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Agglomeration in Metallurgy

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Agglomeration in Metallurgy

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*The book is dedicated to our colleagues,
agglomeration specialists,
who give new power to ... powder*

Preface

Prometheus stole fire from Hephaestus, the patron saint of metallurgy, and presented it to people, for which, as we know, was severely punished by the gods. Finding fire, of course, changed a person's life in the literal and figurative sense, but also, in particular, turned into many problems. The punishment, according to Greek mythology, came to people in the form of Pandora with her ill-fated box. Fire (high-temperature treatment, roasting) of course, plays a very important role in metallurgical processes, being practically the only possible method of smelting metal. Unfortunately, it is Pyrometallurgy that is one of the main sources of harmful emissions into the atmosphere, creating serious threats to the very life of mankind. In the structure of these emissions, a significant proportion (up to 50%) is composed of emissions from sinter plants. Therefore, the efforts of scientists and metallurgists to find ways of the so-called cold agglomeration of raw materials for smelting iron do not stop.

This book was originally conceived by the authors as a continuation of the book by Kurunov and Bizhanov (*Stiff Extrusion Briquetting in Metallurgy*, Springer, 2018) devoted to the description of the new technology of briquetting, based on stiff vacuum extrusion, already widely used in practice. In particular, the authors assumed to compare it comprehensively with the classical agglomeration methods used in modern metallurgy.

But as the content of the book was formed and the manuscript was being prepared, novelties of technical solutions in classical technologies of agglomeration came to light, which were not adequately covered in available literary sources. Not to dwell on such materials would simply be wrong, for this would largely narrow the understanding of the current level of classical technologies and the prospects for their development. These considerations led to the structure of the book, in which, besides briquetting, due process is also given to the processes of roasting agglomeration—sinter and pellets production.

The generalization of information sources is not limited to time periods, but reflects the most significant milestones for the technologies of agglomeration, partly forgotten or unclaimed ideas, hypotheses, technical solutions that have remained relevant to the present time, with an emphasis on the experience of improving the

quality of sinter and pellets, increasing the productivity of sintering and firing machines, resource efficiency, ensuring environmental safety of the production of raw materials.

The chapters “Sinter Production” and “Production of Pellets” were prepared by Dr. Sci., Prof. Valentina Chizhikova, chapter “Briquetting”—by Ph.D. Aitber Bizhanov. Chapter 4 was written by the authors jointly.

The authors in no way claim to the indisputability of the assessments and conclusions, which are built on the arguments currently available at their disposal, and fully allow for the further development of views and ideas in the theory and technology of the agglomeration of dispersed materials.

The authors are grateful to the research teams and researchers who shared in their publications their own ideas, their theoretical rationale and engineering embodiment, as well as colleagues all over the World who helped the authors in their scientific work.

The authors are especially grateful to the publisher for the goodwill and the possibility of publishing this book and efforts to publish it.

The publication is addressed to metallurgical engineers, personnel of metallurgical enterprises, researchers and can be useful to teachers of higher educational institutions of metallurgical or polytechnic profile, graduate students, undergraduates, students studying the specialty “Metallurgy”.

With all the best wishes.

Moscow, Russia

Aitber Bizhanov
Valentina Chizhikova

Introduction

Time to cast away stones and a time to gather stones together...

(Ecclesiastes 3:5, English Standard version)

The scheme of steel production developed by the beginning of the twenty-first century, based on a three-stage processing (preparation of raw materials for the production of primary metal, production of primary metal, processing of primary metal into steel) provides high technical and economic indicators of the industry and, obviously, will remain the preferred scheme of metal production. The dominant position in the production of primary metal is occupied by the blast furnace process [1], the main charge component of which is the agglomerated iron ore raw material (sinter, pellets and briquettes). In 2016 the global production of the hot metal achieved 1164 million tons, which required 398 million tons of pellets and more than 750 million tons of sinter [2].

Sinter is a solid lumpy product with an irregular shape of the pieces, formed as a result of high-temperature treatment of the charge, and isolated from the cake by crushing and screening [3].

Pellet is a solid spherical body obtained by pelletizing fine ore materials with the addition of binders, followed by hardening by firing, cementation or autoclaving [3].

Briquette (briquette)—a prismatic or cylindrical solid formed by mechanical forces, depending on the molding method, containing a binder, with further strengthening by aging under natural conditions or by autoclaving.

The first patent for the method of agglomeration by sintering was obtained in 1887 by the English F. Geberlein and T. Huntington. It was related to the oxidizing firing of sulfide ores and did not provide for the introduction of a special fuel into the charge, since the heat demand of the process was provided by the oxidation of sulfide sulfur. With regard to the agglomeration of iron ores, the engineering solution with the introduction of coke or coal fines was proposed by the German specialist D. Zavelsberg in 1905 [4], who introduced the term “sintering”. Process received commercial distribution after the invention of Dwight A. and R. Lloyd of the belt (conveyor) sinter machine in 1906, and the commissioning of the first installation of its kind in the city of Birdsboro (USA) opened the era of commercial

application of the sintering of charge materials on the conveyor machines. Modern sintering machines have a sintering area of up to 700 m².

The technology of pellet production was born a little later than sintering: the first patent was taken in 1912 by Swedish Anderson [5]. This technical idea was further supported and developed in Germany, starting with the Brakkelsberg patent in 1913 for the method of pelletizing of finely divided iron ore [6] and up to the construction of an industrial pelletizing plant in 1926 in Dillingen. A new stage of interest in this method arose in the 40s in the United States with the advent of industrial volumes of fine concentrates obtained during the enrichment of taconites. It was at this time that the term “pellet” was born (in the Russian version of “okatysh”). The date of the beginning of industrial production of pellets as raw materials for blast furnaces can be considered as 1955, when the first pellet factory was introduced in the United States (Silver Bay). Modern installations for oxidizing firing of pellets can have an area of up to 780 m².

Industrial briquetting began with the first commercially successful project for the production of briquettes from fine magnetite iron ore, implemented in 1899 in Finland. By 1913, there were 38 such briquetting lines in the world (including 16 in Sweden, 12 in England, and 6 in the USA). For the production of briquettes various presses were used (Sutcliffe, lever, revolver, ring, conveyor, roller). The low productivity of briquetting equipment and, often, the insufficient strength of briquettes did not allow this technology to play a significant role in the agglomeration of raw materials for blast-furnace production. The development of briquetting technology with the advent of technologies such as stiff vacuum extrusion allows you to neutralize the shortcomings noted and thus rehabilitate the technology of briquetting as a method of agglomeration of raw materials for blast furnace smelting.

The production of agglomerated raw materials as an industrial technology in modern conditions faces a number of challenges that form additional requirements both for production and for the product or impose certain restrictions:

Increased requirements for the quality of raw materials for blast furnace smelting.

The modern blast smelting technology, aimed at the utmost coke saving, provides for a number of technological innovations that lead to increased demands on the quality of agglomerated raw materials:

- due to the desire to increase the iron content, the proportion of pellets in the charge of blast furnaces increases, since every 1% increase in iron content reduces coke consumption to 1.3% [7]; in recent years in Russia, it has risen to 40%, in the USA, the consumption of pellets in the charge reached 1000 kg/t of pig iron, and some furnaces operate on 100% pellets;
- separation of fine fractions of sinter (with special conditions of its loading into the blast furnace); the increased content of fines in the iron ore part of the blast furnace charge causes coke overruns of up to 2% for each percent increase in the fraction—5 mm in the sinter or pellets [7].
- injection of pulverized coal.

Unlike sinter plants (and briquetting workshops), integrated in the structure of metallurgical production, pelletizing factories are focused on the ore base, and the raw materials produced must be delivered to the consumer with numerous overloads. Transportation of pellets of unsatisfactory quality leads to the actual loss of raw materials up to 50 kg/t of pellets.

Public concern about resource availability and resource saving.

Sustainable development of society according to American scientists [8] is predetermined by the conservation of raw materials, energy, environmental and other resources. At the same time, global public production is characterized by extremely low efficiency with respect to resources: only 2% is used positively, the remaining 98% is transferred to secondary materials or waste. In this regard, the problems of resource saving are global in nature.

The paradigm of sustainable development of civilization, which determined the resource and ecological strategy of industrial development in the 90s of the twentieth century, establishes certain improvement criteria, including the production processes of the primary metal:

1. resource saving (mainly due to the high material consumption of the primary metal production processes, focused on the maximum involvement of anthropogenic materials into the economic turnover);
2. energy saving due to the need to solve global environmental problems (greenhouse effect);
3. environmental requirements (minimizing the negative impact on the environment).

The level of negative impact is an important resource aspect of the operation of metallurgy. According to [9] in Russia, for example, emissions from metallurgical production (ferrous and non-ferrous metallurgy, production of finished metal products) account for more than 20% of gross national emissions from stationary sources. In the structure of the metallurgical enterprise of a full cycle sinter production represents up to 50% of gross emissions, the volume of which is primarily due to the technological features of the process.

It is easy to see that the terms, such as quality, pollution level, energy saving, are in a close relationship and interdependent. Improving the quality of the agglomerated product (first of all, its durability) ensures a reduction in recycling costs and is accompanied by a decrease in energy consumption for production and a decrease in dust emission.

The way to improve the quality of the product with uncontrolled energy consumption (for example, the mechanical activation of charge components in the production of pellets or sinter) in terms of resource conservation is unacceptable. It should be taken into account that the thermal regulation of the product quality, which is traditional for high-temperature sintering processes, is largely associated with energy waste (approximately 0.5 m³ for every 10 °C of heating).

Actually, these ideas created the basic concept of the book, which consists in highlighting theoretical ideas about the processes of agglomeration of iron

containing raw materials and the ideas, proposals and solutions aimed at managing the quality of raw materials for blast-furnace smelting while minimizing energy consumption and limiting environmental impact (environmental aspects).

The concept is based on the principle of sustainable environmental management, the observance of which is guaranteed by:

- preservation of material resources (in the form of metallurgical coke) while increasing the strength of the agglomerated material and the quality of pellets by reducing the content of fines and other measures;
- saving energy resources (process fuel) in the implementation of effective technical and technological solutions in the agglomeration;
- reduction of emissions in the technological process (effective technologies, including environmental), due to the production of high-quality raw materials, the use of stiff extrusion briquettes, waste disposal, the use of new binders in the production of pellets and briquettes.

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About the Authors

Aitber Bizhanov was born on October 6 1956 in Buinaksk, Russia. Graduated from the Moscow Physical-Technical Institute in 1979. Aitber spent eleven years as a senior researcher with the Institute for High Temperatures, USSR Academy of Sciences, focusing on solar heat storage technologies. In 1992, he left academia, joining EVRAZ, a large, vertically integrated steel and vanadium enterprise with global assets. Following two years as Commercial Director and Executive Plant Director with ChTPZ-Complex Piping Systems, Aitber joined Kosaya Gora Iron Works in 2005 as Commercial Director, introducing a briquetting technology that used metallurgical wastes. Since then, he's worked on agglomeration and briquetting of the metallurgical wastes as Wastes Management Expert for HARSCO Metals. Today, Aitber is an Independent Representative of the J.C. Steele & Sons, Inc. Company in Russia & CIS, Eastern Europe and Turkey. Has Ph.D. degree in the agglomeration of natural and anthropogenic materials in metallurgy. Author of more than 60 publications and is owner and co-author of 14 Russian Patents in the field. Author and owner of the "BREX" trademark. With his personal participation, projects of briquetting of natural and anthropogenic raw materials of ferrous metallurgy were successfully implemented in a number of countries. Aitber is a member of Institute for Briquetting and Agglomeration (IBA) since 2011.

Valentina Chizhikova was born and lives in Moscow. Graduated with honors from the Moscow State Institute of Steel and Alloys (MISiS) with an engineer-metallurgist qualification. Her Ph.D. thesis marked the beginning of the study of solid-phase sintering processes in relation to pellet firing, her doctoral (Dr. Sci.) thesis was devoted to a wide range of tasks related to sinter and pellet production, namely, improving the quality of agglomerated raw materials, resource saving and environmental safety. She has more than 30 years of teaching experience at MISiS (now the National University of Science and Technology), as a professor. In scientific terms, the activities of Valentina Chizhikova have always been devoted to solving industry-specific tasks. Under her leadership and direct participation, more than 30 major research projects were successfully implemented. She is the author of about 200 publications, including 80 copyright certificates and

patents, the author and co-author of 8 books on the theory of metallurgical processes, techniques and technologies for the production of agglomerated raw materials and pig iron smelting, environmental problems of metallurgy. In practical terms, she served for 13 years (until April 2018) at a large metallurgical enterprise (PJSC Novolipetsk Metallurgical Plant) as a chief ecologist.

Chapter 1

Sinter Production



1.1 General Information About the Sintering Process

In the sintering, a preliminary prepared mixture of charge components and solid fuel is being burnt in air flow filtered layer (vacuum sintering). Let's describe the phenomenon of sintering technology.

The charge components (see Sect. 1.2) are delivered to the sinter plant in a certain way, guaranteeing the averaging of the composition of the components, are stored, then dosed out in the prescribed proportion to ensure the specified composition of the sinter, are mixed, moistened, and fed to the pelletizing, during which they can be wetted additionally if necessary.

The pelletized charge is loaded on the grate of the conveyor machine (pallet) with a layer height of 300–600 mm, and an exhaustor is switched on to provide the necessary vacuum under the layer and conditions for filtering air through the sintered layer.

The sintering process begins with the combustion of solid fuel in the layer. To initiate the subsequent autonomous combustion of the fuel, the loaded pallet charge passes under the ignition hood, where the upper layer of the charge warms up to temperatures of about 1000–1100 °C (not above 1200 °C), and the solid fuel ignites, forming a specific distribution of temperature regions (zones) in the sintered layer for the sintering process.

The instantaneous picture of such distribution (thermogram) with more detailed structure of zones is shown in Fig. 1.1.

Recorded the time of sintering on Fig. 1.1 reflects the following macrostructure (temperature zoning) of the sintered layer (Fig. 1.1a, b) in sequence along the airflow:

1. layer of finished sinter;
2. combustion zone (melting zone);
3. heating and drying zone;
4. over-wetted charge area;

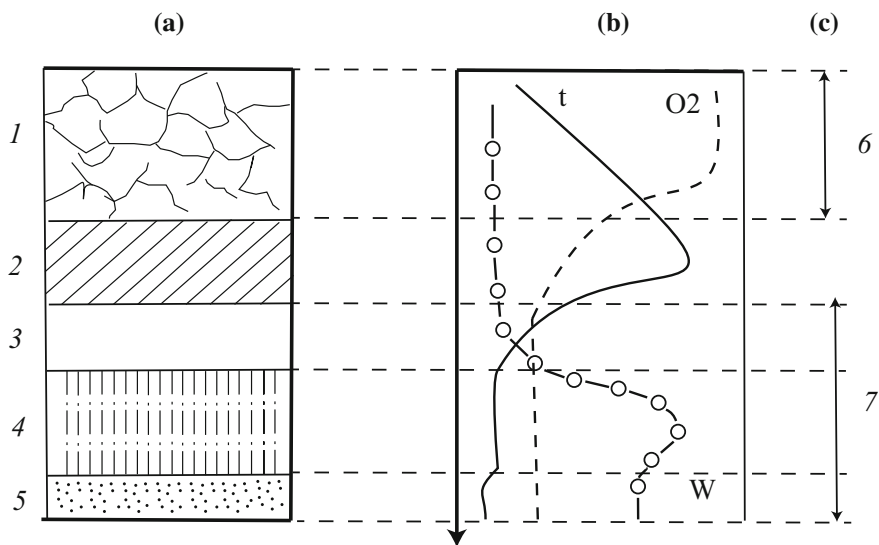


Fig. 1.1 Instantaneous temperature distribution pattern in the sintering layer (interrupted sintering). **a** Macrostructure of the layer: 1–5 layers of finished sinter, combustion zone (melting zone), heating and drying zone, over-wetted charge area, layer of the initial charge; **b** thermogram of the layer, t layer temperature, W moisture content of materials in sinter layer, O_2 —oxygen content in the gas to be sucked, %; **c** stages of heat exchange in a layer: 6—upper heat transfer stage, 7—lower heat transfer stage

5. layer of the initial charge.

The particles of solid fuel ignited at a certain temperature (for coke breeze $\sim 700^\circ\text{C}$) continue to burn, creating a temperature around themselves in the micro-volume of the charge layer at the level of $1300\text{--}1500^\circ\text{C}$ (zone 2). The melt formed as a result of heating to the specified temperatures (oxide-silicate phase) during the subsequent crystallization upon cooling by the sucked air forms a porous sinter cake (zone 1).

The air heated during filtration through a layer of sinter enters the underlying zones, heats the mixture up to the fuel ignition temperature (zone 3), and at the same time dries it, cooling to $50\text{--}60^\circ\text{C}$ (estimated dew point temperature). The gas saturated with water vapor, which comes when the layer is dried, partially condenses on contact with the cold mixture, creating an over-wetted charge zone (zone 4).

Getting into the area of the initial charge (zone 5), the gas is cooled to $15\text{--}20^\circ\text{C}$.

The distribution of the corresponding zones in the space–time coordinates (in the longitudinal section of the layer on the sintering machine) is given in Fig. 1.2.

The arrow shows the direction of movement of the agent.

In general, the duration of sintering can be characterized by three periods [1]:

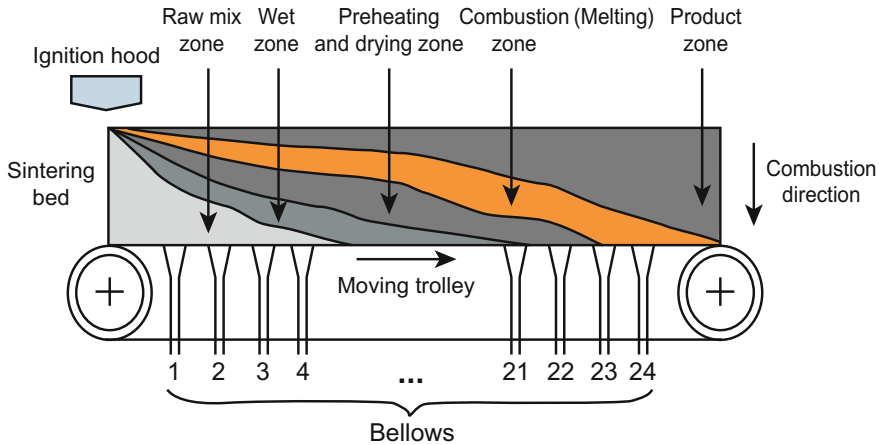


Fig. 1.2 Location of individual zones in the sintered charge layer on the sintering machine

- the initial period τ_i (during this period, the main zones of the sintered layer are formed when the charge is ignited; approximately during the same time, the entire layer of the charge is over-wetted);
- the main period τ_o , when the thermal and gas-dynamic regimes of the sintered layer have stabilized;
- final τ_f , during which the macrostructure of the layer disappears and only the sinter cake zone remains (the sintering process is considered complete when the sinter formation zone reaches the grate of the sintering trolleys, as evidenced by the increase in the temperature of the exhaust gas (Fig. 1.2).

The duration of sintering is determined by the sum ($\tau_i + \tau_o + \tau_f$) and is approximately estimated at 15–25 min depending on the characteristics of the charge and sintering conditions.

A general idea of the sintering process allows us to highlight its features, which, on the one hand, will need in-depth study and coverage, and on the other hand, will allow to identify and develop effective solutions for managing the sintering process with optimization of the objective function for the most important parameters.

1. Sintering is a layered process (in a fixed layer), but, in fact, it is characterized by the cross-movement of gas and material flows, which is easily seen by analyzing the image of the distribution of zones in Fig. 1.2. And if the movement of the material layer is provided by the drive of the sintering machine, then the gas flow is a necessary condition for the sintering process that requires special care in terms of the gas dynamics of the layer (the optimal dispersion composition of the charge components, the charge pelletizing to give it the required grain size and granule strength, and the correct placement on the grate).
2. The sintering process is characterized by the most complicated conditions of heat transfer (Fig. 1.1b):

- In the upper heat transfer stage [2], cold air cools the melt and then the formed sinter cake and heats up; filtration conditions in this zone significantly affect the quality of the sinter, primarily its strength.
 - The lower stage of heat exchange [2] is formed by heat transfer from the heated air to the cold charge (in the presence of other sources and heat sinks in the layer) and is characterized by a high degree of completeness; but this means that the residence time of the elementary volume of the layer in the high-temperature zone is very small, which requires not only detailed knowledge about the physicochemical reactions and their kinetic characteristics, but also appropriate technical solutions for their intensification (size and fuel consumption, the particle size blending of the components of the gas-dynamic regime, the thermal conditions of the process).
3. Solid fuel as a component of the sintering charge is distributed in its volume, which creates special conditions for its combustion (and heat generation)—in separate volumes. In order to ensure the quality of the sinter in view of this distinctive feature, additional measures are required for the thermal regime of the process (additional heat sources).
 4. Due to the use of solid fuels, high processing temperatures, and the circulation of bulk materials, it is possible to predict significant emissions to the atmosphere both in the form of gas components and in the form of dust.
 5. Sinter charge is multi-component, which must be taken into account in the analysis of physical and chemical interactions in the solid phase and the formation of the melt from which the sinter is formed, for the purposeful management of these processes and, ultimately, the strength of the agglomerated raw materials.

To implement the sintering process, an appropriate infrastructure is required, which is shown in the form of a technological scheme in Fig. 1.3.

Due to the consumption of a significant amount of materials and their various nomenclatures, sinter production (sinter plant) includes an ore stockpile (1), where all components of the sinter blend are accepted. The charge components are placed in stacks. In determining the amount of stocks of charge materials are guided by the requirements for the quality characteristics of the sinter (chemical and granulometric composition, strength) and, above all, the variability of the characteristics of the sinter. According to [3], the dependence of the chemical composition of the sinter on the stack capacity is of an extreme nature: The variability decreases with a stack capacity of 80–100 thousand tons and increases again with an increase in the stack capacity above the specified values.

For iron ore materials, the minimum stock (and, accordingly, the volume of the stack) must ensure the operation of the sinter plant for at least 5 days; with the remoteness of the supplier, the stock of materials in the ore warehouse can be increased depending on the delivery time.

The ore stockpile is intended not only for the formation and storage of stocks of charge materials, but also provides for the averaging of materials, mainly iron ore, due to their diversity.

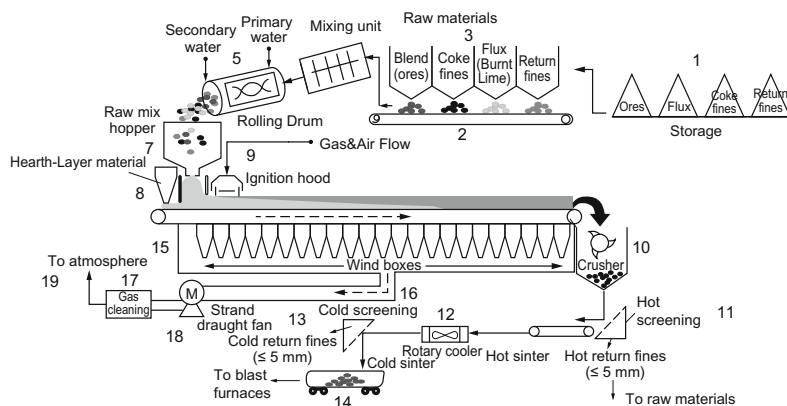


Fig. 1.3 Flow diagram of sinter production. 1—ore warehouse; 2—charge department of sinter plant; 3—charge bunkers; 4—mixing equipment; 5—pelletizing equipment; 6—sintering machine; 7—charge hopper; 8—loading unit “beds”; 9—ignition hood; 10—crusher of sinter; 11—screen of hot sinter; 12—cooler of sinter; 13—screen of the cooled sinter; 14—sinter carrying trucks for feeding to the blast furnace; 15—vacuum chamber; 16—exhaust gas manifold; 17—the system of purification of exhaust gas; 18—exhauster; 19—chimney

Various technologies of averaging materials are possible and are used, which also contribute to the reduction of variability in the composition of the sinter:

- forming a stack using a stacker with a material intake from the end of the stack with an intake-averaging machine or from a slope using a scraper reclaimer;
- the formation of a separate stack for each material, the subsequent dosing of components, and the formation of a stack of “mono-charge”;
- the formation of a separate stack for each material, the subsequent dosage of the components, and their mixing in intensive mixers («Eirich» type mixer).

The charge department of the sinter plant (2) provides for the preparation of the charge components, namely solid fuel and flux (limestone, lime). To obtain the required fineness of fuel and limestone, these materials are subjected to crushing followed by sieving (screening).

Usually, fuel is crushed in four-roll crushers or in two pairs of two-roll crushers, less commonly used is rod mills or hammer crushers, and flux—in hammer, sometimes rotary, crushers [4].

Charge bins (3) of the charge (dosing) department of the sinter plant are designed for receiving and dosing in a given ratio of the components of the sinter. Each component of the charge has a certain hopper (hoppers), where materials are fed along the path by belt conveyors with unloading devices (trolley or shuttle conveyor). Modern bunkers have a conical or cone-cylindrical shape, and their volume can reach 600 m³. Belt weighers are used for continuous and batch dosing of charge materials.

The dosed charge composition enters the mixing device (4), which is usually a rotating drum, where some part of the water is supplied. Mixing of bulk materials is

a process of mutual movement of particles of one material relative to another to ensure their uniform distribution in the volume of the material. The achieved degree of homogeneity of the mixture depends on the physical and chemical properties of the materials, the number of components in the mixture, the nature of the movement of the material in the mixing device; it can be determined by the coefficient of homogeneity of K_o as the ratio of the average minimum content of the element to the average maximum content [5]:

$$K_o = (c - \Delta c) / (c + \Delta c)$$

To form a proper granulometry of the sintered layer after the mixing device, the charge enters the pelletizing, usually in a rotating drum (5), where all the water necessary for the process is dosed. In relation to the process of pelletizing, it is possible to distinguish the following fractions of the charge:

- lumping fraction, which includes particles of the charge, being able to perform the role of nucleating centers (particle size 1.6 mm);
- lumped fraction in the form of charge particles size 0–0.4 mm, which are rolled onto the surface of the nucleating centers (or may form nucleating centers);
- intermediate fraction, which include conditionally “inert” particles of size 0.4–1.6 mm, which practically do not participate in the pelletizing process.

The potential ability of sinter charge to pelletizing can be estimated by the granulation rate coefficient (K_{GR}) as the ratio of the size of the surface of the lumping fraction of the charge (S_C) to the volume of the lumped fraction (V_K):

$$K_{GR} = S_C / V_K$$

In the physical sense, the granulation rate coefficient is the inverse of the thickness of the layer rolled onto the surface of the nucleating center, respectively; the greater the value of the coefficient, the thinner the rolled layer, in other words, the faster it is formed.

Loading of the pelletized charge on the sintering machine (6) is made from the loading hopper (7). From a special hopper (8), a “bed” is pre-fed to the pallets of the sintering machine, which is a fraction of the sinter with a size of 5–8 mm. Then, the pallets loaded with bed and charge pass successively under the ignition hood (9). At the end of sintering, sinter cake comes off the pallet and falls into the gear crusher (10). After the hot return (11) is eliminated, which is fed into the mixing drum, the suitable sinter cake fraction is sent to coolers (12) and after cold screening (13), the sinter cake is loaded into wagons for delivery to the blast furnace shop (14).

The air sucked through the sintered layer through the vacuum chambers (15) and the collector (16) is evacuated by the exhaustor (17) through the gas cleaning system (18) and removed to the chimney (19).

Separate processes of the technological scheme of sinter production, as well as a brief description of the equipment, will be discussed in the sections below.

1.2 Raw Materials of the Sintering Process

Sintering is a universal method for the agglomeration of finely dispersed components, which is applicable to a wide range of materials (in both chemical and granulometric compositions).

Fundamentally, in the composition of the sintering charge, there are three groups (parts) of components:

- iron ore charge;
- flux part of the charge;
- fuel part of the charge.

In addition to the regular groups of components, additives can be introduced into the sintering charge for various purposes (see Sect. 1.7). The structure of the sintering charge and the requirements for its components are illustrated in Fig. 1.4. Based on the practice of sintering, certain requirements are established for the components of the sintering charge, which further form their physicochemical properties. In addition to the regular groups of components, additives can be added to the sinter blend for various purposes (see Sect. 1.7). The structure of the sintering mixture and the requirements for its components are illustrated in Fig. 1.4. Based on the practice of sintering, certain requirements are established for the components of the sintering charge, which further form their physicochemical properties.

The iron ore part of the charge includes components in which the predominant compounds are iron oxides. It should be noted that at present, industrially recoverable iron ores are predominantly represented by oxides, carbonates, and iron hydroxides.

Basic requirements for the iron ore part of the charge:

- the highest possible iron content;
- granulometric composition (for sinter, 0–8 mm, for concentrate, less than 0.1 mm);
- preferably basic gangue;
- the minimum content of harmful impurities.

The composition of the iron ore part of the charge includes: sinter ore, iron ore concentrate, or a mixture of concentrates (in a certain proportion with respect to the ore up to 100%). Various waste products from metallurgical plants are also used: sintering and/or blast furnace sludge (products of a wet gas cleaning system), collected dusts from metallurgical plants and aspiration systems (casting yards and bunker racks of blast furnaces, mixing sections of converter shops, discharge stations of sinter and coke fines in blast furnaces units, etc.), mill scale; 0–10 mm magnetic fraction released during the crushing and screening of steelmaking slags. In addition, a returnable product (or return), which is formed during screening (separation) after the initial crushing of sinter cake and subsequent sieving of sinter at the sintering plant, in the blast furnace shop, during stabilization of sinter (if applicable), is necessarily introduced into the sintered mixture. A minus 5 mm fraction is released into the return, and the chemical composition of the return approximately corresponds to the composition of the produced sinter.

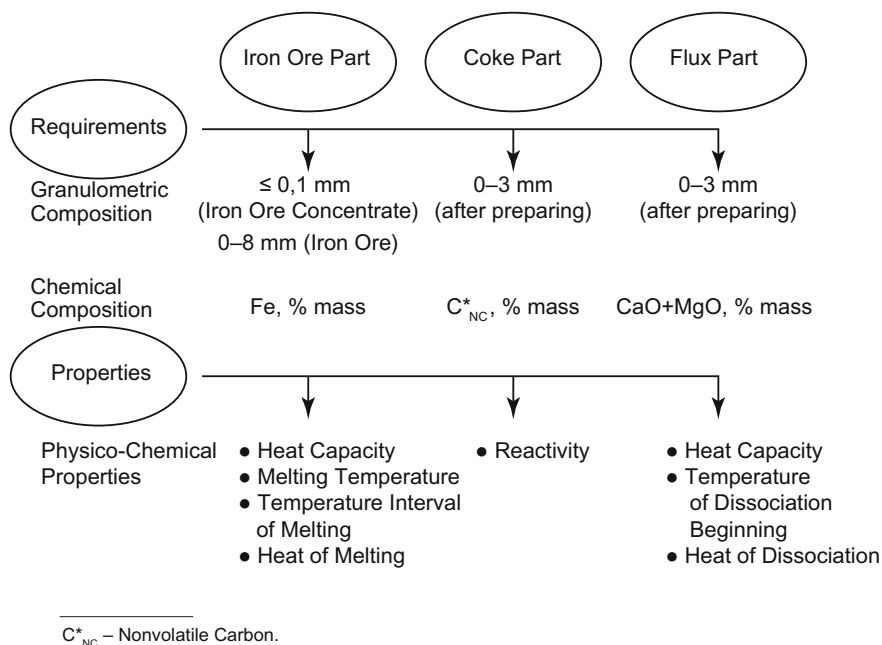


Fig. 1.4 Requirements for the components of the sinter charge

The number of components of the iron ore portion of the mixture can reach up to 15 [6].

Despite the wide range of surrogate products indicated for use in sintering charge, certain restrictions are imposed on them. The requirements for the conditions of use of waste and by-products in the sintering charge are not related to the sintering process itself, but are determined by the accompanying circumstances:

- minimum sulfur content to avoid emissions of sulfur compounds in the sintering process, as well as alkaline elements that are undesirable in the blast furnace (the requirement applies to all charge components, not only by-products and waste);
- Zinc-containing dusts and sludge (more than 1.5% of zinc) are not allowed due to the limitation of zinc load in blast furnaces (not more than 0.15 kg per ton of hot metal).
- Oily mill scale (with oil content more than 15%) is undesirable in the charge due to the possible formation and release of dioxins in the waste sinter gas.
- The volume of total waste use in the sintering charge is also optimized under the conditions of the granulometric composition of the charge.

The composition of the iron ore part of the charge (for example) is given in Table 1.1 [7]. By chemical nature, iron ores are represented by mineral phases—hematite (Fe_2O_3), magnetite (Fe_3O_4), martite (semi-oxidized magnetite), and Bakalskaya ore-siderite (FeCO_3). Iron ore concentrates are exclusively magnetites.

Iron content in the ore is usually lower than in the concentrate, which makes the concentrate a very attractive component of the sintering charge, but at the same time

requires serious technological efforts to ensure the gas permeability of the layer. Sinter plants in Russia operate with a very high share (more than 80%) of concentrate in the iron ore part.

Some properties of the components of the iron ore part of the charge, such as heat capacity, melting temperature, melting range, significant for the sintering process according to [7, 8] are given in Tables 1.2 and 1.3.

In the temperature range 273–1473 K (0–1200 °C), the dependence of the heat capacity on the temperature is described by a polynomial (see Table 1.2). The calculation of heat capacity for different iron ore materials for the boundary temperatures of the interval shows that the minimum values of heat capacity for iron ores lie in the range of 0.705–0.878 kJ/kg °C, and in the high temperature range—within 0.941–1.157 kJ/kg °C. The heat capacity of concentrates at 373 K (with rare exceptions) does not exceed 0.800 kJ/kg °C; at 1473 K, the range increases to 0.911–1.029 kJ/kg °C.

The highest melting temperatures of 1245–1284 °C (Table 1.3) have quartz-containing ores. Here, the formation of the first portions of the melt mainly involves Fe_3O_4 (FeO) and SiO_2 .

Lower temperatures of the beginning of melting (up to 1100 °C) are recorded for ores, which contain sulfur in their composition. The appearance of the primary melt in this case is caused by the formation of low-melting compounds in the ternary systems FeS – Fe_3O_4 – SiO_2 .

The increase in the content of the basic iron-containing oxide (in the transition from ores to concentrates) shifts the beginning of melting to higher temperatures (1281–1312 °C). Due to the heterogeneous mineral composition of iron ore materials, the melting process takes place in a certain temperature range, the value of which varies in a rather wide range from 118 to 402 °C.

As early as the 1950s, for the first time in Russia, industrial production of fluxed sinter was mastered; currently, only fluxed sinter is produced in Russia and in the world. This allowed the raw limestone to be removed from the blast furnace charge, which in turn guaranteed coke consumption decrease in blast furnace smelting up to 5% while reducing the flux consumption by 100 kg/t of pig iron [9].

Since, as can be seen from Table 1.1, the gangue¹ in iron ores and concentrates is mainly characterized by a siliceous (silicate) component, and the *flux part* of the sintering charge is mainly limestone.

Basic requirements for the flux part of sintering charge:

- the maximum possible mass fraction of CaO and MgO;
- minimum content of SiO_2 ;
- particle size distribution: 95% of the fraction 0–3 mm;
- minimum moisture content.

To improve the metallurgical properties of the sinter, dolomite or dolomitic limestone is introduced in addition to the limestone, and calcined lime is used to

¹Gangue-part of the mineral composition of ore or concentrate that does not contain the main element (in the case of iron ore materials—iron).

Table 1.1 Approximate particle size distribution and chemical composition of some iron ores, concentrates of the enterprises of the Russian Federation [7, 10]

Material	Size	Content (% mass)				CaO	SiO ₂	Al ₂ O ₃	MgO	MnO	S _{tot}	LOI
		Fe _{tot}	Fe ₂ O ₃	FeO								
Ores												
Bakalskaya	0–10 mm	29.10	2.57	35.10	2.96	10.10	3.00	8.92	1.2	–	–	–
Lebedinskaya		50.11	47.45	21.72	1.90	9.31	2.34	0.68	0.09	0.32	12.73	–
Mikhailovskaya [6]		55.10	75.16	3.20	0.77	17.40	0.21	1.50	0.39	0.32	5.46	–
		52.00	–	–	0.50	20.00	1.19	0.14	0.02	0.33	–	–
Stoilenskaya (1)		49.70	55.67	13.80	1.10	10.20	3.30	0.47	–	0.24	5.57	–
(2)		53.52	68.85	6.85	0.87	9.77	6.13	0.46	0.12	0.23	6.45	–
Concentrates												
Vysokogorskiy	<45 μm	58.20	56.20	24.30	3.10	6.50	2.90	1.70	–	0.23	–	–
Kachkanarskiy		64.30	61.06	27.80	0.90	3.72	1.76	0.96	–	TiO ₂ /2.57	–	–
		60.99	56.97	27.19	1.45	4.60	2.66	2.75	–	TiO ₂ /2.70	1.16	–
Kovdorskiy		64.04	64.27	24.58	1.10	1.06	0.27	4.94	0.58	0.33	1.12	–
Olehegorskiy		64.40	64.10	25.20	0.72	8.30	0.34	0.68	0.078	0.07	0.40	–
Kostomukhskiy		60.00	55.44	27.30	0.43	13.90	0.47	0.30	–	0.25	–	–
Lebedinskiy		68.20	65.76	28.50	0.21	4.70	0.36	0.20	–	0.03	–	–
Mikhailovskiy		67.49	64.40	28.80	1.02	5.21	0.20	0.21	0.06	0.043	–	–

Table 1.2 Coefficients for calculating the average specific heat^a of some iron ore materials, kJ/kg °C [8]

Material	Temperature, t_i , (°C)	Values of the coefficients of a polynomial		
		a	b	c
<i>Ores</i>				
Lebedinskaya	100	0.744	0.316	0.00856
Mikhailovskaya	300	0.925	0.2803	0.00847
Stoilenskaya	300	0.960	0.2743	0.00609
<i>Concentrates</i>				
Kachkanarskyi	100	0.851	0.137	0.00163
Kovdorskyi	300	0.806	0.431	0.00117
Olenegorskyi	200	0.7296	0.3268	0.01614
Lebedinskyi	200	0.7278	0.2327	0.00457
Mikhailovskyi	100	0.747	0.213	0.00149

^a $C_p = a + b \times 10^{-3} \cdot (T_i - T_B) - c \times 10^{-5} \cdot (T_i - T_B)^2$, where T_i , T_B are temperatures (Kelvin degree), respectively, current and initial in the range 473–1473 K

Table 1.3 Melting temperatures (°C) and heat of some iron ore materials [7]

Material	Transformation temperature (°C)				Temperature interval $t_{\text{B}} - t_{\text{F}}$	Melting heat (kJ/kg)
	t_{B} (DTA)	t_{B} visually ^a	$t_{0.5}$ visually ^a	t_{F} (DTA)		
<i>Ores</i>						
Lebedinskaya	1245	1255	1380	1400	155	590.4
Mikhailovskaya	1282	1300	1360	1400	118	566.3
Stoilenskaya (1)	1284	1295	1380	1442	158	621.3
(2)	1262	1275	1435	1465	203	–
<i>Concentrates</i>						
Kachkanarskyi	1281	1290	1431	1499	218	–
Kovdorskyi	1312	1320	1460	1514	210	611.0
Olenegorskyi	1278	–	1410	1493	215	608.3
Lebedinskyi	1294	1300	1445	1480	158	580.3
Mikhailovskyi	1308	1315	1465	1510	202	600.9

^aVisually determined by a high-temperature microscope; t_B , t_F are temperatures, respectively, initial softening and finishing melting

improve the pelletizing conditions and granule strength. In addition, for the recycling of by-products and/or metallurgical wastes, screenings of limestone from refractory production, screenings of lime from steel-smelting workshops, trapped lime kiln dust, dust from aspiration systems of production and technological sections of transportation and handling of lime and limestone are used.

The chemical composition of some limestones (examples) is given in Table 1.4. As follows from Table 1.4, the composition of limestone in both the main

component and the gangue does not change significantly (appearing as part of dolomitic limestone MgO replaces CaO) on the conditions of its genesis. Probably for this reason, the values of heat capacities for limestones of Table 1.4, determined in the range of 273–973 K, differ slightly from each other and cover the range of values from 0.834 to 1.306 kJ/kg °C [7].

The *fuel part* of the sintering charge is usually represented by a mixture of combustible components.

Basic requirements for the fuel part of the sintering charge:

- high content of combustible carbon;
- minimum ash content;
- restriction on the content of volatile (no more than 15%);
- limiting the content of fraction –0.5 mm;
- limiting the content of fraction +3 mm;
- calorific value;
- reactivity.²

The above requirements are justified by the practice of sintering: Thus, an increase in the ash content of 1% in the fuel is accompanied by an increase in fuel consumption by 1.4–1.6%; an increase in the volatile content by 1% gives an increase in fuel consumption by 0.6% [4]; in addition, due to the deposition of low-volatile components on the extractor blades, complications of its operation are possible. An increase of 1% in the fraction minus 0.5 mm increases its consumption by 0.35% [11].

In the best way, the aggregate of the indicated requirements is met by coke breeze, but because of its scarcity and high cost, coke breeze substitutes or surrogate fuels are used: fossil coals (anthracite is preferred, but lean coals are also used), semi-coke, and other materials.

For coke breeze fraction of 0–3 mm is recommended, the use of other fuels requires optimization of particle size distribution.

For the sintering process, the most important characteristic of solid fuel is its composition, in other words, technical analysis, which reflects the carbon content of the fuel and the volatile content, sulfur content (see Table 1.5).

No less important in connection with environmental aspects is the content of nitrogen in solid fuels (N), which is usually in the range of 1.0–2.7% [4].

The genesis of the fuel material and its composition determine the essential properties of the fuel for its role in the sintering process: the fuel ignition temperature, its calorific value, and reactivity (Table 1.6).

The calorific value of solid fuels, estimated by the lowest calorific value, for coal (lean coals, anthracites, semi-anthracites) lies in the range from 27.0 to 34.8 MJ/kg; for coke breeze, this value is slightly higher—36.5 MJ/kg.

For example, Table 1.7 shows the average composition of sinter charge of Russian sinter plants [12].

²The reactivity of solid fuels is determined by a special test on the rate constant of interaction with CO₂ at a temperature of 950–1100 °C [10].

Table 1.4 Approximate granulometric and chemical composition of some flux materials [7, 10]

Material	Size (mm)	Content (% mass)									
		Fe _{tot}	Fe ₂ O ₃	FeO	CaO	SiO ₂	Al ₂ O ₃	MgO	MnO	S _{tot}	LOI
Vysokogorskyi	0–10	–	–	–	50.84	1.80	–	2.00	–	–	40.80
Dolomitized limestone	0–10	–	–	–	49.40	2.40	–	3.80	–	–	43.20
Pikalevskyi	0–10	–	–	–	52.10	2.06	–	0.78	–	0.036	41.62

Note

Mentioned in Tables 1.1, 1.2, 1.3, and 1.4 the materials that make up the components of the sintering charge characterize the basic iron ore deposits of Russia, which are part of large industrial groups of producers and exporters of iron ore raw materials and metal products

Kachkanarsky Deposit (concentrate)—KachGOK, Sverdlovsk region, a part of PJSC EVRAZ;

Vysokogorsky mine (concentrate)—VGOK, Sverdlovsk region, formerly part of PJSC EVRAZ, currently in NMD “Ural”;

Lebedinsky Deposit (ore and concentrate)—LebGOK, Belgorod region, is a part of PJSC Metalloinvest;

Mikhailovsky Deposit (ore and concentrate)—Mikhailovsky GOK, Kursk region, is a part of PJSC Metalloinvest;

Kovdor field (concentrate)—JSC “Kovdor GOK”, Kola Peninsula;

Olenegorsky mine (concentrate)—OLCON, Kola Peninsula, a part of PJSC “Severstal”;

Kostomuksha Deposit (concentrate)—JSC Karelsky Okatysh, the Republic of Karelia, a part of PJSC “Severstal”;

Stoilenskyi Deposit (ore, concentrate)—StoilGOK, Belgorod region, a part of NLMK Group;

Bakalsky Deposit (ore)—LLC “Bakal Rudoupravlenie”, Chelyabinsk region, was previously part of PJSC MMK, now in NMD “Ural”

Table 1.5 Technical analysis of some of solid fuels [4, 11]

Solid fuel	Size	Technical analysis (share, % mass)			
		Non-volatile carbon C _n	Ash content A ^d	Volatiles V ^b	Sulfur organic S ^d
Coke breeze	0–3 mm	83–87.0	8–13	1.5–2.5	0.4–2.0
Anthracite [GOST 8180-75] ^a					
A _f	13–25 mm	80.4	14.0	3.5	1.8
A _m	6–13 mm	“_”	“_”	“_”	“_”
A _c	<6 mm	69.7	25.0	2.8	1.9
Semi-anthracite	–	75.6	16.8	8.0	2.0
Lean coals	–	82.7	4.9	12.7–17.0	0.27–0.46
Semi-coke (from brown coals)	Up to 2 mm	58.04	14.54	26.77	0.25

^aA_f—Anthracite fine; A_m—Anthracite medium; A_c—Anthracite culm

1.3 Preparation of Charge Components for Sintering (Crushing, Dosing, Mixing, Pelletizing)

Since the processes of crushing and mixing were briefly described in Sect. 1.1, let us consider the processes of dosing and pelletizing.

Table 1.6 Reactivity of some solid fuels [11]

##	Solid fuel	Reactivity (ml/g s)	Specific surface area (m ² /g)	Ignition temperature (°C)
1	Coke breeze	0.76–1.85	17.0–40.5	620–700
2	Anthracite	0.51	–	470–560
3	Semi-coke	6.23–12.9	182.0–217.0	150–400
4	Charcoal	11.1	243.0	250–270

Table 1.7 Approximate component composition of the charge of sintering plants of ferrous metallurgy of the Russian Federation [12]

##	Charge component	Granulometric composition (fraction, mm)	Content in the charge (kg/t of sinter)
1	Sinter ore and heavy concentrates of dry magnetic separation	<8.0	274
2	Wet magnetic separation concentrate	<0.074	637
3	Sinter fines	<5	36
4	Manganese ore	<8	11
5	Flue dust	<3	27
6	Mill scale	<5	26
7	Converter slag	<5	2
8	Limestone	<3	192
9	Lime	<1	23
10	Iron-bearing sludge	<0.1	10
11	Different waste	<8	17
12	Coke breeze	<3	42
13	Anthracite culm	<6	22

1.3.1 Dosing of the Components of the Sinter Charge

The dosing of components is the determination of the flow rate of each component, the allocation of this measure from the total material flow of a particular component, and discharge of this material to the charge conveyor for transportation to the mixing device.

Determination of component flow rate is carried out by calculation methods:

- according to the material balance at the specified fuel consumption and additives (used as an operational calculation);
- according to the material balance on the basis of the analogues of the base variant (for the choice of fuel consumption) with subsequent amendments for the expenses of the components obtained by model calculations (unfortunately, the reliability of the result in this case depends on the reliability of the model);

- based on the solution of the system of equations for the material and heat balance of the sintering (full calculation), which involves some assumptions, resulting in additional errors.

Due to the noted circumstances in practice the operational calculation is usually applied.

The initial data for the calculation of the material balance are:

- required content of FeO in sinter;
- given basicity of sinter, B;
- solid fuel consumption (coke) T;
- consumption of additives D (return is not taken into account in the calculation, because it is a circulating load);
- chemical composition of all components of sintering charge.

The calculations for 100 kg of sinter are determined by the flow rate of the mixture of iron ore and limestone.

The calculation is carried out on 100 kg of sinter, and the consumption of iron ore mixture and limestone is determined.

The solution of the problem with two unknowns is found from the system of equations of material balance (1.3.1) and the basicity of the charge (1.3.2):

$$O + T + D + F - (\Delta_1 + \Delta_2) = 100 \quad (1.3.1)$$

$$\frac{(O \cdot (\text{CaO}) + T \cdot (\text{CaO}) + D \cdot (\text{CaO}) + F \cdot (\text{CaO}))}{(O \cdot (\text{SiO}_2) + T \cdot (\text{SiO}_2) + D \cdot (\text{SiO}_2) + F \cdot (\text{SiO}_2))} = B \quad (1.3.2)$$

where O, T, D, F—flow rates of ore mixture (the ratio of concentrate/sinter is given by the proportion), fuel, additives, flux (limestone), respectively.

Δ_1 —weight loss of the charge during sintering due to the burning of solid fuel carbon, removal of hydrated moisture, dissociation of carbonates, oxidation of sulfur compounds (for sulfide and organic components, the degree of removal during agglomeration is taken in 95%); Δ_2 —weight loss (increment) as a result of redox reactions of iron oxides;

B—basicity of sinter.

For a simplified calculation, the material balance Eq. (1.3.1) can be written using the index “sinter yield” from the charge component β_i [13]:

$$O \cdot \beta_O + T \cdot \beta_T + D \cdot \beta_D + F \cdot \beta_F = A \quad (1.3.3)$$

where β_O , β_T , β_D , β_F —the outputs of sinter from ore mixture, solid fuels, additives, flux, respectively.

In turn, the yield of the sinter from the charge component is determined by its chemical composition and possible reactions during sintering. Thus, the yield of the sinter from the ore mixture is calculated by (1.3.4):

$$\beta_O = (100 - \text{LOI} - 0.95 \cdot [\text{S}])/100 \quad (1.3.4)$$

where LOI—loss on ignition;
[S] is the sulfur content of the iron ore mixture.

From the ore mixture into the sinter (1.3.4), all the material will be transferred with the exception of hydrated moisture (which is reflected in the chemical composition of the LOI index), as well as burnt sulfur (in this case we ignore the redox reactions; however, this will be reflected in the general result when checking: If reduction reactions take place, then the sum A (sinter yield) will be less than 100 kg, if oxidative, then more than 100 kg).

Only the ash part of the solid fuel will pass to the sinter (1.3.5):

$$\beta_T = A^c/100 \quad (1.3.5)$$

Fluxes in the sinter will be represented by oxide components:

$$\beta_F = (100 - \text{LOI})/100$$

Based on the calculation, the components of the charge after the mixing device are fed to the pelletizing through a conveyor.

1.3.2 Pelletizing of the Sinter Charge

The pelletizing of bulk materials, such as components of the sinter blend, is a process of aggregation of dispersed (small) particles of the charge into lumps (granules) under the influence of a complex of forces, among which the forces of capillary and molecular interaction are the most important [14].

Potentially, the system of dispersed particles is capable of spontaneous aggregation due to the tendency to reduce the free surface energy, but to obtain a pelletized charge that meets the requirements of the sintering process, special technological measures and equipment are needed.

Technological operation of pelletizing must ensure [15]:

- production of fine-grained charge with a high degree of pelletizing;
- uniform granulometric composition of the pelletized charge;
- sufficient strength (density) of the granules, guaranteeing their stability during overloads, waterlogging of the layer, in the processes of drying and heating during sintering.

The pelletizing process generally proceeds in three successive stages: the formation and growth of granule nuclei, an increase in the linear dimensions of the granules, compaction (hardening) of finished granules.

The formation of granules during pelletizing can be carried out in two schemes:

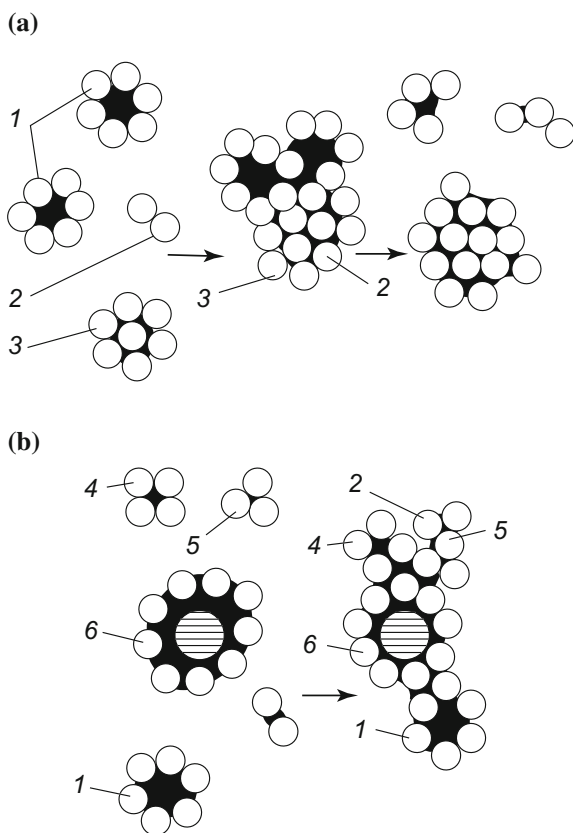
- on the basis of the nucleating centers present in the charge in the composition of the crumpling fraction (granule type A, Fig. 1.5b);
- nuclei formed from the crumpled fraction when moistened by capillary forces (type B granules, Fig. 1.5a); moreover, in the moistening zone, the ratio of the number of granules of types B and A in the mixture containing 80–90% of the concentrate in the iron ore part is 3: 1 (their number does not exceed 30% at the exit from the pelletizer).

The evolution of sintering charge during pelletizing with the participation of nucleating centers of different nature (type A and B) is illustrated in Fig. 1.5.

When drops of moisturizing liquid get into the clumped material, the process of formation of nuclei of type B is mainly developed, which in turn is preceded by the formation of aggregates from a certain number of material particles and their coalescence (1, 2, 3; Fig. 1.5); then, on the basis of the most stable unit (critical nucleus), the growth of the pellet takes place (4) by attaching additional units. The difference between the aggregate and the critical nucleus is obviously in smaller

Fig. 1.5 Evolution of the sinter charge in the process of a pelletizing [15].

a Nucleating centers of type B; **b** nucleating centers of type A; 1–6—aggregates of particles of charge components; dark—pores filled with water, light—particles of crumpled fraction, hatched—particle of crumpling fraction



mass and linear dimensions. In the case of nucleating centers of type A, namely around such nuclei, a granule is formed by joining the particle aggregates (5).

The efficiency of pelletizing is certainly influenced by the initial granulometric composition of the charge components. For sintering charge with a high proportion of fine concentrates, optimal conditions of pelletizing correspond to the ratio between the lump and the crumpled and crumpling fractions of the sintering charge (2.75–3.25): 1 [14].

Pelletized sinter mixture is characterized by a certain average grain sizes (average, weighted average, average harmonic, on averagely equivalent), but the most common is based on averagely equivalent diameter d_e (mm), defined by the ratio:

$$d_e = P / (\sum P_i / d_i) \quad (1.3.6)$$

P is the mass of the pelletized charge.

Σ is the sum taken by fractions (i varies from 1 to n).

P_i is the mass of the i -th fraction of the pelletized charge.

d_i is the average size of the i -th fraction of the pelletized charge.

The formation of granules of crumpled charge in the drum pelletizer

Pelletizing of sintering charge in industrial conditions is carried out in devices, which are called drum pelletizers. The typical size of the drum pelletizer can vary depending on the required capacity: There are devices with diameters from 2.8 to 4.2 m and a length from 7.5 to 24 m [13].

The size and mode of operation of the drum pelletizer (angle of inclination to the horizontal, speed, degree of filling, water supply mode) significantly affect the formation of sintering charge granules. For the drum pelletizer with a diameter of 3.2 m and a length of 12.5 m, the following modes are characteristics: The angle of inclination of the drum to the horizontal is 1.5–4.0°; rotational speed 4–8 min⁻¹; drum filling with charge 5–13%; the residence time of the mixture in the drum 1–4 min.

The movement of the mass of the charge material in the pelletizer drum is determined by the speed of its rotation and corresponds to four types of schemes (Fig. 1.6) [13]:

- Running mode (a) occurs when the friction force is balanced by gravity; the center of gravity of the load is deflected from the vertical by an angle less than the angle of the natural slope of the material.
- In roll back mode (b), the center of gravity of the load is deflected from the vertical by an angle exceeding the angle of the natural slope; the center of gravity of the charge does not shift, but around it (along circular trajectories) rotates (at the speed of the drum) the bulk material, rising up along the wall of the drum, and crumbling down the surface of the charge.
- Waterfall mode (c) occurs at high speeds of rotation of the drum with the possible trajectories of the particles: BA—circular, AC—parabolic (separation from the surface of the drum, free fall), CB—the site of bulking.

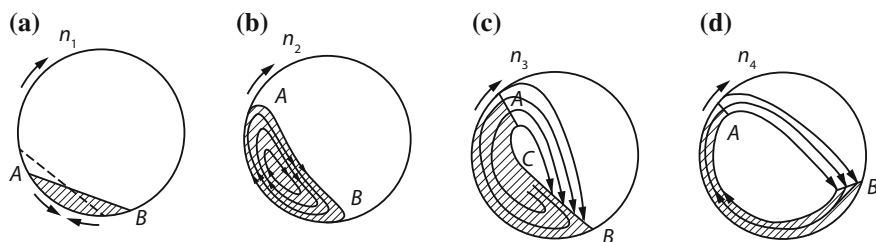


Fig. 1.6 Modes of charge movement in the drum pelletizer [13]. **a** Running mode; **b** roll back mode; **c** waterfall mode, **d** cyclic mode

- Cyclic mode (d) takes place at very high speeds of rotation of the drum; it has only a circular BA and parabolic (AB) trajectory.

It is established [15] that the most favorable mode of pelletizing in pelletizers is the mode of roll back. For this mode, the kinetics of charge pelletizing in an industrial drum pelletizer with a diameter of 2.8 m and a length of 7.5 m is analyzed, the results of which are shown in Fig. 1.7.

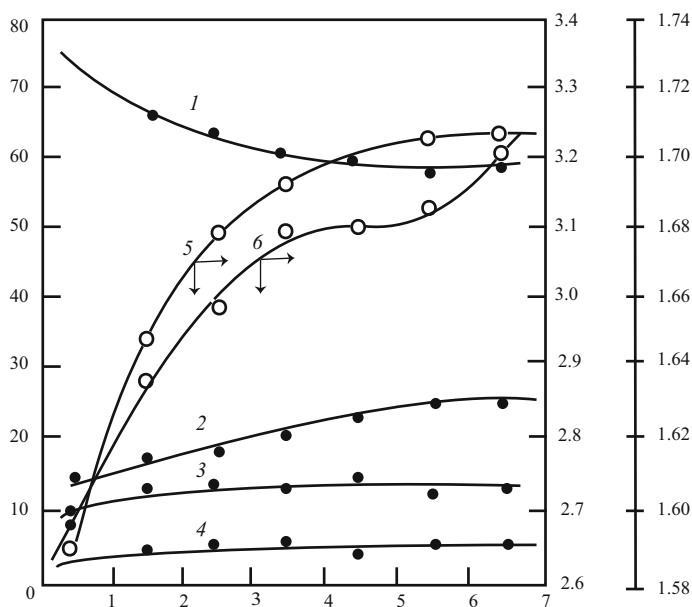


Fig. 1.7 Changes in granulometric composition, average equivalent diameter and the bulk density of the sinter charge pelletized in the industrial drum pelletizer [15] 1–4—classes of size of the pelletized charge, respectively, 0–3, 3–5, 5–8 mm and more than 8 mm; 5—average diameter of granules (far right y-axis), 6—bulk weight of charge (closest right y-axis); left y-axis—content of classes of size 1–4, %

During pelletizing of the charge compositions containing finely divided concentrates, it is necessary to distinguish two periods of the process: transient and steady state. The variable granulometric composition of the charge corresponds to the unsteady period of pelletizing: The number of granules of small classes (less than 3 mm) decreases, and the number of classes more than 3 mm increases (in other words, this period corresponds to the process of formation of nucleus and growth of granules), as a result of which the bulk mass of the charge significantly increases (Fig. 1.7, curve 6). In the steady-state period of pelletizing, the granulometric composition of the charge remains practically unchanged, but the bulk mass increases (which is caused by the compaction of granules in each class of fineness).

The patterns of mass transfer during pelletizing predetermine a completely relevant connection between the granulometric composition of the pelletized mixture and its other characteristics, namely the average equivalent diameter of the granules and the degree of pelletizing of the mixture (Fig. 1.8). Each value of the degree of granulation of the charge corresponds to a certain average equivalent diameter of the granules and the particle size distribution, regardless of the size of the pelletizer and the modes of its operation. In other words, the granulometric composition is predetermined only by the pelletizing phase, or the degree of completion of the pelletizing process.

The formation of the charge granules during pelletizing (granulometric composition, strength) significantly depends on the nature of the mechanical action inherent in the pelletizing device, as shown in Table 1.8.

The nature of the particles movement in the vibrofluidized layer (Table 1.8) is fundamentally different from that in the processing of the charge in the pouring layer typical of the drum pelletizers. In contrast to the drum pelletizers in the vibrofluidized layer due to lower dynamic loads, the destruction of fragile aggregates is limited and the growth of granules goes by coalescence of small aggregates without their preliminary destruction. The charge, pelletized in the vibrofluidized layer, has a more uniform granulometric composition.

Completeness of the pelletizing process is estimated by the indicator “degree of pelletizing” K , which characterizes the proportion of small particles (crumpled fraction of the charge) that went to the formation of shells around the particles playing the role of nucleus of granules:

$$K = m_{-0.4}^{+1.6} / m_{-0.4}^{\Sigma} \quad (1.3.7)$$

where $m_{-0.4}^{\Sigma}$ —quantity of class 0–0.4 mm in sintering charge; $m_{-0.4}^{+1.6}$ —quantity of class 0–0.4 mm in lumps with a minimum size of 1.6 mm.

The efficiency of pelletizing η , which is the result of the operation of the pelletizer drum and the strength of the granules, is determined from (1.3.8):

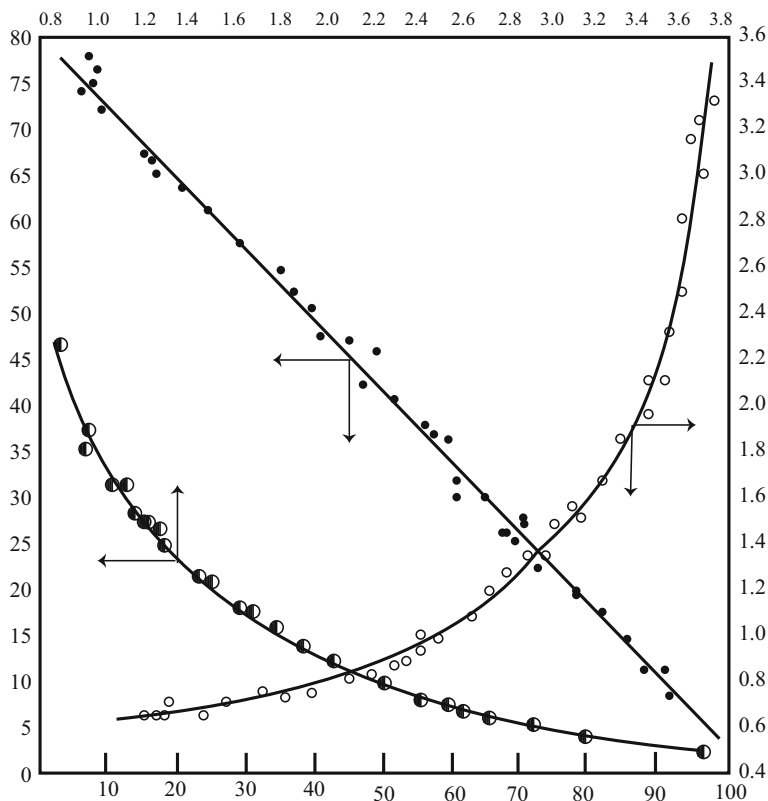


Fig. 1.8 Relationship between the degree of work (The degree of granulation C_b is determined according to Korotich $C_b = [(m - 0.4)^{+1.6}] / [(m - 0.4) \sum]$), the content of the class of 0–1.6 mm and the average equivalent diameter of the granules of the charge (charge of Kachkanarskyi GOK); the abscissa axis is the degree of granulation; ordinate axis—average equivalent diameter of granules [15]

Table 1.8 Comparison of the granulometric composition of the charge obtained by pelletizing in different devices [15]

Pelletization method ^a	W (%)	de (mm)	Granulometric composition (%)				Coefficient of variation
			10.0–5.0	5.0–2.5	2.5–1.6	–1.6 mm	
D	7.10	2.44	21.0	50.5	13.5	15.0	0.56
VF	7.40	3.04	16.0	67.5	10.0	6.5	0.43
D	7.10	3.37	42.5	41.0	9.0	7.5	0.47
VF	7.46	3.37	33.0	52.0	9.0	6.0	0.43

^aPelletizing method: D—drum pelletizer; VF—vibrofluidized layer; W, %—moisture content of the charge (sintering charge of Kachkanarskyi GOK); de—average equivalent diameter of the particles of the pelletized charge; fraction of the charge are specified in mm

$$\eta = ((C^{-1.6})_{in} - (C^{-1.6})) / (C^{-1.6})_{in}, \quad (1.3.8)$$

where $(C^{-1.6})_{in}$ —content of the class minus 1.6 mm in the initial charge, %;
 $(C^{-1.6})$ —class content minus 1.6 mm in the pelletized charge, %.

The role of physicochemical interactions in the “lumped material–water” system

The strength of granules obtained by wet granulation depends on the strength of single contacts between the particles of charge materials, mainly due to the action of capillary forces due to the formation at the points of contact of individual particles of the material of water interlayers of ring shape with the surface of double curvature [16, 17].

The element of the capillary dispersed structure of the clumped material is a pair of solid particles connected by the cuff of the moisturizing liquid (Fig. 1.9a). In the state of static equilibrium, the resultant coupling force, which binds the particles of the moistened lumped material, is determined by the complete surface of the liquid cuff and the fluid pressure [18, 19].

In the general case, the capillary attraction force f_c of two particles connected by a liquid cuff is described by a differential equation of the form:

$$f_c = -2 \cdot V \cdot d \cdot \Delta P_{L-G} / dl + \sigma_{L-G} \cdot (\partial W_{L-G} / dl + \cos \theta \partial W_{S-L} / dl) \cdot \Delta P_{L-G}, \quad (1.3.9)$$

where V —the volume of fluid in the cuff;
 d —the distance between the particles (the diameter of the capillary);
 ΔP_{L-G} —Laplace pressure drop at the liquid–gas interface;
 σ_{L-G} —fluid surface tension;
 W_{L-G} —liquid–gas interface;
 W_{S-L} —solid–liquid interface;
 θ —wetting angle.

The expression for the force of capillary attraction in a simplified form can be written as follows [20]:

$$f_c = \Delta P_{L-G} \cdot W_{L-G} + \sigma_{L-G} \cdot L \quad (1.3.10)$$

where L —wetting perimeter.

Taking into account the structure of the Eq. (1.3.10), it can be noted that the interaction force of moistened particles is the result of two components:

- negative capillary pressure that occurs during the formation of the meniscus of the liquid $F\Delta p$ (1.3.11);

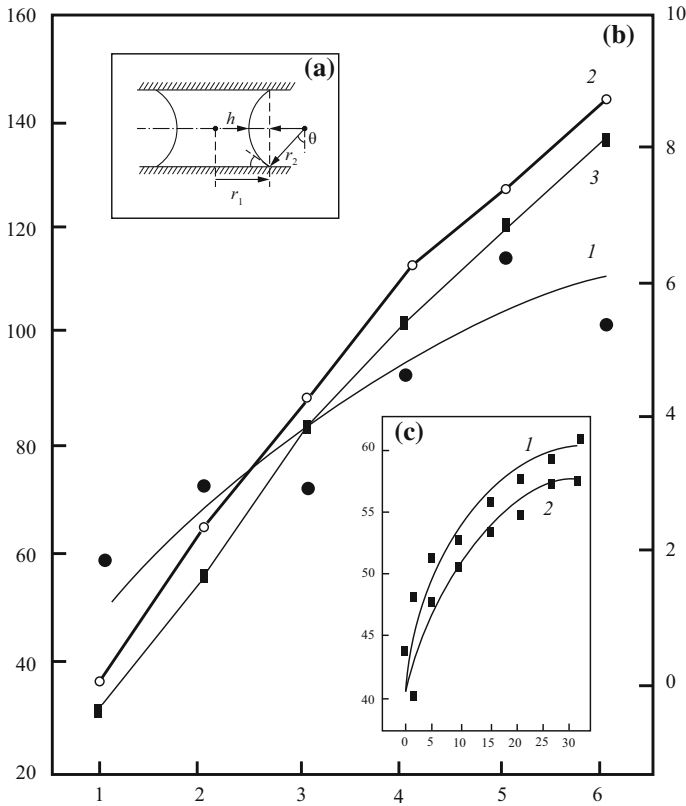


Fig. 1.9 Capillary interaction in the magnetite–magnetite contact system **a** the structure of the contact of two particles connected by a liquid cuff **b** the magnitude of the interaction forces depending on the volume of liquid in the cuff; abscissa axis—the volume of fluid in the cuff, $U_L \times 10^3, \text{cm}^3$; ordinate axis (left)— F_{Σ} , F_L , $N \times 10^5$; ordinate axis (right)— $F_{\Delta p}$, $N \times 10^5$; curves 1— $F_{\Delta p}$, 2— F_{Σ} ; 3— F_L ; **c** the size of the nuclei of granules with drip moisture; abscissa axis—the volume of fluid in the cuff, $U_L \times 10^3, \text{cm}^3$; ordinate axis—the diameter of the nucleus granules with drip moisture, mm; curves 1, 2—calculated values according to the Formula (1.3.18) for cases of wetting with distilled water and an aqueous solution of phenol (concentration $5.45 \times 10^{-3} \text{ mol/l}$); points—experimental values

- surface tension of the moisturizing liquid during interaction on the wetting perimeter F_L (1.3.12).

$$F_{\Delta p} = \Delta P_{L-G} \cdot W_{L-G} = \sigma_{L-G} \cdot (1/r_2 - 1/r_1) \cdot 2 \cdot \pi \cdot r_2 \cdot h \quad (1.3.11)$$

where r_1 , r_2 are the radii of curvature of the liquid meniscus (Fig. 1.9a); h —the height of the meniscus curvature surface (meniscus concavity)

$$F_L = \sigma_{L-G} \cdot L = \sigma_{L-G} \cdot \pi \cdot C \cdot (\cos \theta_1 + \cos \theta_2) \quad (1.3.12)$$

C —capillary length;

$\cos \theta_1, \cos \theta_2$ —wetting angle of the surfaces of the contacting particles.

Transforming (1.3.11) and (1.3.12) on the basis of simple geometric considerations and accepting the assumption of preferential contacts of particles of the same nature (i.e., equality $\theta_1 = \theta_2$), we obtain for $F\Delta p$ and F_L , as well as for the total adhesion force F_Σ following ratios [21, 22]:

$$F\Delta p = 2 \cdot \pi \cdot \sigma_{L-G} \cdot r_2 \cdot (1 - r_2/r_1) \cdot (1 - \sin \theta) \quad (1.3.13)$$

$$F_L = 4 \cdot \pi \cdot \sigma_{L-G} \cdot (r_1 + r_2(1 - \sin \theta)) \cos \theta \quad (1.3.14)$$

$$F_\Sigma = 2 \cdot \pi \cdot \sigma_{L-G} \cdot (r_2 \cdot (1 - r_2/r_1) \cdot (1 - \sin \theta) + 2 \cdot (r_1 + r_2(1 - \sin \theta)) \cos \theta) \quad (1.3.15)$$

Thus, the strength of the capillary interaction of two particles of arbitrary shape (generally parallel plates) or the strength of an aggregate depends (1.3.15) on the magnitude of the surface tension of the moisturizing fluid σ_{L-G} , the degree of hydrophilicity of particles of a crumpled material (wetting angle θ), as well as the wetting perimeter L .

The share of the Laplace force $F\Delta p$ in the capillary interaction of the particles of the crumpled material is small and is not more than 10% of the total adhesion force (curve 1, Fig. 1.9b).

The main contribution to the capillary interaction force is made by the interaction on the wetting perimeter F_L (curve 3, Fig. 1.9b). As the cuff volume increases, the F_L force increases due to an increase in wetting perimeter.

In the process of formation of granules in the sinter charge, the size of the gap between particles of the charge materials is not maintained constant. The change in the distance between the particles affects the ratio of the radius of curvature of the cuff, which will affect the adhesion force of the particles according to (1.3.15). This conclusion is illustrated in Fig. 1.10.

With an increase in the distance between the plates, the force of capillary pressure $F\Delta p$ decreases to the greatest extent (curve 3, Fig. 1.10). Starting from a certain distance (0.7 mm), this force makes a negative contribution to the total adhesion force F_Σ and reduces it.

Due to the fact that the iron ore mixture is the main basic component of the sintering mixture, the interaction processes are considered for the most likely contacts (magnetite–magnetite). When the sintering mixture is multi-component, contacts of particles of various degrees of hydrophilicity are possible, which undoubtedly will affect the force of adhesion of particles (the strength of their aggregates). Table 1.9 presents the calculated by (1.3.13), (1.3.14), (1.3.15) and experimental data for some contact pairs of materials (F_{exp}).

Fig. 1.10 Influence of the distance between the particles on the capillary interaction in the magnetite–magnetite system. The volume of liquid in the cuff $1 \times 10^{-3} \text{ cm}^3$; 1—the total force of interaction F_{Σ} ; 2—the force of interaction on the perimeter of wetting F_L ; 3—the force of interaction from the capillary pressure $F\Delta p$. Abscissa axis—the gap between the plates, mm; ordinate axis (left)— F_{Σ} , F_L , $N \times 10^5$; ordinate axis (right)— $F\Delta p$, $N \times 10^5$

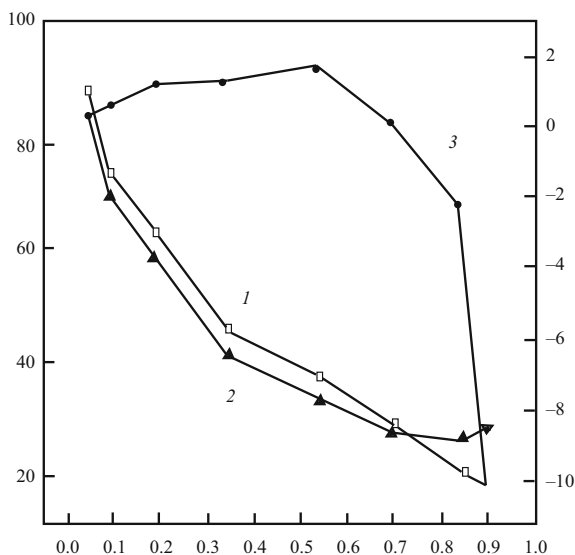


Table 1.9 Magnitude of the forces of adhesion of aggregates at the contact of particles of different nature in the crumpled sintering mixture^a [21]

Material	Contact pair	Capillary length (cm)	Interaction force ($H \times 10^5$)			
			$F\Delta p$	F_L	F_{Σ}	F_{exp}
Magnetite $\cos \theta = 0.42\text{--}0.50$ (± 0.01)	Magnetite	0.147	2.5	33.5	36.0	36.0
	Hematite	0.126	1.9	25.9	27.8	28.0
	Graphite	0.105	—	16.8	16.8	16.5
Hematite $\cos \theta = 0.39\text{--}0.40$ (± 0.01)	Magnetite	0.131	2.5	26.8	29.3	30.0
	Hematite	0.117	1.5	21.5	23.0	23.5
	Graphite	0.084	—	11.5	11.5	11.0
Graphite $\cos \theta = 0.20\text{--}0.25$ (± 0.01)	Magnetite	0.121	2.1	21.3	23.4	23.0
	Hematite	0.105	0.4	14.4	14.8	15.0
	Graphite	0.095	—	8.6	8.6	9.0

^aFor moistening distilled water was used with $\sigma_{L-G} = 72.4 \times 10^{-3} \text{ N/m}$

The volume of fluid in the cuff 10^{-9} m^3

Coke breeze was simulated by graphite due to the inability to obtain a non-porous sample

For the case of contact of plates of the same materials, the force of capillary interaction during wetting (F_{exp}) decreases with an increase in the wetting angle (with a decrease in $\cos \theta$) of these materials: the force of capillary interaction of magnetite plates is $36 \times 10^{-5} \text{ N}$ against $9 \times 10^{-5} \text{ N}$ for graphite plates. When replacing one of the plates with a material having a worse wettability, the force of capillary interaction decreases when going from magnetite to graphite. In other words, the strength of the capillary interaction depends on the hydrophilicity of the materials, and this fact opens up the possibility of controlling the strength of the

Table 1.10 Effect of surfactants in a moisturizing fluid on capillary interaction in a crumpled sinter charge^a

Material	Contact pair	Capillary length (cm)	Interaction force ($H \times 10^5$)			
			$F\Delta p$	F_L	F_Σ	F_{exp}
Magnetite $\cos \theta = 0.64\text{--}0.72 (\pm 0.02)$	Magnetite	0.190	2.2	39.8	42.0	41.5
	Hematite	0.184	1.8	33.0	34.8	34.0
	Graphite	0.147	1.5	25.7	27.2	27.0
Hematite $\cos \theta = 0.45\text{--}0.48 (\pm 0.01)$	Magnetite	0.168	1.5	30.2	31.7	32.0
	Hematite	0.137	1.0	18.7	19.7	19.5
	Graphite	0.116	1.3	16.6	17.9	18.0
Graphite $\cos \theta = 0.37\text{--}0.42 (\pm 0.01)$	Magnetite	0.158	1.8	27.5	29.3	30.0
	Hematite	0.137	2.1	19.6	21.7	21.5
	Graphite	0.137	2.0	18.9	20.9	21.0

^aFor moistening distilled water was used with concentration 5.45×10^{-3} mol/l with

$\sigma_{L-G} = 52 \times 10^{-3}$ N/m; the volume of fluid in the cuff 10^{-9} m³

Coke breeze was simulated by graphite due to the inability to obtain a non-porous sample

pelletized charge through the influence on the hydrophilicity (wettability) of the materials of the sintering charge.

Note that with the deterioration of wetting, $F\Delta p$ remains almost unchanged, as the F_L decreases sharply, which is caused by a decrease in the wetting perimeter.

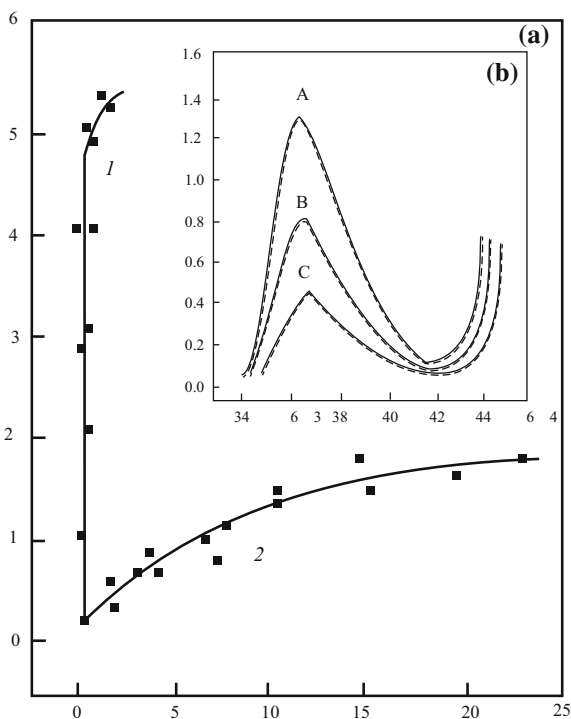
Effect of surfactants on the strength of granules of pelletized charge

One of the methods of improving the wettability of materials is the introduction of surfactants into the moisturizing liquid.

Phenol was considered and studied as a model surfactant. As shown by studies (Table 1.10), the introduction of surfactants proved to be an effective means of increasing the strength of aggregates during pelletizing [22]. At a concentration of phenol in moisturizing water 5.45×10^{-3} mol/l, there is an increase in capillary interaction of all types of contacts. So F_{exp} for contacts “magnetite–magnetite” increased from 36.0×10^{-5} N (when moistened with water) to 41.5×10^{-5} N (when moistened with a solution of phenol), i.e., 15%. To the greatest extent, the capillary adhesion force F_{exp} increased for contacts of magnetite, graphite, and their combinations; to a lesser extent, this affected hematite–hematite contacts.

The increase in the strength of capillary adhesion when moistened with water with surfactant additives is associated with an increase in F_L , while the strength $F\Delta p$ remains almost at the same level, and in some cases even decreases. The increase in the degree of hydrophilicity of materials in the case of humidification with surfactant additives leads to an increase in the length of the capillary (Table 1.10): In the case of contact of magnetite plates, the length of the capillary increased from 0.147 to 0.190 cm. This circumstance led to increased interaction at the wetting perimeter (F_L) from 33.5×10^{-5} N (Table 1.9) to 39.8×10^{-5} N (Table 1.10).

Fig. 1.11 Adsorption isotherms of phenol from aqueous solution on sintering charge materials: **a** 1—magnetite, 2—graphite, $T = 34^\circ\text{C}$; abscissa axis—concentration of phenol in solution, $C_1 \times 10^3$, mol/l; ordinate axis—phenol adsorption value, $n_1 \times 10^5$ mol/g, **b** absorption spectra on hematite of aqueous solutions of phenol, line—initial solutions, dotted line—after 3—day contact; A, B, C—optical path length, respectively, 9.13×10^{-4} m; 5.42×10^{-4} m; 3.05×10^{-4} m; abscissa axis—wave number, $\nu \times 10^3$, cm^{-1} ; ordinate axis—optical density



According to the Young–Dupré equation [23], a decrease in σ_{L-G} should inevitably lead to an increase in $\cos(\theta)$, and for the case of a solution of phenol in water by 1.39 times ($72.4 \times 10^{-3}/52 \times 10^{-3}$); however, this ratio is not maintained for any of the cases (Tables 1.9 and 1.10). Based on the balance of forces at the interface according to Young–Dupré, it can be assumed that the wettability mechanism also has an effect of σ_{L-G} due to the adsorption of phenol at the solid–liquid interface. The fact of phenol adsorption on magnetite and graphite was confirmed experimentally (Fig. 1.11).

Phenol is more actively adsorbed on magnetite than on graphite. In the same range of concentrations, phenol adsorption on hematite could not be detected even after prolonged contact of the material and solution (Fig. 1.11b).

The adsorbent capacity and adsorption intensity as comparative characteristics of the materials studied can be obtained from the parameters of the Langmuir Eq. (1.3.16), which approximates the experimental data Fig. 1.11:

$$n^v = (n_s \cdot b \cdot C_1) / (1 + b \cdot C_1), \quad (1.3.16)$$

where

n^v —excessive adsorption of phenol on sintering charge materials;

C_1 —concentration of phenol solution;

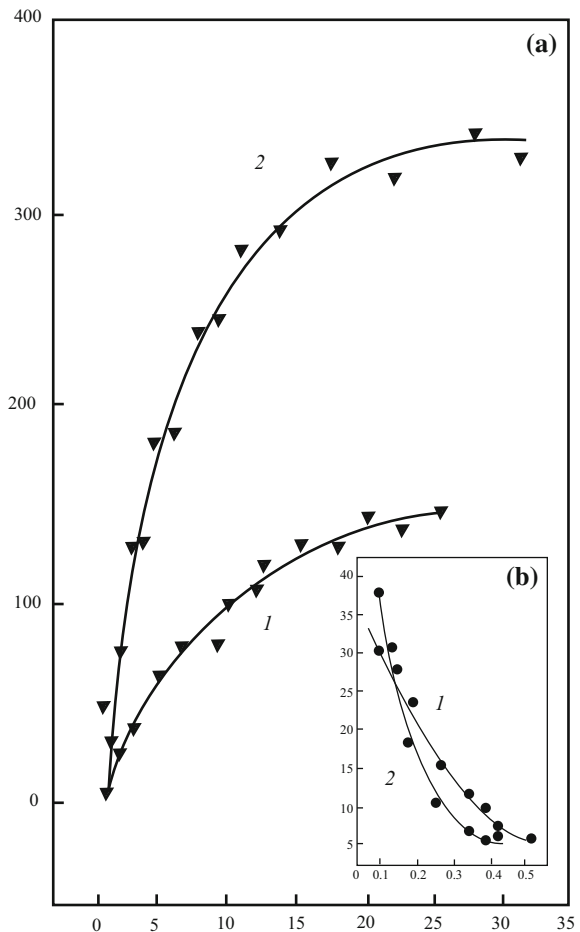
n_s, b —constants: n_s characterizes the capacity of the adsorbent, b is the intensity of adsorption.

The capacity of adsorbent (n_s) on magnetite exceeds the similar value on graphite by 5 times 5.12×10^{-5} mol/g against 1.08×10^{-5} mol/g, and the intensity of adsorption (b) on magnetite is about an order of magnitude higher than on graphite (1.04×10^4 and 0.894×10^3 l/mol).

To identify the limiting element of the wetting process [21, 22], we used the time dependence of the wetting driving force, shown in Fig. 1.12.

The kinetic mode of limiting the spreading of a liquid when wetted (Fig. 1.12b) provides that the main resistance to wetting is exerted by the formation of bonds between the spreading liquid and the material on the wetting perimeter. This is

Fig. 1.12 Characteristics of wetting conditions during pelletizing sintering charge: 1—distilled water; 2—aqueous solution of phenol 5.45×10^{-3} mol/l. **a** The driving force of wetting; abscissa axis—driving force for wetting, $\text{N/m} \times 10^3$; ordinate axis—wetting rate, degree/s, **b** wetting rate; abscissa axis—wetting time, sec; ordinate axis—wetting driving force, $\text{N/m} \times 10^3$



accompanied by a change in the ratio of forces at the interface, which determines the speed of movement of the wetting perimeter, or the rate of wetting. The dependence of the rate of wetting on the driving force of wetting in some cases is described by an exponential, which indicates the activation nature of the spreading.

Pelletizing of sintering charges with the use of surfactants

The acceleration of wetting with the introduction of surfactant into the moisturizing liquid has a positive effect on the redistribution of moisture in the granulated volume, which is especially important in conditions of limited contact time of the moisturizing liquid with the clumped material.

The wetting phenomenon determines, in general, such macrokinetic features of pelletizing as nucleation and growth of granules upon wetting.

To determine the dependence of the size of the nucleus during drip moisturizing on the properties of the solid and liquid phases, as well as the parameters of the drop, we take into account the initial conditions and assumptions:

- The base of the nucleus is a drop of moisturizing fluid with volume U_L .
- The nucleus is the formation of a spherical shape.
- The layer of material is represented by a set of capillaries of the same radius (i.e., it is a porous structure).
- In the process of impregnation, a change in the size of the capillaries does not take place, in other words, the porosity remains constant.
- At the initial moment of time, the volume of the nucleus U_L is zero.

From the equilibrium of forces at the gas–liquid interface, the height of the liquid lift L in the capillary of radius r will be equal to:

$$L = 2 \cdot \sigma \cdot \cos \theta / k \cdot \rho \cdot r \cdot g \quad (1.3.17)$$

where ρ is the fluid density;

g —acceleration of gravity;

k —coefficient taking into account the state of the material surface.

The limiting size of the nucleus under ideal wetting is found from condition (1.3.17). With non-wetting ($\cos(\theta) = 0$), the penetration of fluid into the capillaries is excluded and the volume of the nucleus U_n will be equal to zero.

Taking into account the boundary conditions and the effect of wetting on the movement of the liquid in the capillary, we obtain for the volume of the nucleus:

$$U_n = (2 \cdot \pi \cdot \sigma \cdot \cos \theta / k \cdot \rho \cdot g) \cdot \sqrt[3]{(6 \cdot U_L / \pi \cdot \varepsilon)} \quad (1.3.18)$$

where ε is the porosity of the crumpled material layer.

The size of the nucleus depends not only on the volume of the droplet, but also on the interfacial tension at the liquid–gas boundary and the degree of wettability of the materials.

The calculated values of the nucleus size by (1.3.18) satisfactorily (with an error of not more than 2%) coincide with the experimental data obtained by the “free drop” method, as shown in Fig. 1.9c.

The use of surfactants in moisturizing water for pelletizing has an impact on the critical size of the nucleus by changing the surface tension of the liquid–gas (σ) and the edge wetting angle $\cos(\theta)$. In the layer of loose material, even with uniform moistening, there are volumes of moisture fluctuations, which are potential centers of nucleus formation. A decrease in the critical size of the nucleus, while all other granulation conditions remain unchanged, means that the number of such nuclei in the volume increases due to an increase in the probability of the appearance of a smaller fluctuation volume.

To illustrate the conclusion about the reduction of the critical size of the nucleus, let us describe [24] the process of nucleation during pelletizing in the concepts of nucleation theory during phase transformations developed by Gibbs [25] and used for analyzing dispersion media [26], although strictly speaking, this approach does not apply to similar systems.

The change in Gibbs free energy ΔG_n during the formation of a nucleus is written as follows:

$$\Delta G_n = n \cdot \Delta F + \sigma \cdot S \quad (1.3.19)$$

where n —the number of moles of material in the nucleus;

ΔF —the difference between the molar free energy of the nucleus and the matrix volume of the material;

σ —surface tension of the nucleus phase;

S —surface of the nucleus.

Let's transform (1.3.19) with reference to the crumpled system. The number of moles of material in the embryo of a granule is determined from the equality:

$$n = m/M = \rho \cdot (1 - \varepsilon) \cdot U_n/M = \rho \cdot (1 - \varepsilon) \cdot 4/3 \cdot \pi \cdot r^3/M \quad (1.3.20)$$

where m is the mass of the nucleus;

M —molecular mass of the material being granulated; it is found from the additivity rule for the mineralogical composition of the mixture;

ρ —density of the granulated material (for the charge, the bulk mass should be taken);

ε —porosity of the nucleus;

U_n —the volume of the nucleus;

R —the radius of the nucleus.

Taking into account that during pelletization, the surface of the nucleus is limited by a film of a moisturizing fluid, we assume σ is equal to σ_{L-G} as in (1.3.19).

The traditional thermodynamic equality for the free energy ΔF for the crumpled system, taking into account the invariance of the enthalpy in the pelletizing process and the isothermal nature of the process, will have the form:

$$\Delta F = F_n - F_c = T \cdot (S_c - S_n) \quad (1.3.21)$$

where T —temperature, K;

S_c, S_n —entropy of the charge and of the nucleus.

After substitution (1.3.20), (1.3.21) in (1.3.19), we obtain an expression for the change of the free Gibbs energy:

$$\Delta G_n = (\rho \cdot (1 - \varepsilon) \cdot 4/3 \cdot \pi \cdot r^3 / M) \cdot T \cdot (S_c - S_n) + \sigma_{L-G} \cdot 4 \cdot \pi \cdot r^2 \quad (1.3.22)$$

From the condition $\partial \Delta G_n / \partial R = 0$, we find the radius of the critical nucleus:

$$r_{cr} = (2 \cdot \sigma_{LG} / T \cdot (S_c - S_n)) \cdot (M / \rho \cdot (1 - \varepsilon)) \quad (1.3.23)$$

Thus, from (1.3.23) it follows a definite conclusion about the reduction of the critical size of the nucleus with a decrease in the interphase tension at the liquid–gas boundary caused by the introduction of surfactants into the moisturizing liquid.

The trend of changes in the statistical concentration of nuclei (N) can be estimated from the ratio:

$$N = A \cdot e^{-\Delta G_n / RT} \quad (1.3.24)$$

where A —constant;

R —universal gas constant;

T —temperature, K.

Decrease of the free Gibbs energy (ΔG_n , 1.3.22) with surfactant additives in the moisturizing liquid due to the decrease σ_{L-G} is accompanied by an increase in the number of nucleus according to (1.3.24).

The positive effects due to the influence of surfactants on the mechanism of interphase interactions in the system of crumpled material-moisturizing liquid allowed to develop and offer for commercial use the technology of pelletizing of industrial charge with the use of moisturizing liquids containing surfactants based on phenol in various concentrations and representing almost a waste of metallurgical production (wastewater of coke oven cooling and gas cleaning systems).

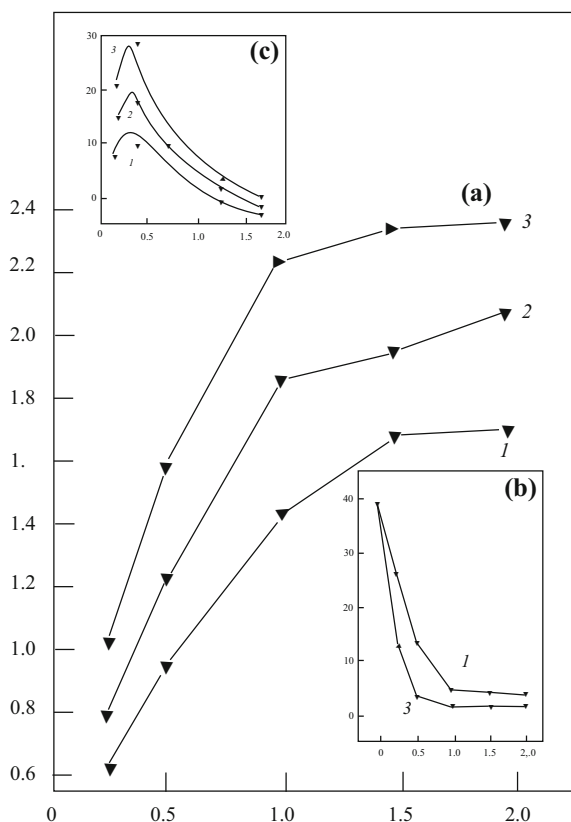
The kinetics of growth of sintering charge granules (e.g., the charge of the sinter plant “Ural steel”) when pelletizing with humidification with various aqueous solutions differing in the content of surfactant (phenol) is shown in Fig. 1.13.

In comparison with the use of recycled water, the use of moisturizing liquids containing surfactants in one or another concentration is accompanied by an increase in the average equivalent diameter of the granule from 1.65 to 2.35 mm

Fig. 1.13 Agglomeration kinetics of the sinter charge moisture mode:

1—circulating water sinter plant; 2—aqueous solution of phenol 5×10^{-3} mol/l; 3—water after ammonia columns (phenol concentration 564.8 mg/l).

a Change in the average equivalent diameter of the granules in time; the x -axis is the time of pelletizing, min; ordinate axis—average equivalent diameter of granules, mm; **b** change in the fraction of 0–0.4 mm during pelletizing; the x -axis is the time of pelletizing, min; the ordinate axis is the content of fraction 0–0.4 mm, %; **c** the growth rate of the granules during pelletizing; the x -axis is the time of pelletizing, min.; the y -axis the growth rate of granules, mm/min



and depends on the concentration of surfactant (phenol). Comparison of the rate constants calculated by the kinetics of changes in the average equivalent diameter shows that pelletizing with surfactants is accompanied by an increase in the pelletizing rate: from 3.57 l/min in the circulating water of the sinter plant against 6.25 l/min when using water with a phenol content of 564.8 mg/l (water after ammonia columns of coke production).

The change in the rate of pelletizing of charge when moistened with solutions with different surfactant content is shown in Fig. 1.13.

The change in the sintering charge pelletizing rate over time (Fig. 1.13c), regardless of the type of moisturizing fluid, has a characteristic dependence, which can be described in three periods (areas):

- The first section is characterized by an increase in the speed of pelletizing from a certain value inherent in each type of moisturizing liquid to a maximum value.
- In the second section, the growth rate of the granules decreases from the maximum value.
- The third phase is distinguished by the invariance of the rate of growth of the granules at the level, characteristic for each type of the moisturizing liquid.

At the same time, although at the second and third areas a higher growth rate of granules with surfactant additives is maintained, the difference in speeds is insignificant. Consequently, the defining stage is the initial pelletizing stage, described by the first portion of the curve.

The maximum speed of pelletization of the charge, moistened with water with a surfactant, is achieved two times faster than when moistened with circulating sintering plant water (23 and 45 s). The shift of the maximum growth rate of the granules to the ordinate axis indicates an increase in the number of nuclei in the volume of the material being granulated, which is confirmed by a decrease in the content of the crumpled fraction of 0–0.4 mm with time (Fig. 1.13b).

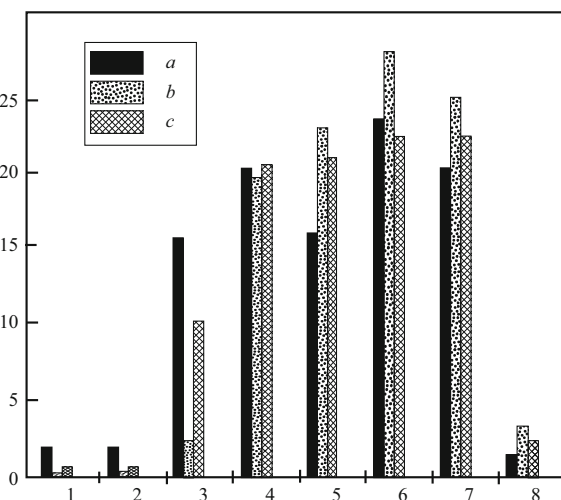
The strength of the aggregates, moistened with water and surfactants, is 16% higher compared with moistening with water (modeled on briquettes).

Changing the macrokinetic parameters of granulation with the introduction of surfactants leads to a more uniform particle size distribution (the coefficient of variation of the particle size distribution of the charge, pelletized with the use of water after ammonia columns, is 51% less than for the mixture, pelletized using recycled water (Fig. 1.14).

Summarizing, it should be noted that the introduction of surfactant into the moisturizing liquid qualitatively changes the mechanism of the charge pelletizing as a result of the impact on the interphase processes:

- nucleus formation (the critical size of the nucleus decreases and the number of nucleus per unit volume of lumps increases);
- kinetics of granule growth (increased growth rate, more uniform granulometric composition is formed);
- increases the strength of the granules.

Fig. 1.14 Granulometric composition of the mixture pelletized with the use of surfactants. **a** Recycled water of sinter plant; **b** aqueous solution of phenol 5×10^{-3} mol/l; **c** water after ammonia columns; abscissa axis—designation of fractions: 1—0 to 0.4 mm, 2—0.4 to 0.63 mm, 3—0.63 to 1.0 mm, 4—1.0 to 1.6 mm, 5—1.6 to 2.5 mm, 6—2.5 to 5.0 mm, 7—5.0 to 8.0 mm, 8 to >8 mm; ordinate axis—fraction content, %



The patterns found on one of the surfactants (phenol) are general and applicable to any other surfactants that are appropriate for use in pelletizing technologies.

Pelletizing of sintering charges with the use of additives

Involvement in the extraction and processing of increasingly poorer iron ores, the development of technologies for their deep enrichment to produce fine concentrates, increasing the share of such concentrates in the sinter charge increasingly complicate the technology of pelletizing sinter charge.

Various researchers and practitioners [27] attempted to improve the quality of pelletizing of charge with a high content of concentrates by introducing special binding additives regardless of the pelletizing mechanism: aqueous solutions of polyacrylamide (up to 1.5 kg/t of the charge); sodium humate (up to 70 kg/t of the charge); polyvinyl acetate (up to 50 kg/t of the charge); liquid glass; sulfite liquor; iron sulfate; fuel oil heated to 60–70 °C (0.25–1% of the charge mass). However, these additives did not become commercially available for various reasons: the lack of proper theoretical justification in terms of the limiting mechanism of influence, due to the relatively low efficiency, complexity of the technological scheme, for reasons of negative impact on the environment and subsequent processing, in some cases due to high prices.

The quality control of pelletizing should be based on the pelletizing mechanism and should be directed to:

- (1) strengthening of the interfacial interactions due to the improvement of wettability (additives in moisturizing water surfactants);
- (2) changes in the ratio of crumpling and crumpled fractions towards their optimization;
- (3) increase the strength of granules of pelletized charge.

The mechanism of interphase interactions and its management to increase the efficiency of pelletization (position 1) is discussed above, and then we will focus on additives that contribute to the implementation of positions 2 and 3.

The practice of agglomeration confirmed that the preferred options for additives for these tasks are either natural ore materials with proper properties, which should rather be considered as components of the charge, rather than additives (e.g., aluminosilicates or hydrohematite ores), or specially made products from natural non-metallic materials (e.g., lime).

The introduction of aluminosilicates in the sintering charge

The strength of the granules of the sintering mixture can be significantly adjusted by introducing colloidal or colloid-forming additives, in other words, dispersed components (with a particle size of less than 0.01 mm) having binding properties.

Magnetite concentrates usually contain few such particles due to the fact that they are washed out during wet magnetic enrichment; therefore, the addition of natural ores containing clay waste to such concentrates has a positive effect on the pelletization of the charge. According to [28], the addition of 25% alumohematite

Table 1.11 Pelletization efficiency of mix^a containing polydisperse martite and hydrohematitic ores

Additives	Share (%)	Crumpling ratio (%)	
		Moisture content 10%	Moisture content 12%
Without additives	0	33.7	40.5
Martite ore	15	44.9	92.4
	30	55.2	93.8
	45	50.4	89.6
Hydrohematite ore	15	38.3	81.4
	30	43.2	92.3
	45	35.7	85.1

^aThe mixture is based on iron ore concentrate of KMA

ore to iron ore concentrate produced by magnetizing roasting enrichment made it possible to improve the gas permeability of the pelletized charge layer and raise the vertical sintering rate by more than 50% due to the formation of a gel when the thinnest $\text{Al}(\text{OH})_3$ particles interact with water.

Application of ore of martite and hydrohematite nature

In order to reduce the yield of small fractions during pelletizing of sintering charge containing finely dispersed iron ore concentrates, it is advisable to add polydisperse martite and hydrohematitic ore fractions of minus 5 mm in an amount of 15–30% by weight, which improves the pelletization of the charge (at optimum humidity) by 2.0–2.3 times (Table 1.11) [29] due to the correction of the ratio of the crumpled and crumpling fractions (in the martite ore about 17% of the crumpling fraction (+1.6 mm), in hydrohematitic—more than 20%, Table 1.12).

Table 1.12 Granulometric composition of martite and hydrohematitic ores of fraction minus 5 mm

##	Size (mm)	Yield (% mass)	
		Martite ore	Hydrohematitic ore
1	−5.0 + 2.5	6.20	10.20
2	−2.5 + 1.6	10.53	10.46
3	−1.6 + 0.63	13.64	16.33
4	−0.63 + 0.25	10.23	15.47
5	−0.25 + 0.14	11.13	19.55
6	−0.14 + 0.071	11.84	12.03
7	−0.071	36.41	13.96
Total		100	100

To assess the efficiency of the charge pelletization, the index “lumpiness coefficient” $K = ((m + 1.6)_2 - (m + 1.6)_1) \cdot 100 / ((m + 1.6)_2 + (m + 1.6)_1)$ is used, where $(m + 1.6)_2$ and $(m + 1.6)_1$, respectively, the mass of the fraction +1.6 mm in the charge after pelletizing and in the initial charge

Addition of lime in sintering charge

Lime is a product of dissociation of calcium carbonate (limestone) CaCO_3 at high-temperature (1000–1200 °C) firing. There are calcined lime (CaO) and hydrated lime (slaked lime) $\text{Ca}(\text{OH})_2$, obtained from calcined lime by treating it with water.

The first experiment of the application of lime for pelletizing the charge was made by Ural scientists [27], and later the efficacy of lime was confirmed by German scientists [30]. The widespread industrial application of lime in the pelletization of the sinter charge in order to intensify the process began in the 1950s of twentieth century.

The action of lime in sintering charge is determined by many factors, first of all, the quality of lime. To assess the quality of lime, a number of indicators are used:

- the degree of calcination of lime $\zeta = (\text{CaO} + \text{MgO})_{\text{act}}/(\text{CaO} + \text{MgO})_{\text{total}}$, where
- $(\text{CaO} + \text{MgO})_{\text{act}}$ —CaO and MgO content (% wt.) capable of hydrating with water heated to 60–70 °C at an exposure of 5–7 min and slow cooling (GOST 9179-77); in relation to sintering, lime activity should be determined under conditions close to real temperatures [31] (i.e., the water temperature should not exceed 20–25 °C);
- $(\text{CaO} + \text{MgO})_{\text{total}}$ —the content of CaO and MgO (% of the mass) in the calcined product (for high-grade lime content $(\text{CaO} + \text{MgO})_{\text{tot}}$ must be higher than 90%;
- the yield of lime paste—the volume of the mixture when mixing quicklime with water; high-quality lime has this indicator not lower than 2.5–3.5 l/kg of lime;
- reactivity is measured by the quenching time from the moment of mixing with water until the maximum temperature of the mixture is reached: Soft-burned lime has a quenching time of 0.75 min, medium-burnt—8 min, hard-burnt—36 min.

Depending on the firing mode, it is possible to obtain soft-calcined lime (calcination temperature 950–1050 °C), medium-calcined (calcination temperature 1050–1200 °C), and hard-calcined (calcination temperature more than 1200 °C).

Lime affects both interfacial processes and, to a greater extent, the content of the binding colloidal fraction resulting from the self-dispersing of lime when it is mixed with water. The action of this mechanism is confirmed by the fact that the most effective use of lime is for blends containing a high proportion of finely divided concentrates with a minimum content of colloidal components. The increase in strength of granules of the pelletized mixture, as well as during sintering (in areas of waterlogging and drying), is caused by hydration hardening according to the scheme—removal of moisture, crystallization, and partial carbonization of calcium hydroxide.

The consumption of lime in the sintering charge to achieve optimal indicators of pelletizing is also due to its granulometric composition: The finer the lime, the smaller its consumption is required in the sintering charge that can be described by statistical dependence [31]:

$$\text{CaO}_{\text{act}} = 220 \cdot S_{\text{ir}} / (S_{\text{l}} + 3.64 \cdot S_{\text{ir}}) \quad (1.3.25)$$

where CaO_{act} —the required amount of active CaO in the charge;
 S_{ir} , S_{l} —specific surfaces of iron and lime ore part of the charge.

The use of quicklime is associated with the problem of ensuring the maximum assimilation by the lime of the moisture of the charge before it begins to work. The use of lump quicklime requires its aging with charge materials for at least 1–2 days; preliminary grinding of lime to minus 3 mm (and wetting of batch materials up to 6–8%) reduces the required holding time to 3–5 h.

In order to achieve the greatest efficiency with maximum absorption of moisture from the application of lime, technologies are being developed to feed it to the sinter blend [31]:

- joint supply of iron ore and lime to the loading hopper, then to the pallets of sintering machine;
- lime feed to the concentrate stack (associated effect—drying of the concentrate, which makes it a free-flowing and easily dosed component);
- spraying of water over a layer of lime laid on the sintering charge (the degree of hydration of lime increases from 67 to 83%);
- supply of lime in a mixture with sintering sludge after its layering in the ore yard and maturing the mixture for 8 days (lime consumption is 20% by weight of the sludge, and the sludge mixture in the charge 58–60 kg/t of the sinter; it was noted that up to 40% of the granules of the pelletized charge have a nucleus from the sludge mixture);
- introduction to the composition of the prepared slime–limestone mixture [32];
- spraying (consumption 0.7%) or rolling lime on pellets of the pelletized mixture in the pelletizer (with an additional supply of 1–2% of water);
- mixing of freshly burnt lime with coke fines with moisture up to 15–20% and holding the mixture for 2–3 h (at a rate of 10 kg/t of sinter); the method is particularly attractive for dispersed coke fines: Slaked lime is added to the mixture of coke and anthracite (with a particle size of minus 0.125 mm), the mixture obtained is pelletized (up to 0.5–3 mm) and together with the fuel (fraction plus 0.125 mm) is introduced into the sintering charge.

Along with conventional lime, other lime-based additives can be used in the sintering charge:

- crushed iron flux obtained by firing a mixture of lime (limestone) and iron-containing materials;
- dolomitic and magnesia lime; the ratio of CaO: MgO is recommended to be taken as (60–95)/(30–2), and the burning temperature of limestone should be maintained within 900–1000 °C; to obtain hydrated magnesia lime, it is proposed to burn dolomite at 900–1100 °C, hydrate, and add 0.7–7% in the total charge;
- the complex fluxing additive containing 30–60% of waste of production of acetylene or lime (80–90% CaO), 10–40% of waste of the burned dolomite

- (25–65% CaO and 25–50% MgO), to 15% of waste of fluorite (50–55% Ca and 40–45% F), no more than 20% of calcium hexaortosilicate, up to 10% of bentonite; all components of fineness of 0–5 mm in dry form mix within 8–10 min., then add 7–10% water and pelletized;
- complex additive with a size of not more than 4 mm and a flow rate of 0.5–6% in the composition: pseudogranulated steelmaking slag, quicklime (up to 1%) and slaked lime (up to 15%), gypsum, dolomite.

Pre-granulation of materials as a pelletizing stage

Improving the properties of the pelletized mixture can be achieved by using the technology of producing mini-pellets with preliminary, combined, selective granulation or HPS techniques. Distinctions of the specified technological receptions are reflected in Fig. 1.15.

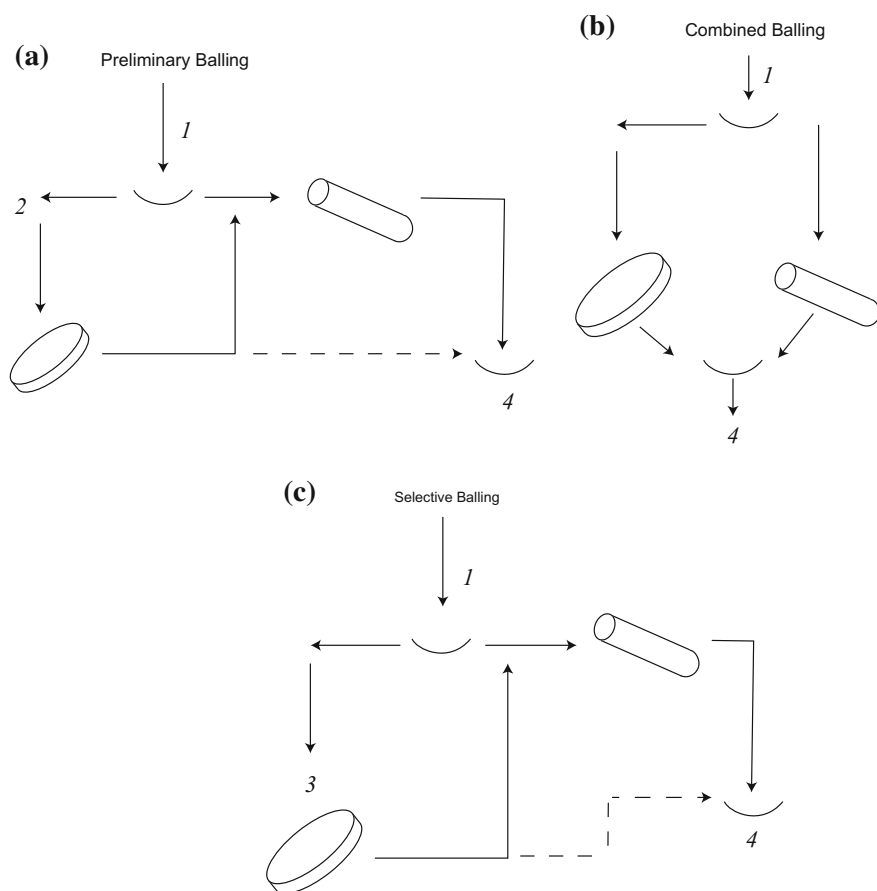


Fig. 1.15 Differences in technological methods of pre-granulation. **a** Pelletizing of the fine part of the charge; **b** combined pelletizing; **c** selective granulation; 1—flow charge; 2—part of the flow of the charge; 3—a separate component of the charge; 4—pelletized charge on the sintering machine

During pre-granulation, the finely divided part of the charge is usually pelletized to a particle size of 2–9 mm (mini-pellets); then it is mixed with the other components of the sintering charge, as a rule, before the drum pelletizer (Fig. 1.15a).

In the combined technology of pelletizing, the charge flows are granulated in parallel in different units and mixed only when fed to the sintering machine (on a conveyor), (Fig. 1.15b).

In the case of selective granulation, a separate component is separated from the sintering flow (usually with poor lumping properties) and granulated separately, and then mixed with the main flow of the charge in the drum pelletizer (Fig. 1.15c).

Combination granulation of the sinter charge

Centrifugal forces, gravity forces, and friction forces act on a flow of sintering mixture moving in a drum pelletizer, providing a sealing effect on the granule. It is possible to conditionally characterize the work of compaction during granulation using the dimensionless index R_d .

$$R_d = k_d \cdot d_{av} \cdot n / \sqrt{D^2 \cdot \tau} \quad (1.3.26)$$

where k_d —coefficient taking into account the proportion of time spent on compaction of the granules;

d_{av} —weighted average diameter of granules, m ;

n —rotational speed, s^{-1} ;

D —diameter of the granulating device, m ;

τ —the residence time of the charge in the pelletizer, s .

The increase in the sealing effect on the granules of the charge contributes to the growth of the number of durable granules that form without germinal centers from the aggregating fraction of the mixture (nuclei of type B).

A feature of the drum pelletizer compared with a disk granulator is a reduced proportion of time spent on pellet compaction ($k_d = 0.1$ for a drum pelletizer and $k_d = 0.5$ – 0.6 for a disk granulator) [33].

In addition, in terms of dynamic loads along the length of the drums, pelletizers do not meet the requirements of hardening of the granules, since the granules approach the discharge section, the dynamic loads decrease in accordance with the decrease in the degree of filling of the drum with the charge (Fig. 1.16).

For these reasons, a plate granulator was chosen as an additional apparatus for granulation. Setting up his work was carried out according to the experimental empirical dependences of the weighted average diameter of the granules (d_{av}) on the moisture content of the charge (W , %), the performance of the granulator (P , t/h), the angle of inclination of the plate (α , degrees), and its rotation frequency (n , $\min^{-1}$):

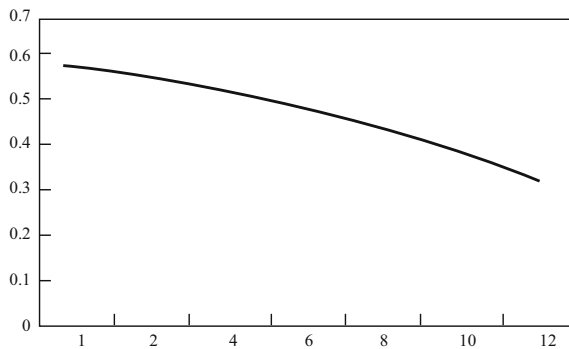


Fig. 1.16 Distribution of the charge along the length of the drum pelletizer. Drum diameter 3.2 m, length 12.5 m, rotation speed of 5 1/min, tilt angle $3^{\circ} 30'$, the load on the charge 360 t/h [33] Y-axis—thickness of the charge layer (in “m”), measured along the length of the drum; the abscissa axis is the length of the drum

$$d_{av} = -0.0048 \cdot P^2 + 0.364 \cdot P - 2.94 \quad (1.3.27)$$

$$d_{av} = -0.257 \cdot \alpha^2 + 2.558 \cdot \alpha - 59.72 \quad (1.3.28)$$

$$d_{av} = -0.1200 \cdot n^2 + 2.290 \cdot n - 6.93 \quad (1.3.29)$$

$$d_{av} = -2.9630 \cdot W^2 + 45.53 \cdot W - 171.07 \quad (1.3.30)$$

The results of comparative laboratory studies [33] of the efficiency of charge pelletizing in the drum pelletizer and disk granulator are summarized in Table 1.13.

As follows from Table 1.13, an increase in the weighted average diameter of the granules occurs due to an increase in the fraction of 3–5 mm and a decrease in the content of the fraction minus 1.25 mm. The weighted average diameter of the charge granules obtained on a disk granulator is 6.0–20.4% larger than that of the charge after the drum pelletizer. At the same time, the indicator of compaction operation is significantly higher when a disk granulator is operating, rather than a drum pelletizer. In industrial condition, the technology of combined granulation is implemented on the complex of sintering machine AKM-312 in the sinter production of NLMK, Russia [33]. To service the pelletizing line of the sintering charge, three disk granulators were installed (a plate diameter of 3.5 m, a bowl inclination angle of 45° – 53° , and a rotation frequency of -12 1/min). The pelletized charge from the granulators and drum pelletizers was fed to a collecting conveyor and a shuttle distributor for loading onto the sinter machine.

Selective granulation of limonite ores with poor sintering characteristics

The need to involve limonite ores in processing is due to their local prevalence, increased consumption of iron ore, and depletion of high-quality iron ore reserves.

Table 1.13 Results of granulation of the mix in the drum pelletizer and disk granulator

Parameter	Initial charge			Pelletized charge					
				Drum pelletizer			Disk granulator		
	Mass fraction of concentrate in iron ore part of charge (%)								
	60	80	100	60	80	100	60	80	100
Fraction content (%)									
<1 mm	34	38	45	5	11	20	2.5	4	5
1–2 mm	15	18	17	17	24	16	7.5	11	12
2–3 mm	12.5	8.5	8	17	14	15	19.5	16.5	16
3–5 mm	11	9.5	8	13.5	13	11	14.5	18.5	14.5
5–7 mm	5.5	9	11	7.5	8	18	33	31	29.5
>7 mm	22	17	11	40	30	20	23	19	23
d_{av}^a , mm	3.35	3.10	3.16	5.10	4.32	3.94	4.44	4.86	4.91
R^b , conv. units	–			3.75	3.18	2.9	5.65	5.35	5.40

^a d_{av} —weighted average diameter of granules^b R —densification performance indicator

Limonite ores contain a lot of alumina and bound water and are represented by quite dispersed fractions, which together cause complications of the sintering process. One of the methods for solving the problem of using limonite ores is their selective granulation [34]. Dispersed limonite ore is separated by a stream from the other charge materials into the granulator to form small granules, the so-called pseudoparticles (Fig. 1.17). Such a preparation scheme prevents the alumina from negatively influencing the formation of the liquid phase and removes restrictions on the use of limonite ores.

Since part of the dispersed limonite ores with a particle size of less than 3 mm contains plastic clay, they can be easily granulated (without adding a binder) when

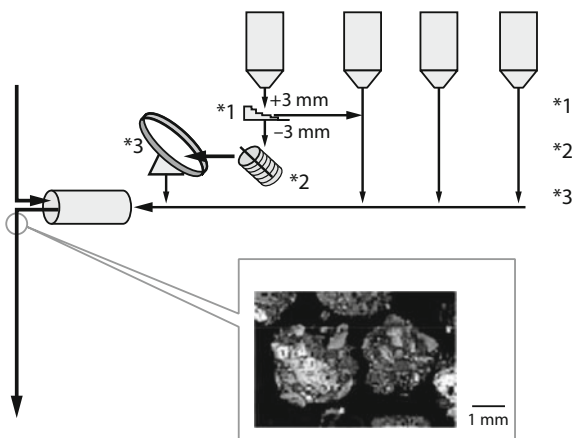
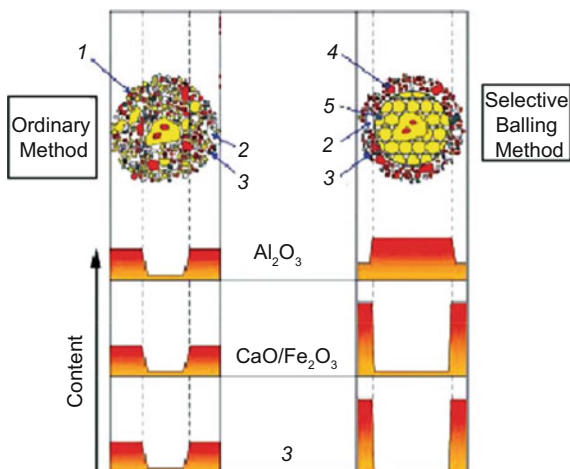
Fig. 1.17 Scheme of selective granulation of limonite ores [34] 1—screen, 2—high-speed mixer, 3—disk granulator

Fig. 1.18 Structure of pseudoparticles obtained by selective granulation [34]

1—Hematite + limonite;
2—limestone; 3—coke breeze;
4—hematite with a low content alumina;
5—limonite ore with a high content of alumina



moistened. Further, pelletization is completed by the formation of granules with a size of 2–5 mm, in which the alumina will be placed inside (Fig. 1.18), and the granule will thus acquire a two-layer structure.

The results of the local X-ray analysis of a two-layer granule showed that during the sintering reactions, the two-layer granules have a very positive effect on the formation of the molten liquid phase and sinter:

- A low concentration of alumina in the outer layer and a high concentration of limestone lead to the formation of a significant amount of fluid-flowing molten liquid phase at lower temperatures compared with the temperatures that occur in the conventional method of work.
- The liquid phase penetrates into the gaps between the ore particles and into the voids inside the particles and acts as a binding agent, which ensures their hardening.

1.4 Mass Exchange Processes in the Sintering Layer

The complexity of the sintering mixtures, the multi-phase nature of each component, the gas phase of an alternating composition during sintering, the elevated and high temperatures in the layer cause a variety of chemical interactions leading to the transformation of the charge system (mechanical mixture of components) into an agglomerated product with a mineralogical composition different from the composition of the charge components.

Depending on the temperature interval in which physicochemical processes take place during sintering, it is advisable to distinguish three significant groups [35]:

- chemical transformations in solid phases in the interaction between the solid phases and the gas phase, as well as between the solid phases (in the temperature range 500–1200 °C);
- processes occurring during the formation of the liquid phase (melting, temperature range 1200–1500 °C);
- processes during solidification (crystallization) of the melt (in the temperature range of 1500–1000 °C).

The mass transfer processes in the sintering layer during sintering, indicated above, can be summarized according to [4] by the scheme shown in Fig. 1.19.

Strictly speaking, for the case of mass transfer in the physicochemical processes taking place in the sintering layer, one can only talk about the qualitative picture and conditions of the reactions, and due to the significant heating rates and short sintering cycle, there is no point in talking about the kinetic parameters.

We briefly describe the main physical and chemical processes (Fig. 1.19).

1.4.1 Chemical Reactions with Participation of Solid Phases

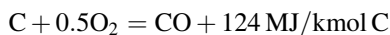
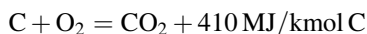
The combustion of solid fuels is one of the processes determining the thermal side of a sintering. On the one hand, the combustion of fuel in the sintering layer can be considered according to the regularities of layer combustion, on the other hand, due to the discrete nature of its distribution in the layer (with a consumption of solid fuel of 4–6%, the volume fraction of carbon in the charge will be 12–20% depending on the share of concentrate) as the burning of an individual particle. The structure of the sintering layer with discretely distributed carbon is shown in Fig. 1.20.

Combustion of solid fuel precedes the stage of drying and removal of the volatile organic part (usually removed with the exhaust gas), the resulting coke residue interacts with the oxidizing reagents.

By the volume of filtered air, the sintering process refers to combustion technologies with a significant excess of air (excess air ratio $\alpha = 1.5$ –2.0). At the same time, in a layer with discretely distributed carbon, there is a probability of limiting the oxidizer's access to the fuel particle (oxygen deficiency in the combustion zone, e.g., flows 1, 2, 3, 4 in Fig. 1.20).

In general, the combustion of carbon can be described by three processes [11]:

- reaction with oxygen (actually burning)



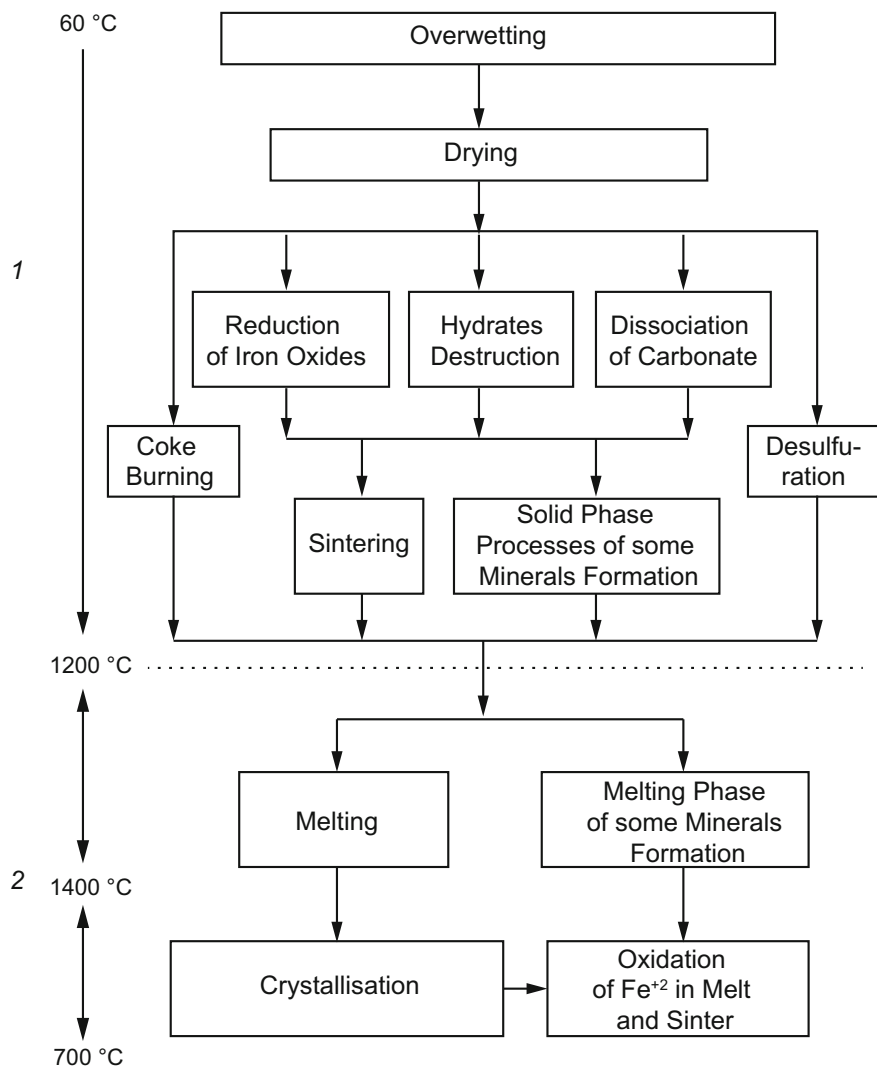


Fig. 1.19 Mass-exchange processes in the sintering layer [4]. 1—processes in the layer of solid ore material; 2—processes involving iron silicate melts

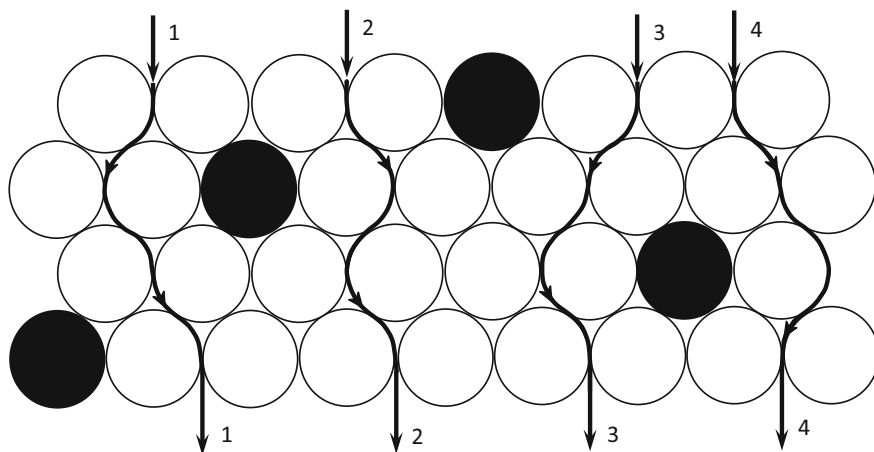
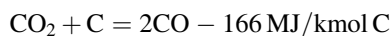
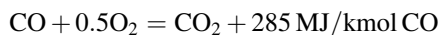


Fig. 1.20 Distribution of fuel particles in the sintering layer. Dark—fuel particles, white—particles of charge materials; 1, 2, 3, 4—filtered airflows ($O_2 + 3.76N_2$)

- decomposition of carbon dioxide



- oxidation of carbon monoxide



At the moment, the point of view about the formation of primary products of carbon combustion in the form of carbon–oxygen complexes is generally accepted.

The formation of CO in the combustion processes of solid fuels is due to the mechanism of chemical interaction of carbon, which differs in location in the carbon structure (single, double, and triple valence bonds). Three options [36] are possible for the formation and desorption of intermediate carbon–oxygen complexes C_xO_y depending on the valence state of carbon (Fig. 1.21), reflecting its position in the structure of solid fuel.

The decay of carbon–oxygen complexes is accompanied by the formation of two products CO and CO_2 . The final composition of the off-gas is formed depending on the ratio of the positions of carbon (i.e., the yield of CO and CO_2 in the chemical reaction) and the potential oxidation of CO. These two processes determine the CO/ CO_2 ratio in the off-gas. During sintering of sinter charges, the CO/ CO_2 ratio is 0.2–0.4 [1.2]. The stability of the CO/ CO_2 ratio reflects both the mandatory presence of CO in the off-gas and the possibility of controlling the CO content in it.

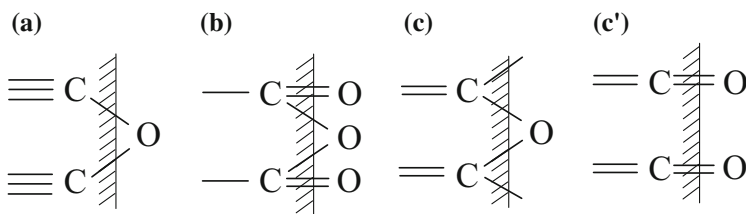


Fig. 1.21 Structure of carbon–oxygen complexes formed during solid fuel combustion [36]. **a** Carbon with triple valence bond, **b** carbon with single valence bond, **c** and **c'** carbon with double valence bond (variants)

In experiments on fuel combustion in a layer of inert material [4, 11], it was confirmed that the ratio of CO/CO_2 in combustion products increases under the following conditions:

- increase in the content of solid fuel (carbon) in the sintered layer;
- reducing the size of solid fuel;
- an increase in the reactivity of solid fuels (the structural positions of carbon in solid fuels (Fig. 1.21) are determined by its nature (reactivity), as well as fractional composition).

The empirical dependence of the ratio of CO/CO_2 on fuel consumption for sintering and particle size of its particles was obtained [37]:

$$\text{CO}/\text{CO}_2 = 0.393 + C_c(0.148 - 0.031 \cdot d_c), \quad (1.4.1)$$

where C_c —carbon content of fuel in the charge;
 d_c —the size of the fuel particle.

The flow of oxidizer (air oxygen) into the layer and its delivery to the fuel particles are determined by the gas-dynamic characteristics of the sinter layer (permeability conditions), which depend on the initial granulometry of the charge components, the characteristics and quality of pelletizing, loading conditions for the charge on the tape, sintering conditions layer height, the method of laying the charge on the tape, the presence of the bed, the presence of onboard outlets, the state of the grate field, etc.). These factors significantly affect the completeness of carbon oxidation and constitute a reserve for reducing carbon monoxide emissions.

Combustion of solid fuel (coke breeze) in the sintering layer occurs in a narrow zone, the width of which can vary according to the sintering conditions within 10–40 mm (the most probable value is 25 mm), i.e., in the conditions of short-term stay of the reaction system in the high-temperature zone (for the gas phase not more than 10 s). The completeness of the interaction of carbon with the oxidant can be achieved both by intensifying the processes on the surface of the fuel particle (sorption–desorption) and by oxidizing CO in the gas phase.

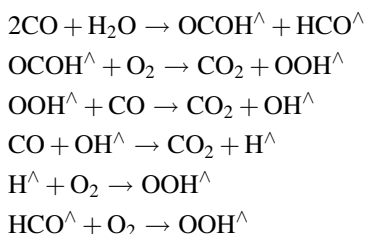
Thus, the formation of carbon monoxide in the sintering layer during fusion is a consequence of incompleteness of combustion processes in thermodynamic (under the conditions of equilibrium of the gas phase composition) or kinetic aspects.

The CO afterburning conditions are due to both the delivery of the oxidant and the time of its contact with CO, which should be revealed by the dependence of the CO/CO₂ ratio on the gas flow rate (filtration rate). In our opinion, this relationship should be extreme: In the area of low filtration rates (0.2–0.3 m/s) with an increase in ω , the CO/CO₂ ratio decreases due to improved oxygen supply, when going to higher filtration rates (more than 0.3 m/s), the CO/CO₂ ratio increases due to the restriction in this case of the contact time of CO with oxygen in the combustion zone.

To improve the conditions of CO afterburning in the sintered layer, special measures can be taken, for example, by moistening the gas flow entering the combustion zone.

It is known [35] that the interaction between CO and oxygen stops completely in the dry gas mixture and, on the contrary, accelerates proportionally to the square root of the water vapor concentration in the gas mixture.

In the presence of water vapor, the chain reaction of combustion [36] is carried out through the formation of active radicals (marked with ^) according to the scheme:



The intensification of interaction in the supply of water vapor to the gas phase is explained by the participation of active radicals that facilitate the formation of CO₂ during co-combustion.

The positive effect of water vapor on the combustion reactions of gases and solid fuels is a well-known fact [35, 36]. Recently, there has been information [38] about the laboratory testing of the technology of water vapor supply over the sintered layer and the full-scale testing on the sinter machine with water spraying over the layer. It is noted that in the pilot mode, the concentration of CO in the tail vacuum chambers of the sintering machine decreased by two orders of magnitude.

Laboratory experiments on sintering iron ore charge with the supply of fine-atomized water and steam over the sintered layer with the control of the composition of the off-gases (CO, CO₂, NO_x, and SO₂) showed that the water supply is accompanied by a decrease in the concentration of CO in the main sintering period (Fig. 1.22) and provides a reduction of CO emissions during the sintering period by 22%.

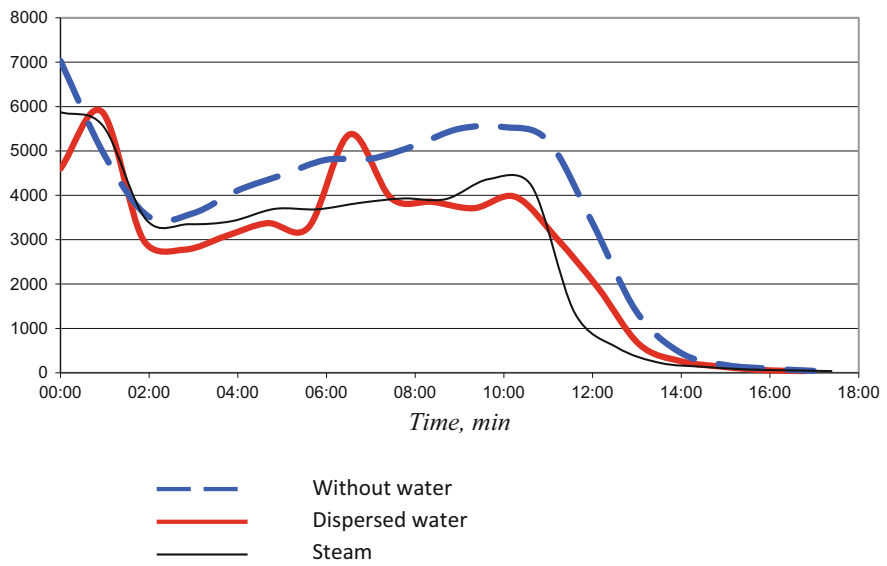
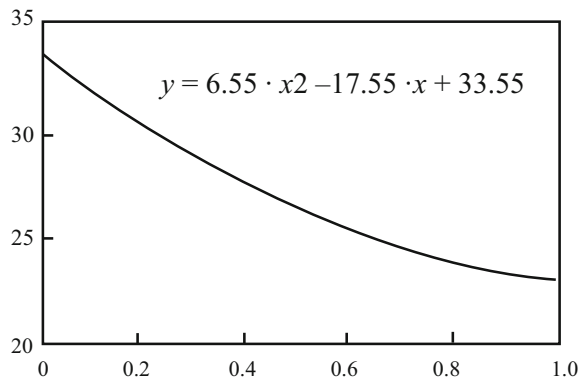


Fig. 1.22 Efficiency of water and steam supply during the sintering period. Y-axis—CO concentration in flue gas, ppm

Fig. 1.23 Relationship between the ratio of CO/CO₂ and the net calorific value [4]. The abscissa axis is the CO/CO₂ ratio, fractions (x); Y-axis—net calorific value, kJ/kg carbon (y)



The CO/CO₂ ratio decreased from 0.34 (in the case of sintering without water supply) to 0.28 for both water and steam.

The ratio of CO/CO₂ reflects the completeness of fuel combustion in the layer, and its increase is accompanied by a decrease in the heat of fuel combustion (and heat transfer to the layer). The relationship between these characteristics obtained by calculation is shown in Fig. 1.23.

The duration of combustion of the fuel particle and the intensity of heat release determine both the temperature level of the sintering process and the residence time of the charge micro-volumes in the high-temperature zone.

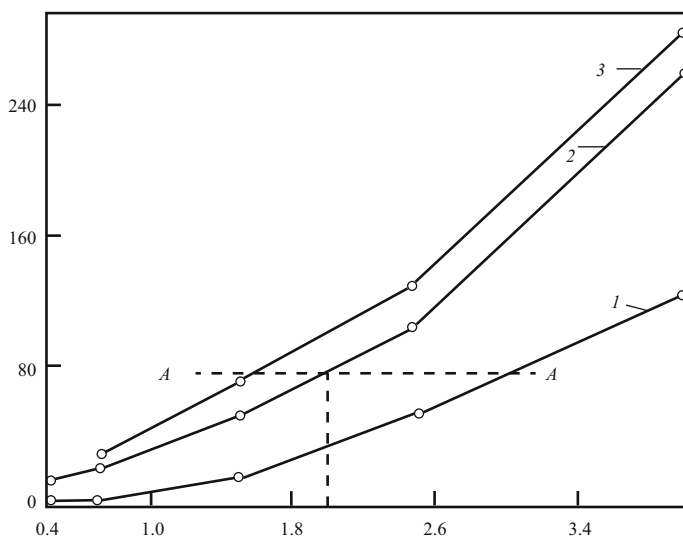


Fig. 1.24 Effect of particle size on the burn-up time [11]. 1—brown-coal semi-coke, 2—coke breeze, 3—anthracite culm. The abscissa axis is the average particle size of the fuel, mm; ordinate axis—time of complete burning out of a particle of the corresponding size, sec

The study of burn-up rates of fuel particles of different size and nature (a special device with a heating table [11]) allowed to determine the duration of combustion of the fuel particle (Fig. 1.24).

The time of burning particles of coke fines of size 2 mm is 75 s. Having accepted this optimal burnout time, we obtain a recommendation for changing the particle size for solid fuels of different reactivity (see line AA in Fig. 1.24).

Redox interactions of iron oxides

The oldest as a world scientific dispute, whether the sintering process is oxidative or reductive, is now resolved in the form of a compromise: Sintering is the redox process [4, 27, 37].

A diagram illustrating the ratio of redox processes in the sinter according to [27] is presented in Fig. 1.25.

In the part of the high-temperature zone (sinter formation zone), where hot air with high oxygen content enters, and the fuel particles burn down (i.e., little CO is formed), oxidative processes take place (oxidation zone).

In the zone where there is an intensive combustion of fuel particles and a sufficient amount of CO is formed, reduction processes (reduction zone) prevail. The conventional boundary between these zones is the horizon with the maximum temperature. The balance of redox interactions is controlled by changes in the FeO content of the materials.

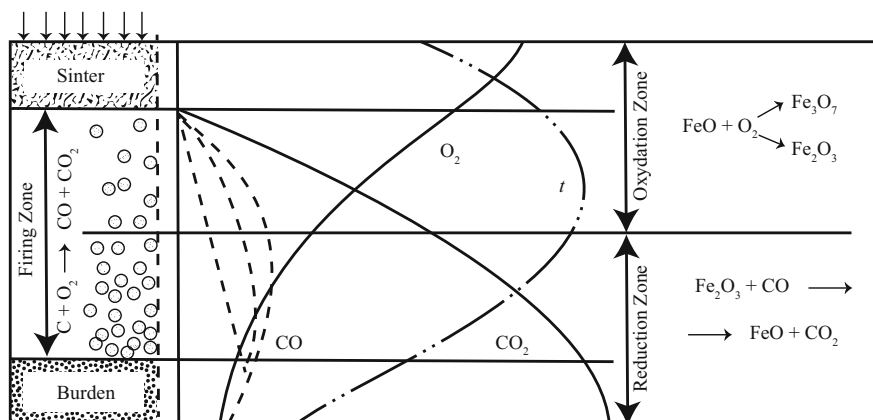


Fig. 1.25 Development of redox processes in the high-temperature part of the sintering layer [27].
 - - - - dotted lines—possible trends of CO content in the gas depending on the ratio of the rates of carbon combustion and reduction of iron oxides; t temperature change in temperature zone

Quantitative indicators of the development of redox reactions depend on the mineralogical type of iron ore material, the content of fluxes in the charge, fuel consumption for the process, which is explained in Fig. 1.26 [37].

With the sintering of oxidized charge (H, L) both at normal and increased fuel consumption, the volume of reduction work will always exceed the volume of oxidizing and the content of FeO in the sinter will exceed the content of FeO in the charge.

During the sintering of magnetite charge (M) depending on the carbon content in the charge, the ratio of the volumes of reduction and oxidation work can vary quite widely, and the content of FeO in the sinter can be less, more or equal to the content of FeO in the charge.

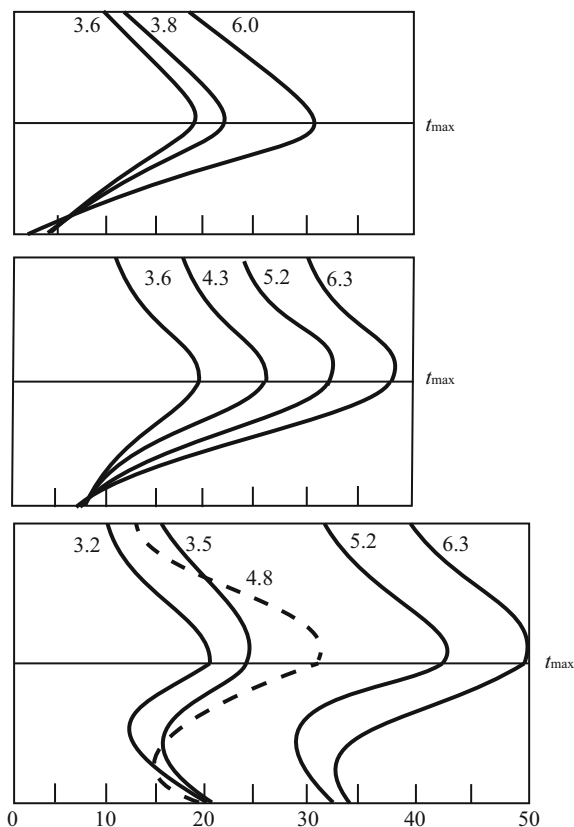
The level (degree) of development of redox reactions significantly affects not only the final composition of the sinter, but also its thermal balance: FeO oxidation, which is an exothermic reaction, provides an additional heat input into the layer, which allows to reduce the consumption of solid fuel for sintering.

Decomposition of hydrate compounds

Some components of the sinter blend can be represented by crystalline hydrates: These are primarily iron ore ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$) and lime, which is part of the flux component, which is converted into calcium hydroxide ($\text{Ca}(\text{OH})_2$) during the preparation of the charge.

Depending on the type of crystalline hydrate (its nature, which determines the strength), the decomposition of hydrate compounds occurs at different temperatures: iron hydroxides (brown ore) dissociate in the range of 120–300 °C, calcium hydroxide (slaked lime) at 450 °C.

Fig. 1.26 Changes in the FeO content in the height of the high-temperature zone of the sintered layer for hematite [37] (H)—upper fragment, limonite (L)—middle fragment, magnetite (M)—bottom fragment charges. The numbers at the curves are the carbon content in the charge, %. The abscissa axis is the content of FeO, %; ordinate axis—layer height (above $t_{\max}$ level—sinter, below $t_{\max}$ level—charge)



At high rates of charge heating inherent in the sintering process, in real sintering conditions, the decomposition of hydrates can be shifted to higher temperatures (up to 1000 °C).

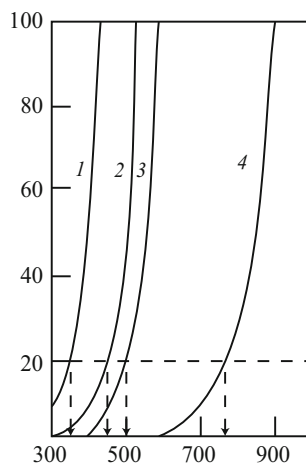
The decomposition of hydrates refers to the endothermic interactions. The increased heat demand of the charge containing oxide hydrates causes an increase in fuel consumption for the process.

The presence of hydrated moisture in the sintering charge significantly changes a number of parameters of the sintering process: the specific effective heat capacity of the charge, the specific yield of the sintering gas, and the evaporation conditions of hygroscopic moisture.

Dissociation of carbonate compounds

We are talking mainly about the fluxing component of the sinter, which is limestone (CaCO_3) or dolomitized limestone (with an increased MgO content). Limestone consumption is due to a given basicity of the charge and varies widely. However, siderite ores, which represent iron carbonates (FeCO_3), can also be sintered.

Fig. 1.27 Dissociation pressure of some carbonates [27] horizontal line—gas phase pressure at sintering (20 kPa); 1— FeCO_3 , 2— MnCO_3 , 3— MgCO_3 , 4— CaCO_3 . The abscissa axis is temperature, $^{\circ}\text{C}$; ordinate axis—partial pressure of CO_2 in the gas phase during sintering, kPa



Carbonate constituents may be present in the gangue of iron ores, concentrates, in the composition of secondary materials involved in magnesium (MgCO_3) and calcium (CaCO_3).

The thermodynamic condition for the beginning of dissociation (and irreversibility of the process) is the fulfillment of the ratio P_{CO_2} (carbonate) $> P_{\text{CO}_2}$ (gas phase). Figure 1.27 [27] shows the dependence of the dissociation elasticity of some carbonates on the temperature.

The strongest carbonate (Fig. 1.27) is calcium carbonate (limestone) CaCO_3 .

For sintering conditions (total gas pressure in the layer is 0.95 atm., the CO_2 content is about 20%, i.e., P_{CO_2} 0.19 atm.) according to Fig. 1.27, the temperature of the start of dissociation of CaCO_3 corresponds to the temperature 790 $^{\circ}\text{C}$. When the elasticity of the dissociation, corresponding to the pressure value of gas in the layer (i.e., of 0.95 atm.) and corresponding to a temperature of 900 $^{\circ}\text{C}$, the intensive decomposition of CaCO_3 begins, which has the character of “chemical boiling”.

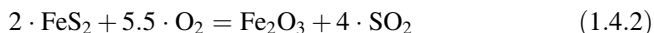
Given the short duration of stay of the charge in the temperature region 800– t_{max} $^{\circ}\text{C}$ to complete the process of dissociation, it is necessary to remove the kinetic limitation, i.e., to provide the proper particle size of limestone (practice shows that this condition corresponds to the particle size 3 mm).

In the processes of dissociation, an active surface is formed, which facilitates the solid-phase interaction.

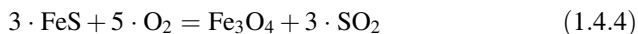
Behavior of sulfur during sintering

Sulfur comes with the components of the sintering charge (ores, concentrates, secondary products, solid fuel) and can be in the form of: sulfides (FeS , FeS_2), sulfates CaSO_4 (rarely BaSO_4), as well as in the fuel in the form of organic sulfur S_{org} .

Sulfide sulfur. At low temperatures ($t < 700$ $^{\circ}\text{C}$) and limited development of the sulfide dissociation mechanism (1.4.3) due to its subsequent absorption by the underlying layers of the charge (as if recombination), the mechanism of sulfur oxidation with the formation of gaseous sulfur dioxide is developing:



At $t > 700^\circ\text{C}$, removal of sulfide sulfur with the formation of sulfur dioxide is possible through a multi-stage process in which the dissociation of FeS_2 (1.4.3), its oxidation (1.4.3), and oxidation of dissociation products (1.4.4) occur in parallel:



Any sulfide oxidation reactions are exothermic.

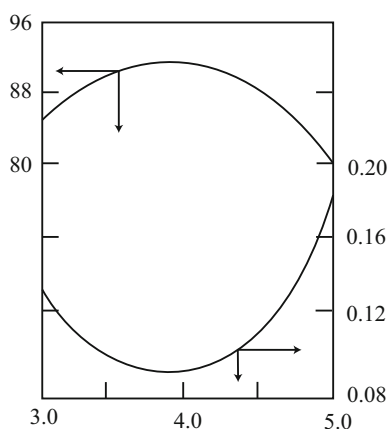
The completeness of sulfide sulfur oxidation during sintering is determined by a number of factors, which are actually characteristic for chemical interactions of this type:

- dispersion of ore components containing sulfides (for a fraction of minus 2 mm, the degree of sulfur removal in 95% is achieved);
- temperature rise in the layer (without melt formation);
- maximum achievable oxygen content in the gas phase.

Due to the fact that increasing the temperature in the layer requires an increase in fuel consumption, and this inevitably reduces the concentration of available oxygen, for this reason, the degree of sulfur removal from fuel consumption is extreme (Fig. 1.28 [35]): Using the example of fluxed sinter production with a carbon content below 3%, the degree of sulfur removal is low due to low temperatures; when the carbon content in the charge is higher than 4%, the degree of sulfide sulfur removal decreases due to oxygen deficiency.

Sulfate sulfur. Calcium sulfate CaSO_4 is a strong compound, and its decomposition requires a temperature not lower than 1100°C :

Fig. 1.28 Dependence of the degree of removal of sulfide sulfur during sintering on the solid fuel consumption in the production of an offset sinter with basicity of 1.25 [35]. The abscissa axis is the coke breeze content in the charge, %; ordinate axis (left)—degree of sulfur removal, %; Y-axis (right)—the sulfur content in the sinter, %



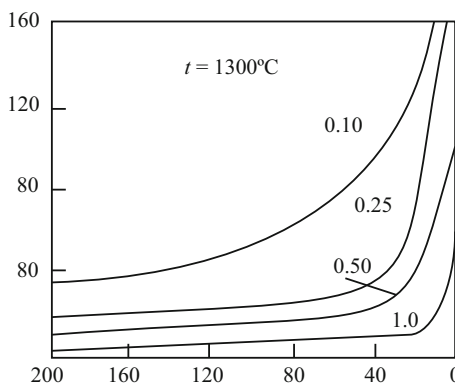
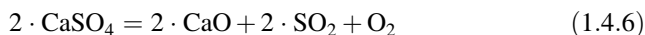


Fig. 1.29 Partial pressure of SO_2 dissociation of calcium sulfate depending on oxygen concentration in the gas phase and activity of calcium oxide [27]. The numbers at the curves—the activity of calcium oxide a_{CaO} . The abscissa axis is the oxygen partial pressure $P_{\text{O}_2} \times 10^3$, atm.; Y-axis—equilibrium dissociation pressure CaSO_4 , $P_{\text{SO}_2} \times 10^3$, atm.; temperature 1300 °C



From a thermodynamic point of view, the reaction (1.4.6) is hampered by the presence of oxygen in the gas phase. On the contrary, reaction (1.4.6) is intensified when CaO is removed from the reaction zone (due to interaction with other oxides of charge materials), i.e., while reducing its activity a_{CaO} . These provisions are illustrated in Fig. 1.29.

The degree of removal of sulfate sulfur during sintering does not exceed 70%, usually 60%.

Organic sulfur. It is present in the coke breeze, anthracite culm, or in other coke breeze substitutes. When burning coke breeze at a temperature above 700 °C, organic sulfur of the fuel is oxidized by oxygen in the air:



At temperatures below 600 °C and in the presence of catalysts (iron oxide, for example), sulfur dioxide can be oxidized by reaction:



Interaction between solid phases

Heating the charge materials in the sintered layer creates the conditions for the chemical interaction between the solid phases, which together form the substance of the charge. The mobility of charge particles that are in the solid-crystalline state is limited; therefore, the interaction of solid phases occurs exclusively in contact zones (Fig. 1.30).

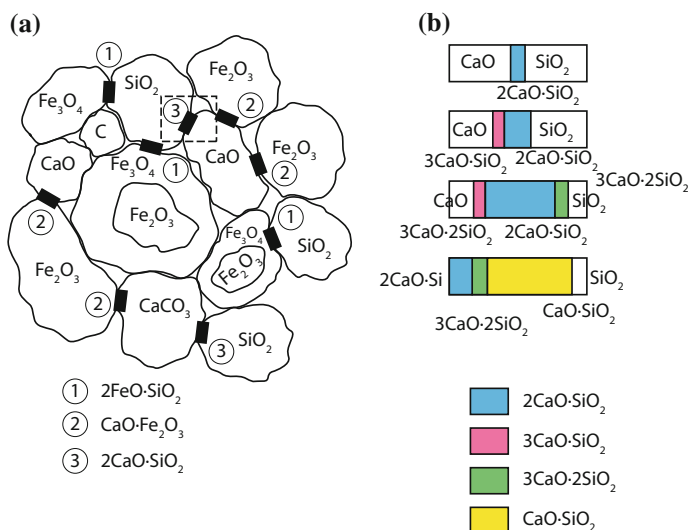


Fig. 1.30 Scheme of interaction of sintering charge components in the solid phase. **a** Scheme of formation of contacts in the production of fluxed sinter [12]: 1— $2\text{FeO} \cdot \text{SiO}_2$; 2— $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$; 3— $2\text{CaO} \cdot \text{SiO}_2$; **b** the mineral structure of the contact zone [35]

The features of solid-phase interactions as a type of reaction in general, supplemented by the specific conditions of the sintering process, form exactly the set of compounds that is presented in Fig. 1.30 and Table 1.14:

- Thermodynamically, solid-phase interactions are possible only in case of reduction of free energy of the system, i.e., exothermic reactions.
- The primary product of interaction in the solid phase (regardless of the mass ratios of the reacting components) is the same compound (probably characterized by the simplest structure of the crystal lattice [35]).
- The interaction between the particles is carried out exclusively in the contact zones, and it is the component composition of the charge (e.g., the consumption of iron ore concentrate is responsible for contacts with Fe_3O_4 , the consumption of lime—for contacts with CaO) forms the types of such contacts and their number (Fig. 1.30a); the number of contacts per unit volume depends on the granulometric composition of the charge components.
- Due to the short-term heating of the charge and stay at elevated temperatures during sintering, the transformation of the zonal contact (as shown in Fig. 1.30b), which requires considerable time due to the low diffusion rate in solid crystal materials, does not develop.

Table 1.14 shows the main chemical compounds formed as primary reaction products during solid-phase interaction in the sintered layer [39].

Interaction in solid phases begins at moderate temperatures; the degree of completion of the process significantly depends on the temperature level: In [35],

it is shown that at 1000 °C in a mixture of dispersed CaO and SiO₂ up to 60% of the reagents pass into calcium silicates in 1 min. (on average, heating of the sintering charge layer requires 2–3 min).

Solid-phase interactions have the important consequence that the products formed as a result of these reactions form the basis for obtaining fusible eutectic involved in the formation of the sinter structure.

1.4.2 Processes in the Formation of the Liquid Phase During Melting

The temperatures developed in the combustion (melting) zone are determined by the consumption of solid fuel for the process (and by heat in general), the type of iron ore component of the sintering charge, its basicity. The high-temperature zone of the layer is characterized by temperatures of 1200–1500 °C, sufficient for the formation of melts of individual phases (Table 1.14).

The formation of the melt in the sintering layer involves the products of solid-phase interaction, iron ore, and other components of the charge through such mechanisms:

Table 1.14 Solid-phase interaction products in iron ore sintering and their characteristics

#	Contacting phases (reactive solid substances)	Primary reaction product	Temperature (°C)	
			Beginning of interaction	Melting [10]
1	CaO–SiO ₂	2CaO · SiO ₂	500, 610, 690	2130
2	CaCO ₃ –SiO ₂	2CaO · SiO ₂	No data	2130
3	CaO–Fe ₂ O ₃	2CaO · Fe ₂ O ₃	400	1480
4	CaO–Fe ₂ O ₃	CaO · Fe ₂ O ₃	500, 520, 600, 610, 650	1227
5	CaO–Fe ₃ O ₄	–	Interaction is not possible	
6	CaCO ₃ –Fe ₂ O ₃	2CaO · Fe ₂ O ₃	590	1480
7	CaO–Al ₂ O ₃	CaO · Al ₂ O ₃	No data	1602
8	CaCO ₃ –Al ₂ O ₃	CaO · Al ₂ O ₃	No data	1602
9	Fe ₃ O ₄ –SiO ₂	2FeO · SiO ₂	800, 950, 990, 1100 ^a	1217
10	Fe ₂ O ₃ –SiO ₂	–	Interaction is not possible	
11	MgO–Fe ₂ O ₃	MgO · Fe ₂ O ₃	600	1750
12	MgO–SiO ₂	2MgO · SiO ₂	680	1890

^aDepending on the type of silica

Table 1.15 Description of the main low-melting eutectics related to sintering [35]

##	System	Characteristics of phases	Melting temperature (°C)	Notes
1	FeO–SiO ₂	2FeO · SiO ₂	1205	Non-fluxed sinter
		2FeO · SiO ₂ –SiO ₂ eutectic	1178	
		2FeO · SiO ₂ –FeO eutectic	1177	
2	Fe ₃ O ₄ –2FeO · SiO ₂	2FeO · SiO ₂ –Fe ₃ O ₄ eutectic	1142	Fluxed sinter
3	2FeO · SiO ₂ –2CaO · SiO ₂	(CaO) _x · (FeO) _{2–x} · SiO ₂ ; $x = 0.19$ lime-ferrous olivines	1150	
4	CaO–Fe ₂ O ₃	CaO · Fe ₂ O ₃ –+ 2CaO · Fe ₂ O ₃ incongruent melting	1216	
		CaO · Fe ₂ O ₃ –CaO · 2Fe ₂ O ₃ eutectic	1200	
5	Fe ₂ O ₃ –CaO–SiO ₂	2CaO · SiO ₂ –CaO–Fe ₂ O ₃ –CaO · 2Fe ₂ O ₃ eutectic	1192	

- melting with dissociation;
- melting with a complete collapse of the connection;
- dissolution (oxides of iron, calcium, magnesium, aluminum).

The mobility of the melts is provided by the formation of low-melting eutectic in accordance with the diagrams of the state, the experimentally determined temperatures of which are given in Table 1.15.

Thus, the easily mobile melt is formed at a temperature of about 1200 °C for both non-fluxed and off-fluxed charge.

1.4.3 Processes During Solidification (Crystallization) of the Melt

The melt formation in the sintering by the example of the Fe₃O₄–2FeO · SiO₂ system state diagram can be seen in Fig. 1.31 [35].

The melt formed at 1217 °C (according to experimental data is 1205 °C) 2FeO · SiO₂ (fayalite) dissolves Fe₃O₄ (line from C to A in Fig. 1.31), and its melting point rises. The final composition of the melt is shown by the hatched area in Fig. 1.31, in which the concentration of 2FeO · SiO₂ covers a range of ~20–40% (in the area of liquidus between fayalite and magnetite, there is an unlimited mutual solubility). Consider the melt crystallization of the approximate composition of 34% 2FeO · SiO₂ with a temperature of ~1550 °C. Upon cooling till reaching the solidus line (point 1), the crystallization process begins: Fe₃O₄ crystals precipitate from the melt up to the temperature corresponding to point 2. At the same time, the melt composition changes according to curve AB with increasing 2FeO · SiO₂ concentration up to the eutectic composition 83% of the mass. 2FeO · SiO₂ and 17%

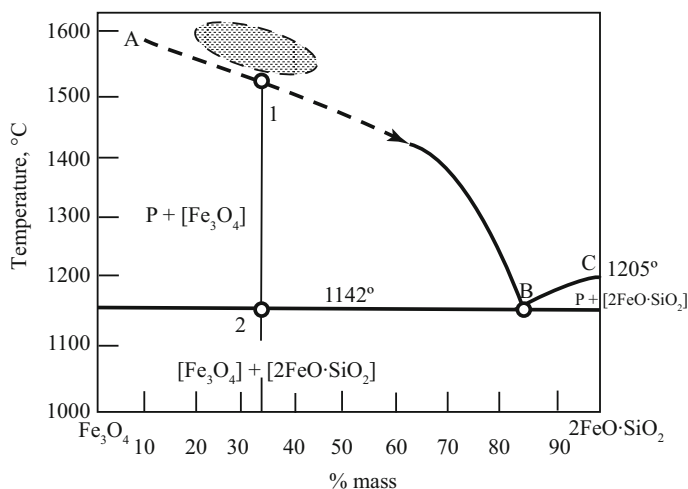


Fig. 1.31 Diagram of the state of the system Fe_3O_4 - 2FeO [35]. The composition of eutectic melt is 83% of the mass. $2\text{FeO} \cdot \text{SiO}_2$ (fayalite), 17% of the mass. Fe_3O_4 (magnetite)

of the mass. Fe_3O_4 . Below point 2, magnetite crystals, eutectics (a mixture of fayalite and magnetite crystals) will exist in the crystallized melt, and at high cooling rates, fayalite may appear in the eutectic as an amorphous phase.

The structure of the crystallized melt (sinter), confirming the described picture of melt crystallization, is presented in Fig. 1.32: magnetite crystals (a), magnetite and olivine eutectics (b).

1.5 Heat Transfer in the Sintering Layer

1.5.1 General Information on the Sintering Heat Exchange

The patterns of heat transfer in layered processes with internal heat sources, which include the sintering layer, are extremely complex.

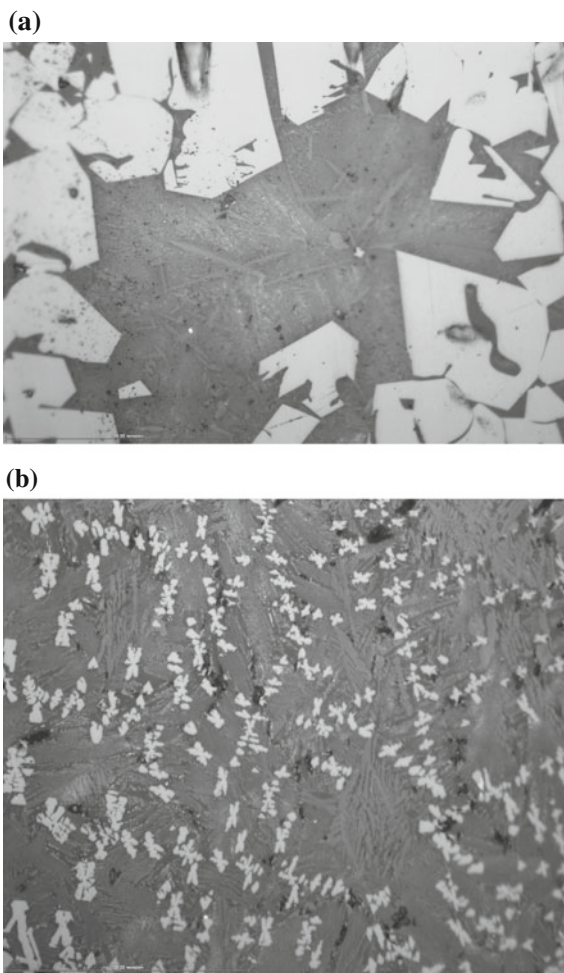
Research in the field of heat transfer in the sintering layer has been conducted for a long time, starting with the work of Wendorborn [40], who determined the distinctive feature of sintering by the method of suction—the zonal nature of the processes occurring in the layer of sintered charge.

When sintering by air suction, two fundamentally different stages of heat transfer are distinguished (Fig. 1.33), the boundary between which is the horizon with maximum temperatures:

- the upper stage, located above the combustion zone, which represents sinter cake being crystallized and already crystallized sinter cake, in which the air drawn in through the heated cake is heated and the cake is cooled;

Fig. 1.32 Mineral phases of crystallized sinter melt.

a Magnetite crystals (white), gray—olivine crystals;
b magnetite eutectic (white) and olivine (gray)



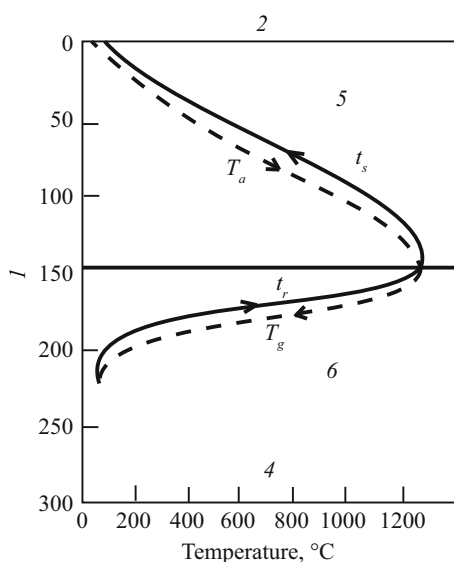
- the lower stage, located under the combustion zone, which is a raw mixture, where the drying and heating of the mixture with hot exhaust gases take place.

Such a temperature curve (Fig. 1.33) is called a thermogram. Due to the high velocity of the gas being filtered in the porous layer, the heat exchange does not reach equilibrium and in most parts of the high-temperature zone, there is a temperature difference between the gas and the material (the solid and dotted lines in Fig. 1.33).

A characteristic feature of the thermogram is the asymmetry of its shape: fast heating of the charge (in the lower heat exchange stage) and slow cooling of the sintering cake (in the upper heat exchange stage), which is quite natural, if we take into account the dependence of the heat exchange intensity on the specific surface of the materials. When the specific surface area of the sintering charge is about

Fig. 1.33 Change of material temperature t (solid line) and gas temperature T (dotted line) in the height of the sintered layer (at some moment of sintering) [27].

t_r , t_s —the temperature of the charge and sinter, respectively; T_a , T_g —the temperature of air and gas, respectively, 1—distance from the surface of layer 2, mm; 4—grate; 5—the upper step of heat exchange, 6—the lower step of heat exchange



3000 m²/m³, the temperature of the combustion products from the maximum level of 1300–1400 °C is reduced to 300–400 °C in height of 20–30 mm (the temperature gradient in the intensive heating zone reaches 400 °C/cm). The specific surface area of the sintering cake is significantly smaller, which determines the reduced cooling rate of the sinter.

The heat exchange intensity in the lower stage is also facilitated by the endothermic process of evaporation of moisture (until the complete evaporation of moisture from the charge material, its temperature cannot rise above the equilibrium evaporation temperature of about 60 °C).

To solve practical problems, the method of direct measurement of temperature in the layer is used (it is more informative to use several thermocouples on different horizons in height), which continuously record the temperature during sintering. A typical example of thermal images obtained in experimental studies (laboratory sinter pot) is shown in Fig. 1.34.

The thermogram allows you to determine a set of parameters that are extremely important for controlling the sintering process:

- maximum temperature level;
- the residence time of the material in the high-temperature zone τ (we take a conditional boundary of 1100 °C, characterizing the temperature of the formation of the first portions of the melt and solidification of the sinter cake); for example, in Fig. 1.34 for the first horizon τ_1 is 1.5 min, for the third horizon 2.5 min;
- the speed of the sintering process (vertical sintering rate), or the rate of movement over the layer of maximum temperatures (from Fig. 1.34, we find the rate of the maximum moving between horizons 2 and 6: 170 : 8 = 21 mm/min);

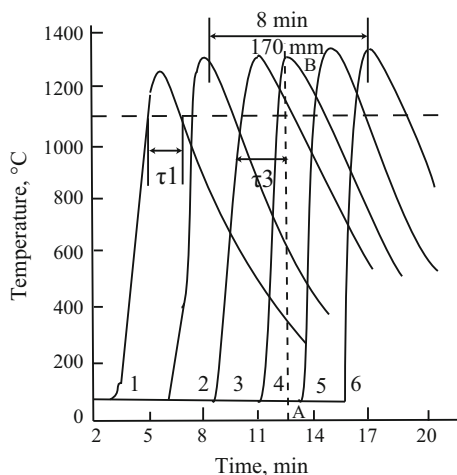


Fig. 1.34 Changes of temperature in the sintered layer at different horizons at the height [27]. Height of the sintered layer 300 mm; vacuum of 13.6 kPa; the distance of the horizons of temperature measurement from the surface of the layer: 1—30 mm, 2—70 mm, 3—110 mm, 4—150 mm, 5—190 mm, 6—240 mm; AB line—temperature distribution along the layer height for 12.5 min of sintering. The abscissa axis is the sintering time, min; ordinate axis—temperature in the layer, °C

- the temperature distribution along the height of the layer at any time of sintering (line AB);
- the intensity of heat transfer in different parts of the layer (the rate of temperature change in time dT/dt , or the temperature gradient in the layer dT/dh).

1.5.2 Zonal Heat Balances of Sintered Layer

Another method for evaluating thermal processes during sintering, in addition to direct temperature measurement in the layer, is the method of zonal heat balances.

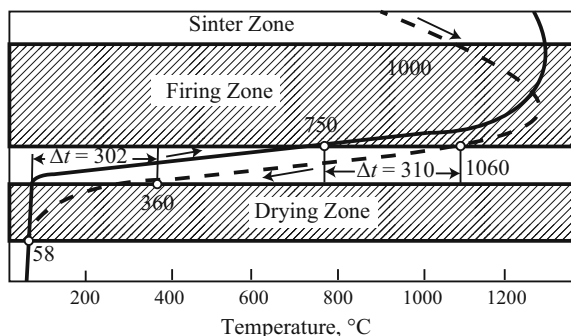
Like any balance method, the zonal heat balance takes into account heat input and consumption, but not integral for the sintering process, but for its individual blocks (zones).

Zonal heat balances are calculated for the following zones:

- a zone of burning solid fuel;
- intensive heating zone;
- drying zone;
- condensation zone.

The location of these zones (and the values of individual temperature parameters obtained from the zonal thermal balances) is illustrated in Fig. 1.35 [27].

Fig. 1.35 Boundaries of temperature zones for the calculation of zonal heat balances [27]. Solid line—material temperature t , °C; dotted line—gas phase temperature T , °C



The heat balance of the combustion zone

In accordance with the boundaries indicated in Fig. 1.35, in the combustion zone, the charge is heated from the ignition temperature of the fuel (750 °C is accepted here) to $t_{\max}$.

The incoming components of the thermal balance of the combustion zone are:

- heat of combustion of solid fuel carbon;
- heat of exothermic reactions (combustion, oxidation of FeO, the formation of new minerals);
- heat released when cooling the gas from $T_{\max}$ to T_{out} ;
- “Expenditures” of the heat balance of the combustion zone are presented by:
- heat of endothermic reactions (dissociation of carbonates, reduction of iron oxides to FeO, melting of materials);
- heat consumption for heating sintered material from 750 °C to $t_{\max}$;
- heat consumption for heating the air entering the combustion zone to $T_{\max}$.

$$Q_c + Q_{\text{exr}} + \Delta Q_g = Q_{\text{enr}} + \Delta Q_a + \Delta Q_{\text{sc}}, \quad (1.5.1)$$

where

Q_c —heat of combustion of solid fuel in the layer;

Q_{exr} —heat of exothermic reactions;

ΔQ_g —the enthalpy change of the sintering gas;

Q_{enr} —heat endothermic reactions ($Q_{\text{enr}} = Q_{\text{ca}} + Q_m + Q_r$);

Q_{ca} —heat for dissociation of carbonates;

Q_m —heat for melting materials;

Q_r —heat for reduction of Fe_3O_4 to FeO;

ΔQ_a —change of enthalpy of air flowing into the combustion zone from the cooling layer of the cake;

ΔQ_{sc} —change in the enthalpy of sintered charge in the combustion zone

$$\begin{aligned}
\Delta Q_g &= V_g \cdot C_g \cdot (T_{\max} - T_{\text{out}}) \\
\Delta Q_a &= V_a \cdot C_a \cdot (T_{\max} - T_{\text{en}}) \\
\Delta Q_{\text{sc}} &= 0.9 \cdot C_{\text{sc}} \cdot (t_{\max} - 750)
\end{aligned} \tag{1.5.2}$$

where V_g , V_a —specific gas yield and specific consumption of air for process (m^3/kg of charge);

C_g , C_a , C_{sc} —heat capacity of gas ($\text{kJ}/\text{m}^3 \text{ } ^\circ\text{C}$), air ($\text{kJ}/\text{m}^3 \text{ } ^\circ\text{C}$), and charge ($\text{kJ}/\text{kg } ^\circ\text{C}$); 0.9—ratio of sinter cake yield;

T_{en} —air temperature at the upper boundary of the combustion zone.

Substituting Eqs. (1.5.2) into (1.5.1) and solving the latter with respect to $t_{\max}$, we get:

$$\begin{aligned}
t_{\max} &= \{ (Q_c + Q_{\text{exr}} + 0.9 \cdot C_{\text{sc}} \cdot 750 + V_a \cdot C_a \cdot T_{\text{en}}) \\
&\quad - (Q_m + Q_{\text{ca}} + V_g \cdot C_g \cdot T_{\text{out}}) \} / (0.9 \cdot C_{\text{sc}} + V_a \cdot C_a - V_g \cdot C_g)
\end{aligned} \tag{1.5.3}$$

Example of the calculation of $t_{\max}$.

The initial conditions for the calculation:

The calculation is made per 1 kg of the charge.

Consumption of coke breeze in the charge; thermal effect of carbon burning 21 MJ/kg C (with a ratio of $\text{CO}/\text{CO}_2 = 1.2$); heat from other exothermic processes is 10% of the thermal effect of combustion; the consumption of limestone in the charge is 9% ($\text{CaCO}_3 = 97\%$), the thermal effect of dissociation of limestone is 1785 kJ/kg; in the $t_{\max}$ zone, 50% of the charge melts with an endothermic effect of 580 kJ/kg melt; $T_{\text{en}} = 1000 \text{ } ^\circ\text{C}$; $T_{\text{out}} = 1060 \text{ } ^\circ\text{C}$; specific gas yield 0.41 m^3/kg of the charge; specific air flow rate 0.37 m^3/kg of the charge; heat capacity: of the mixture—1.1 kJ/kg $^\circ\text{C}$, of the gas—1.4 kJ/ $\text{m}^3 \text{ } ^\circ\text{C}$, of the air—1.4 kJ/ $\text{m}^3 \text{ } ^\circ\text{C}$

heat from the combustion of carbon charge $Q_c = 1 \cdot 0.048 \cdot 0.85 \cdot 21,000 = 857 \text{ kJ/kg}$;

heat from exothermic processes $Q_{\text{exr}} = 857 \cdot 0.1 = 86 \text{ kJ/kg}$;

heat for melting materials $Q_m = 1 \cdot 0.9 \cdot 0.5 \cdot 580 = 261 \text{ kJ/kg}$;

heat dissociation of limestone $Q_{\text{ca}} = 1 \cdot 0.09 \cdot 0.97 \cdot 1785 = 145 \text{ kJ/kg}$.

$$\begin{aligned}
t_{\max} &= (857 + 86 + 0.9 \cdot 1.1 \cdot 750 + 0.37 \cdot 1.4 \cdot 1000 - 261 - 145 \\
&\quad - 0.41 \cdot 1.4 \cdot 1060) / (0.9 \cdot 1.1 + 0.37 \cdot 1.4 - 0.41 \cdot 1.4) = 1273 \text{ } ^\circ\text{C}
\end{aligned}$$

The heat balance of the drying zone

In the main period of sintering, the heat of the gas entering the wet mixture (“credit article”) is spent on the evaporation of moisture:

$$\Delta Q_g = Q_{\text{vap}} \\ L_g \cdot C_g \cdot (T_{\text{ed}} - T_p) = q_{\text{vap}} \cdot b_{\text{sc}} = (2490 - 2.3 \cdot T_p) \cdot b_{\text{sc}}, \quad (1.5.4)$$

where

L_g —specific gas consumption (kg) for the evaporation of water from 1 kg of the charge;

C_g —heat capacity of gas, kJ/kg °C;

T_{ed} —gas temperature at the entrance to the drying zone, °C;

T_p —equilibrium evaporation temperature, °C;

q_{vap} —specific heat of vaporization, kJ/kg (approximated by the equation $2490 - 2.3 \cdot T_p$);

b_{sc} —moisture content of the charge, kg H₂O/kg of the charge.

$$L_g = l \cdot b_{\text{sc}} = b_{\text{sc}} / (x_{\text{ss}} - x_o), \quad (1.5.5)$$

where l is the required gas consumption for evaporation of 1 kg of water, equal to $1 / (x_{\text{ss}} - x_o)$;

x_{ss}, x_o —moisture content of gas in the saturated state and initial, kg H₂O/kg of gas.

Solving (1.5.5) for x_{ss} , we get:

$$x_{\text{ss}} = b_{\text{sc}} / L_g + x_o \quad (1.5.6)$$

Example of temperature calculation in the drying zone

Initial data for calculation:

The calculation is carried out on 1 kg of the charge. The moisture content of the mixture b_{sc} is 0.075 kg/kg of the charge (humidity 7.5%), the density of the sintering gas is 1.4 kg/m³; specific gas yield is 0.41 m³/kg of the charge; the initial moisture content of the gas is x_o 0.007 kg/kg dry gas.

Specific gas yield (by weight):

$$L_g = 0.41 \cdot 1.4 = 0.574 \text{ kg d.g.}^* / \text{kg of dry charge} \quad (* \text{ d.g. --- dry gas})$$

Moisture content of gas in a saturated state:

$$x_{\text{ss}} = 0.075 / 0.574 + 0.007 = 0.138 \text{ kg/kg d.g.}$$

From the tabular data, we find that the temperature $T_p = 58$ °C corresponds to this moisture content, and by Eq. (1.5.4), we determine T_{ed} , equal to 360 °C.

Heat balance of the intensive heating zone

In this zone, the charge is heated from the temperature t_p (equilibrium evaporation temperature) to the fuel ignition temperature (adopted at 750 °C).

The heat balance of the zone of intense heating (taking into account the arrival of heat from oxidation during sintering of magnetite concentrates) can be written as follows:

$$\begin{aligned} \Delta Q_g + Q_{ox} &= \Delta Q_{sc} \\ V_g \cdot C_g \cdot (T_{outh} - T_{ed}) + q_{ox} \cdot \{O_2\} &= 1 \cdot C_{sc} \cdot (750 - T_p) \end{aligned} \quad (1.5.7)$$

where ΔQ_g —change in gas enthalpy;

Q_{ox} —exothermic effect of magnetite oxidation (14,440 kJ/kg of O_2);

ΔQ_{sc} —change of enthalpy of sintered charge;

T_{outh} —the gas temperature at the exit from the zone of intensive heating, °C;

T_{ed} —the gas temperature at the entrance to the drying zone, °C;

$\{O_2\}$ —the amount of oxygen that has gone to the oxidation of magnetite, kg/kg of charge.

We rewrite Eq. (1.5.7) for T_{outh} :

$$T_{outh} = T_{ed} + [C_m \cdot (750 - T_p) - q_{ox} \cdot \{O_2\}] / V_g \cdot C_g \quad (1.5.8)$$

Example of calculation of T_{outh}

Initial data for calculation: specific air flow rate 0.37 m³/kg of the charge; heat capacity of the charge—0.8 kJ/kg °C, of gas—1.4 kJ/m³ °C; 2% (abs) of oxygen is consumed for the oxidation of magnetite ($0.37 \cdot 0.02 = 0.0074$ m³/kg of charge); gas and charge temperatures at the lower boundary of the intensive heating zone are 360 and 58 °C.

Substituting the initial data into (1.5.8), we obtain $T_{outh} = 1060$ °C and the temperature difference between the gas and the charge at the exit from the intensive heating zone will be 310 °C.

1.5.3 Mathematical Model of Heat Exchange During Sintering

With regard to the sintering process, the priority heat transfer mechanisms are convection (the flow of heated air from the sinter and the flow of off-gases to the charge) and thermal conductivity (inside the charge and sinter pieces), the contribution of thermal conductivity is negligible due to the developed porosity of the layer and the porosity of the sinter and granules of the pelletized charge.

We formulate a model of heat transfer in the sintered layer, taking the following initial assumptions [4]:

- Consider the model only for the upper stage of heat transfer (sintered air).
- Consider only convective heat transfer.
- The temperature distribution in the lower stage and the charge temperature entering the combustion zone are assumed constant (not strictly, but acceptable, because these parameters are stable enough for a wide range of charge and sintering conditions).
- We accept a countercurrent process scheme: The gas comes from above, and the material (sinter or charge) with temperature $t_{\max}$ from below (through the upper limit of the combustion zone); $t_{\max}$ is from the heat balance of the combustion zone according to (1.5.3).
- The origin corresponds to the position of the upper boundary of the combustion zone.
- The velocity of the media is given constant and independent of the heat exchange conditions.
- The thickness of the layer of the cooled sintered cake varies with the velocity $U(\tau)$, where U is the linear velocity of the upper boundary of the combustion zone.

Let us write down the heat transfer equations for material (1.5.9) and gas (1.5.10):

$$\begin{aligned} -C_m \cdot \rho_m \cdot Dt/d\tau &= \alpha_v \cdot (t - T) \\ &= -C_m \cdot \rho_m \cdot \{dt/d\tau + (dt/dy \cdot dy/d\tau)\} \end{aligned} \quad (1.5.9)$$

where

C_m —apparent heat capacity of the material (charge), kJ/kg °C;

ρ_m —density of the material (charge), kg/m³;

t —material temperature (charge), °C;

T —gas temperature, °C;

α_v —volumetric heat transfer coefficient, kJ/m³ h °C; applicable equations reflecting the dependence on the filtration coefficient:

$$\alpha_v = 27.07 \times 10^4 \cdot \omega^{0.77} \text{ [41]} \text{ or } \alpha_v = 3.2 \times 10^5 \cdot (1 - e^\omega) \text{ [2]}$$

y —coordinate of the height of the layer

$$-\omega \cdot C_g \cdot \rho_g \cdot dT/dy = \alpha_v \cdot (t - T) \quad (1.5.10)$$

where

C_g —heat capacity of gas, kJ/m³ °C);

ρ_g —gas density, kg/m³;

ω —gas filtration rate, m/h.

Introduce dimensionless variables:

$$Y = \alpha_v \cdot y / (\omega \cdot C_g) \quad Z = \alpha_v \cdot \tau / (\rho_m \cdot C_m) \quad (1.5.11)$$

Define the ratio Y/Z :

$$m = Y/Z = y \cdot \rho_m \cdot C_m / (\omega \cdot C_g \cdot \tau) = U \cdot \rho_m \cdot C_m / (\omega \cdot C_g), \quad (1.5.12)$$

where $U = y/\tau$

On the other hand, the speed of movement of the upper boundary of the combustion zone U (m/h) can be expressed in terms of the filtration rate and the specific air consumption for sintering the charge V (m³/kg):

$$U = \omega / (\rho_m \cdot V) \quad (1.5.13)$$

Substituting expression (1.5.13) into (1.5.12), obtain m :

$$m = C_m / (C_g \cdot V) \quad (1.5.14)$$

Taking into account (1.5.11), (1.5.14), relations (1.5.9) and (1.5.10) in a dimensionless form can be written

$$-Dt/DZ = -\{dt/dZ + m \cdot dt/dY\} = t - T \quad (1.5.15)$$

$$dT/dY = t - T \quad (1.5.16)$$

The solution of the system of Eqs. (1.5.15) and (1.5.16) is carried out by the numerical method according to the finite-difference scheme.

The adequacy of the model to the real process is estimated by the cake temperature at the time of sintering termination, the cake cooling time, and FeO content in it.

1.5.4 Three-Dimensional Mathematical Model of the Sintering Process

Currently, complex three-dimensional mathematical models [42–44] of heat exchange in the sintering layer have been developed.

A three-dimensional mathematical model of the sintering process [45] is a software product that allows predicting in real time the distribution in the sintering layer of temperatures, chemical composition of materials, gas flow parameters, and gas-dynamic characteristics of the sinter machine.

When describing the sintering process in a three-dimensional mathematical model (a system of partial differential equations for charge parameters and ordinary differential equations for gas parameters), the following assumptions were made:

- Sintering charge, consisting of the ore part and solid fuel, is characterized by bulk density and porosity.
- The ore part, limestone, and solid fuel are also determined by the average particle size and moisture.
- The ore part includes CaCO_3 , MgCO_3 , CaO , MgO , FeO , Fe_2O_3 , and chemically inert substances.
- In the composition of solid fuels distinguish carbon and chemically inert substances.
- The gas in the ignition hood (flue gas) and in the layer is represented by a mixture of gases: N_2 , O_2 , CO_2 , CO , H_2O , and CH_4 .
- The time of passage of the gas stream is negligible compared with the time of the development of the sintering process.
- To describe the kinetics of chemical reactions as a function of temperature, the frontal model (model of unreacted nucleus) was adopted.
- Heat exchange between the gas and the charge is assumed to be dependent on the gas flow rate and the total surface of the ore particles and solid fuel.

Mass transfer processes (the degree of development of various chemical reactions, such as the dissociation of carbonates, the formation of FeO and its oxidation to Fe_2O_3 , and the burning of the fuel particle) are described by changing the particle diameter of D_{Ca} , D_{Mg} , and D_{c} or the movement of the interface between the D_{FeO} and $D_{\text{Fe}_2\text{O}_3}$ phases (1.5.17):

$$\begin{aligned}
 dD_{\text{Ca}}/d\tau + dD_{\text{Ca}} \cdot v_s/dL &= w_{\text{Ca}}(t_{\text{sc}}) \\
 dD_{\text{Mg}}/d\tau + dD_{\text{Mg}} \cdot v_s/dL &= w_{\text{Mg}}(t_{\text{sc}}) \\
 dD_{\text{FeO}}/d\tau + dD_{\text{FeO}} \cdot v_s/dL &= w_{\text{FeO}}(t_{\text{sc}}) \\
 dD_{\text{Fe}_2\text{O}_3}/d\tau + dD_{\text{Fe}_2\text{O}_3} \cdot v_s/dL &= w_{\text{Fe}_2\text{O}_3}(t_{\text{sc}}) \\
 dD_{\text{c}}/d\tau + dD_{\text{c}} \cdot v_s/dL &= w_{\text{c}}(t_{\text{sc}})
 \end{aligned} \tag{1.5.17}$$

where L —the length of the sintering strand (from the point of loading the charge on the sintering machine);

v_s —the vertical velocity of sintering;

w_{Ca} , w_{Mg} , w_{c} , $w_{\text{Fe}_2\text{O}_3}$, w_{FeO} —front speed in a piece of limestone, magnesium carbonate during dissociation, ore particles during reduction, ore particles during oxidation, changes in particle size during the burning of coke breeze as a function of temperature, respectively.

The change in the heat content of the charge Q_{sc} is determined by Eq. (1.5.18):

$$\begin{aligned} \partial Q_{sc} / \partial \tau + v_s \cdot \partial Q_{sc} / \partial L \\ = -Q_{he} + Q_c \cdot d_{sc} + Q_{ox} - Q_{Ca} - Q_{Mg} - Q_{vap} - Q_m + \lambda \cdot \partial^2 t / \partial h^2 \end{aligned} \quad (1.5.18)$$

where Q_{he} —heat supplied by heat exchange;

Q_c —heat of carbon burning;

Q_{ox} —heat of oxidation of iron oxides;

Q_{Ca} , Q_{Mg} —heat of carbonate dissociation ($CaCO_3$, $MgCO_3$);

Q_{vap} —the heat expended on the evaporation of moisture;

Q_m —the heat required to melt the components of the mixture;

d_{sc} —the proportion of the mixture in the heat of combustion of coke;

λ —thermal conductivity (due to the insignificant development of contact heat exchange in the charge layer and in the cake, it is assumed to be zero);

h —height of the sintered layer.

The heat content of the gas (Q_g) can be represented by Eq. (1.5.19):

$$dQ_g / dh = Q_{he} + Q_c \cdot (1 - d_{sc}) + Q_{vap} - Q_{hl} \quad (1.5.19)$$

where Q_{vap} —heat of vaporization, Q_{hl} —heat loss.

According to the heat contents of Q_{sc} and Q_g , the temperatures of the mixture t and gas T are calculated from relations (1.5.20):

$$t = Q_{sc} / (\rho_{sc} \cdot C_{sc}); \quad T = Q_g / (\rho_g \cdot C_g) \quad (1.5.20)$$

where ρ_{sc} , ρ_g —the density of the mixture and gas, respectively;

C_{sc} , C_g —the specific heat of the mixture and gas, respectively.

The change in moisture content of the mixture W will be defined by Eq. (1.5.21):

$$\partial W_{sc} / \partial \tau + v_s \cdot \partial W_{sc} / \partial L = Q_{vap} / 2258 \quad (1.5.21)$$

where 2258—specific heat of evaporation, kJ/kg.

Volumetric flow rates (outputs) of the gas components (V_{CO_2} , V_{CO} , V_{H_2O} , V_{O_2}) can be determined from the corresponding Eqs. (1.5.22–1.5.25):

$$\begin{aligned}
dV_{CO_2}/dh = & (K_{sc} \cdot \pi \cdot D_{Ca}^2 \cdot dD_{Ca}/d\tau \cdot \rho_{Ca}/100) \cdot 22.4 \\
& + \left(K_{sc} \cdot \pi \cdot D_{Mg}^2 \cdot dD_{Mg}/d\tau \cdot \rho_{Mg}/84 \right) \cdot 22.4 \\
& + (K_c \cdot \pi \cdot D_c^2 \cdot dD_c/d\tau \cdot \rho_c/2) \cdot 22.4 \cdot d_{CO_2} \\
& + \left(K_{sc} \cdot \pi \cdot D_{Fe_2O_3}^2 \cdot dD_{Fe_2O_3}/d\tau \cdot \rho_{Fe_2O_3}/160 \right) \cdot 22.4
\end{aligned} \tag{1.5.22}$$

where

K_{sc} , K_c —material, coke breeze concentrations in the charge;
 100, 84, 12, 160—molecular weights, respectively, of $CaCO_3$, $MgCO_3$, C, and Fe_2O_3 ;
 d_{CO_2} —proportion of carbon dioxide in the combustion products of coke breeze.

$$\begin{aligned}
dV_{CO}/dh = & (K_c \cdot \pi \cdot D_c^2 \cdot dD_c/d\tau) \cdot \rho_c/12) \cdot 22.4 \cdot (1 - d_{CO_2}) \\
& - \left(K_{sc} \cdot \pi \cdot D_{Fe_2O_3}^2 \cdot dD_{Fe_2O_3}/d\tau \cdot \rho_{Fe_2O_3}/160 \right) \cdot 22.4
\end{aligned} \tag{1.5.23}$$

$$dV_{H_2O}/dh = (dW_{sc}/d\tau)/18 \cdot 22.4 \tag{1.5.24}$$

$$\begin{aligned}
dV_{O_2}/dh = & (K_{sc} \cdot \pi \cdot D_{FeO}^2 \cdot dD_{FeO}/d\tau \cdot \rho_{FeO}/288) \cdot 22.4 \\
& + (K_c \cdot \pi \cdot D_c^2 \cdot dD_c/d\tau) \cdot \rho_c/12) \cdot 22.4(0.5 + d_{CO_2}/2)
\end{aligned} \tag{1.5.25}$$

The vacuum in the layer dP/dh is characterized by Eq. (1.5.26):

$$dP/dh = \gamma \cdot \rho_g \cdot \omega^2 \tag{1.5.26}$$

where γ is the coefficient of specific resistance of the layer (the base value is set in the source data file).

The heat and mass transfer equations of the model (1.5.17–1.5.26) are solved on a three-dimensional difference grid for the charge layer.

The initial data must be specified in advance:

- dimensions of the sintering machine (length, width of the belt, layer height, zone boundaries);
- consumption parameters (sinter speed, composition of the charge, the distribution of the input characteristics of the charge in height, the cost of natural gas in the zones of the incendiary furnace);
- parameters of chemical reactions and heat transfer;
- calculation parameters (grid step, time step, accuracy parameters of iterative processes).

1.5.5 Calculation of the Specific Yield of the Sintering Gas

The most important parameter of countercurrent heat transfer³ is the ratio of heat equivalents W_g and W_m , which are the heat capacities of the gas flow and the heat capacity of the materials flow:

$$W_g/W_m = V_g \cdot C_g / (M_m \cdot C_m)$$

When calculating one kg of dry charge (i.e., at $M_m = 1$), the ratio of the heat capacity of the gas and material flows for the lower heat exchange stage will be equal to:

$$W_g/W_m = V_g \cdot C_g / C_m \quad (1.5.27)$$

where V_g is the specific yield of the sintering gas, m^3/kg of charge;
 C_g —heat capacity of gas, $kJ/m^3 \cdot ^\circ C$; C_m —apparent heat capacity of the sintered material (taking into account the thermal effects of reactions and processes occurring in the lower heat transfer stage), $kJ/kg \cdot ^\circ C$.

For the case of $W_g = W_m$ from (1.5.27), we obtain for V_g :

$$V_g = C_m C_g \quad (1.5.28)$$

Apparent heat capacity can be calculated from the ratio (1.5.29):

$$C_m = C_{mt} + \Sigma Q / \Delta t \quad (1.5.29)$$

where C_{mt} —the true heat capacity of the material;
 ΣQ —the algebraic sum of thermal effects in the considered temperature interval Δt per 1 kg of the charge (exothermic effects are taken with the “−” sign, endothermic —with the “+” sign).

Comparative calculations of the specific yield of sintering gas by different methods, shown in Fig. 1.36, confirm the theoretical dependence (1.5.28) of the sintering gas yield on the apparent heat capacity of the charge, derived under some assumptions [27].

³Heat transfer in the sintering layer can be viewed in various models: in a fixed bed, as a cross heat transfer, as a countercurrent heat transfer in the case when the origin of coordinates is placed on the maximum temperature horizon.

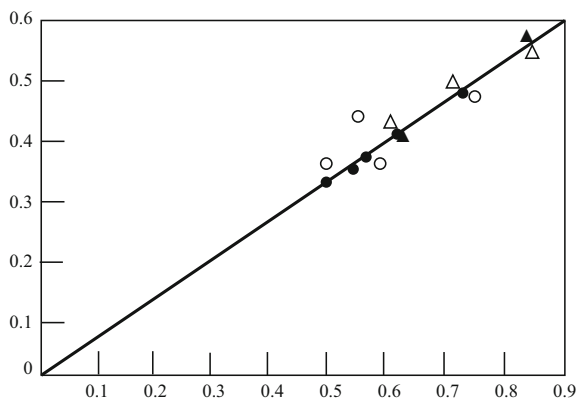


Fig. 1.36 Dependence of the sintering gas yield on the apparent heat capacity of the sintered charge [27] dark points— V_g calculated from apparent heat capacity; transparent points— V_g calculated from carbon balance. The abscissa axis is the apparent heat capacity of the charge, kJ/kg · °C; ordinate axis—specific gas yield, m³/kg dry charge (d.c.)

1.5.6 Vertical Sintering Speed

Formally, the vertical sintering rate (U) is determined by the ratio of the height of the layer to the time for which this layer will be sintered, i.e., converted from raw mixture to cake.

In other words, the vertical sintering rate is $U = h/\tau$.

On the other hand, the formula for the vertical sintering rate can be obtained on the basis of a fairly simple analysis of the thermal balance of the elementary layer of the charge in the lower stage of heat transfer.

When the hot gas flows through the charge layer with an area of 1 m² and a thickness of Δh over a period of time $\Delta\tau$, the gas temperature will decrease by ΔT .

In this case, the heat content of the gas will change by $\Delta Q_g = \omega \cdot \Delta\tau \cdot C_g \cdot \Delta T$.

The charge layer will receive heat $\Delta Q_{sc} = \Delta h \cdot \rho_{sc} \cdot C_m \cdot \Delta t$.

In the conditions of stationary heat exchange, typical for the lower heat transfer stage, ΔQ_g equal to ΔQ_{sc} . Substituting the relations obtained above for the heat content of the gas flow and the charge layer obtains:

$$\Delta h \cdot \rho_{sc} \cdot C_m \cdot \Delta t = \omega \cdot \Delta\tau \cdot C_g \cdot \Delta T \quad (1.5.30)$$

From (1.5.30), we have for $\Delta h/\Delta\tau$:

$$\Delta h/\Delta\tau = (\omega \cdot C_g \cdot \Delta T) / (\rho_{sc} \cdot C_m \cdot \Delta t) \quad (1.5.31)$$

Under the condition $\Delta T = \Delta t$, we have for the vertical sintering rate $U = \Delta h / \Delta \tau$:

$$U = \omega \cdot C_g / (\rho_{sc} \cdot C_m), \quad (1.5.32)$$

where ρ_{sc} —bulk density of sintered charge.

The vertical sintering speed (i.e., the productivity of the sintering process) depends on the filtration rate of gas (air) through the layer ω in accordance with Eq. (1.5.32), derived from theoretical assumptions. This dependence has been repeatedly confirmed by experimental studies and the practice of sintering.

Taking into account the relation (1.5.28) and substituting it in (1.5.32), we express the vertical sintering rate through the specific yield of sinter gas:

$$U = \omega / (V_g \cdot \rho_{sc}) \quad (1.5.33)$$

1.6 The Gas Dynamics of the Sintering Process

1.6.1 The Basic Equation of Dynamics of the Porous Layer

The process of sintering of iron ore materials by suction method implies that the sintered layer is provided with a sufficient amount of air. If the flow (volume) of air (V , m³/s) entering the layer is attributed to the unit area of the cross section of the layer (1 m²) through which it passes, then we obtain the air velocity in the layer [m³/(m² s)], or the filtration rate ω .

To ensure the movement of gas⁴ in the porous layer, it is necessary to create a certain pressure difference at the inlet and outlet of the layer Δp , the value of which depends both on the volume of the filtered gas and the resistance that the layer exerts to the gas movement.

When gas moves in a cylindrical tube, the dependence of the pressure drop (Δp) on the filtration rate ω is known (1.6.1) [27, 46]:

$$(\Delta p) = \gamma \cdot (l/d) \cdot (\rho_g/2) \cdot \omega^2 \quad (1.6.1)$$

where γ —coefficient of gas-dynamic resistance (determined experimentally);

l —tube length;

d —inner diameter of the tube;

ρ_g —gas density;

ω —gas filtration rate.

To apply (1.6.1) to the sinter layer, we create its model in the form of a system (set) of parallel tubes, a conditional (equivalent) diameter d_{eq} of length, equal to the

⁴Here and further “gas” is understood as a gas phase (it is both air and sintering gas).

height of the layer h . The gas filtration rate ω_0 is calculated on the total cross section of the layer; it is associated with the true gas velocity in the channels through the porosity ε :

$$\omega = \omega_0 / \varepsilon.$$

Substituting the last relation in (1.6.1), we obtain the Darcy–Weisbach Eq. (1.6.2), which describes the pressure drop during gas movement in the porous layer:

$$(\Delta p) = \gamma \cdot (h/d_e) \cdot (\rho_g/2) \cdot (1/\varepsilon^2) \cdot \omega^2 \quad (1.6.2)$$

d_e —equivalent diameter of the channels.

Equation (1.6.2) contains several parameters, which for a real layer can be determined only experimentally (γ , ε) or by approximate calculation (d_e).

For example, the known ratio relates the equivalent diameter of the channels in the porous layer to the equivalent diameter of the particles (D_e) that make up this layer:

$$d_e = D_e \cdot \psi \cdot \varepsilon / (1 - \varepsilon), \quad (1.6.3)$$

where ψ —shape factor of the lumps (for the ball is 2/3).

Taking into account (1.6.3), we write the Darcy–Weisbach equation in the final form for the purposes of application in the analysis of gas dynamics of the sintered layer of the sintering charge:

$$(\Delta p) = \gamma \cdot (h/D_e) \cdot (\rho_g/2) \cdot \omega^2 \cdot (1 - \varepsilon) / \varepsilon^3 \quad (1.6.4)$$

1.6.2 Gas-Dynamic Resistance Coefficients

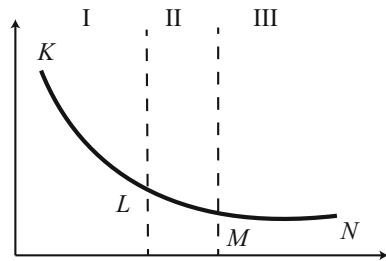
The gas-dynamic resistance coefficient γ depends on many factors: the properties of the gas, its mode of motion, the material of the layer and its structure (porosity, pore tortuosity).

The relationship between the gas-dynamic resistance coefficient and the gas motion regime can be reflected through the Reynolds criterion $Re = \omega \cdot D_e / \zeta$ (ζ —kinematic viscosity of the gas, m^2/s). Figure 1.37 presents the theoretical dependence of the gas-dynamic resistance coefficient γ on the Reynolds criterion.

In the range of values of Reynolds numbers (Fig. 1.37), we can distinguish three characteristic areas:

- I region (for small Reynolds numbers)—the region of laminar gas flow—in this case, the coefficient of gas-dynamic resistance is approximated by the formula $\gamma = A/Re$ (line KL);

Fig. 1.37 Dependence of the coefficient γ of the porous layer on the Reynolds criterion. The abscissa axis— $\lg Re$; the axis of ordinates— $\lg \gamma$



- II region—the region of transition from laminar to turbulent gas flow (this mode is typical for the gas movement in the sintering layer), where the coefficient of gas-dynamic resistance is described by the dependence $\gamma = A_2/Re + B$ (LM line);
- III region (high values of Reynolds numbers)—the region of turbulent gas motion, where the coefficient of gas-dynamic resistance does not depend on the Reynolds number and remains constant, or $\gamma = B_3$ (MN line).

Values A , A_2 , B , and B_3 are empirical coefficients.

Substituting in (1.6.4) the expression for the coefficient of gas-dynamic resistance γ in the transition region of motion and the Reynolds criterion, we obtain for the differential pressure in the layer Eq. (1.6.5):

$$(\Delta p) = \left\{ A_2 \cdot (1 - \varepsilon)^2 / (D_e^2 \cdot 2 \cdot \varepsilon^2 \cdot \psi^2) \right\} \cdot h \cdot \rho_g \cdot \varsigma \cdot \omega + \left\{ B(1 - \varepsilon) / (D_e \cdot 2 \cdot \varepsilon^3 \psi) \right\} h \cdot \rho_g \cdot \omega^2 \quad (1.6.5)$$

Let's denote expressions in curly brackets in the Eq. (1.6.5) by the coefficients k_1 and k_2 :

$$\begin{aligned} k_1 &= A_2 \cdot (1 - \varepsilon)^2 / (D_e^2 \cdot 2 \cdot \varepsilon^2 \cdot \psi^2) \\ k_2 &= B(1 - \varepsilon) / (D_e \cdot 2 \cdot \varepsilon^3 \cdot \psi) \end{aligned} \quad (1.6.6)$$

After substituting the expressions for k_1 and k_2 (1.6.6), the Eq. (1.6.5) is simplified to:

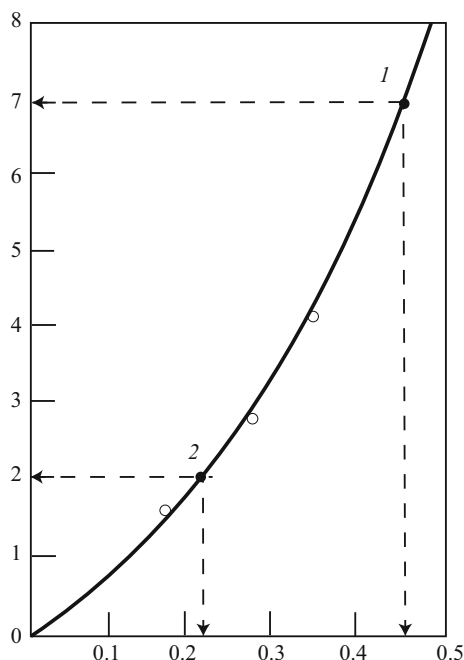
$$(\Delta p) = k_1 \cdot h \cdot \rho_g \cdot \varsigma \cdot \omega + k_2 \cdot h \cdot \rho_g \cdot \omega^2 \quad (1.6.7)$$

The gas-dynamic resistance coefficients k_1 and k_2 are easy to determine experimentally [27] (Fig. 1.38).

The coefficients k_1 and k_2 are determined from a system of equations compiled on the basis of (1.6.7) for two arbitrarily selected points of the gas-dynamic characteristics of the layer (e.g., points 1, 2 shown in Fig. 1.38).

The pressure drop in the bed Δp is a function of the properties of the gas phase (density, viscosity, volume, or velocity) and also depends on the temperature and pressure in the bed.

Fig. 1.38 Gas-dynamic characteristic of the pelleted sinter blend layer when atmospheric air is sucked through it [27] (layer height is 330 mm, air temperature is 20 °C, air density is 1.205 kg/m^3 , viscosity is $1.5 \times 10^{-5} \text{ m}^2/\text{s}$). The abscissa axis is the filtration rate, m/s; Y-axis—pressure drop Δp , kPa



1.6.3 Porosity of the Sintering Layer

The coefficients k_1 and k_2 of the gas-dynamic Eq. (1.6.7) essentially depend on the porosity⁵ of the charge layer ϵ .

The porosity of the charge layer is the amount of free space between the particles available for the passage of gas, and expressed as a proportion of the total volume of the layer. The effect of free space in the layer occurs due to loose stacking (packing) of particles due to their shape (spherical, clastic).

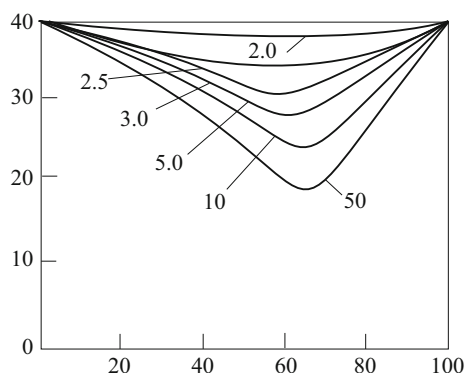
When placing balls of the same size in a layer, the porosity of the layer does not depend on their size, but only on the density of the package, and theoretically certain porosity values lie in the range of 0.26–0.48. For the case of polydisperse sinter charge, this rule cannot be fulfilled.

For a two-component mixture of solid particles, the dependence of the porosity of the layer on the ratio of the coarse and fine fractions in the mixture and their sizes is known, summarized in the form of S. Fournes curves [47], shown in Fig. 1.39.

As can be seen from Fig. 1.39, the porosity of the layer varies according to a complex law: The layer porosity decreases not only when adding a small fraction to

⁵There are different concepts of “porosity”: fraction of the free space in a single particle or a single aggregate of micro particles (for example, a granule of a pelletized charge or pellet), and as a fraction of free space in a set of macro-particles (layer). Denoted by the same symbol ϵ .

Fig. 1.39 Dependence of the layer porosity on the ratio of coarse and fine fractions and their diameters [47] (large fraction of size D , small fraction of size d ; numbers on curves— D/d ratio); the abscissa axis is the content of the coarse fraction, %; ordinate axis—layer porosity, %



a large one (which is quite expected), but also when adding a large fraction to a small one. At the same time, the particle size ratio affects the effect of the porosity reduction: The more different are the sizes of the coarse and fine fraction (the higher their ratio), the more significant the decrease in the porosity of the layer. The desire to ensure the greatest porosity of the sintered layer is due to the requirement to obtain the most homogeneous (granulometry) charge when pelletizing.

1.6.4 Gas Dynamics of Sintering Technology

The basic gas-dynamic parameter is the rate of air filtration through the layer of sintered charge ω_0 . The value of ω_0 depends on the characteristics of the layer (height, coefficient of gas-dynamic resistance, the presence of a bed), the parameters of the gas in the layer (temperature and composition), the resistance of the grate, the characteristics of the elements of the gas-exhaust tract (vacuum chambers, collector, gas cleaning device), exhausters and the chimney tract, as well as the design features of the sintering machine (geometric dimensions, type, and condition of seals).

A typical scheme of the sintering machine in terms of its gas-dynamic operation is shown in Fig. 1.40 [4].

The total resistance of the gas-exhaust path of the sintering machine consists of the resistances of its individual components. Then the total gas-dynamic resistance (expressed through the differential pressure Δp), taking into account the scheme of Fig. 1.40, is as follows:

$$\Delta p = \Delta p_{sc} + \Delta p_p + \Delta p_{vc} + \Delta p_c + \Delta p_{gc}, \quad (1.6.8)$$

where Δp , Δp with indices: total pressure drop, pressure drop on separate structural elements of the gas-discharge path of the sintering machine, respectively, in the charge layer (sc), on the pallet grate (p), in vacuum chambers (vc), in the collector (c), on the gas cleaning apparatus (gc).

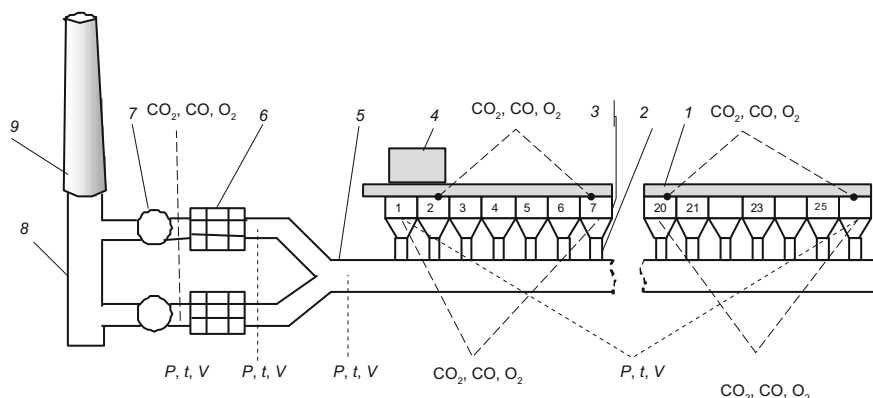


Fig. 1.40 Typical scheme of the gas-discharge path of the sintering machine [4] 1—layer sintered charge, 2—grate pallet, 3—vacuum chamber, 4—ignition hood, 5—collector, 6—gas cleaning device (apparatus), 7—exhauster, 8—chimney path, 9—chimney P, t, V , CO_2, CO, O_2 —points of control parameters (vacuum, temperature, gas rate, gas composition)

The gas-dynamic resistances of the components of the gas-exhaust path of the sintering machine are experimentally found separately for each element of the path.

The structure of the gas-dynamic resistance of the sinter production technology, or the contribution of each component to the total gas-dynamic resistance of the tract, is presented below:

	Pressure drop (kPa)	Share ^a , %
Layer of charge	5.5–10.2	65–76
The grate	0.17–0.45	2.3–2.9
Vacuum chambers	0.09–0.86	1.2–5.5
Collector	0.3–1.4	4.1–8.9
Gas cleaning apparatus (battery cyclones)	1.20–2.80	16.5–17.8

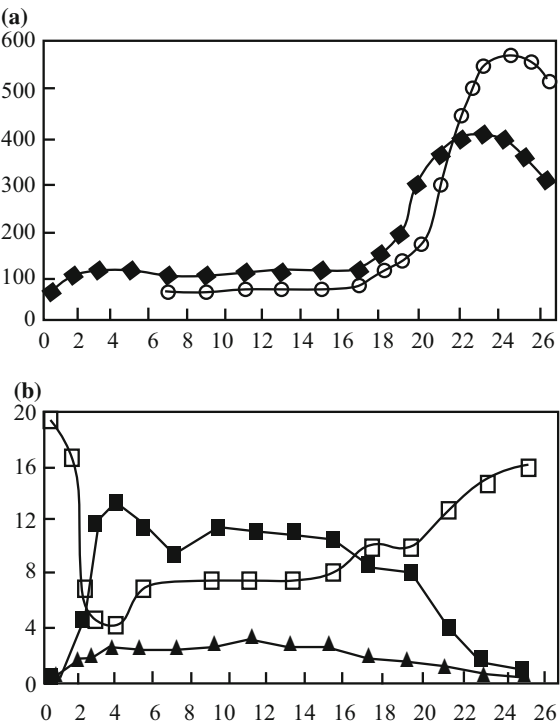
^aCalculated by the author according to [4]

The layer of sintered charge has the highest gas-dynamic resistance.

The determined gas-dynamic characteristics of the sintered charge layer include such indicators (Fig. 1.40):

- air filtration rate at the inlet to the layer (measured flow rate, temperature, pressure and gas composition in the nozzles of the vacuum chambers; chemical composition of the gas at the outlet of the layer);
- air suction in the exhaust duct (by the difference of gas flow in the vacuum chambers, the collector, and after the gas cleaning device);
- specific consumption of air for sintering of the charge;

Fig. 1.41 Temperature and composition distribution of the exhaust gas along the length of the sintering machine (AKM-312, JSC ZSMK, PJSC EVRAZ) [4]. **a** Temperatures (dark points—in the nozzles of the vacuum chambers; light points—under the grate grid at a distance of 1100 mm from the side); abscissa axis—numbers of vacuum chambers; Y-axis—temperature, °C; **b** change in concentration of CO (triangular points), CO₂ (diamond-shaped points), O₂ (transparent points); abscissa axis—numbers of vacuum chambers; ordinate axis—content of components, %



– Figure 1.41 [4] shows the characteristic temperature (a) and composition of the exhaust sinter gas (b) obtained from measurements on an industrial sinter machine (they are practically typical indicators).

In Table 1.16, for example, the gas-dynamic characteristics of the layers of the sintered blend of some sinter production plants are given (the actual data are approximated by a simplified power-law relation of the form $\Delta p^* = \gamma \cdot h \cdot \omega^n$ with

Table 1.16 Gas-dynamic characteristics of the sintered charge layer [4]

Sinter plant	Parameters			
	ω_o (m/s)	h (m)	Δp_{sc} (kPa)	γ
Russia, PJSC NLMK, s/m No. 3	0.338	0.430	10.22	134.8
Russia, JSC MMK, s/m No. 4	0.340	0.220	6.43	189.4
Russia, PJSC EVRAZ, ZSMK	0.274	0.305	9.42	194.0
Russia, JSCMet. Plant named after A.K. Serov	0.409	0.340	5.47	66.7
India, Durgapur plant, s/m No. 1	0.262	0.400	5.50	117.6
India, Bhilai plant, s/m No. 2	0.231	0.290	7.05	253.4

* γ —the coefficient of flow resistance, h is the height of sintered layer, ω —rate air filtration

$n = 1.60$. Comparison of the values of the gas-dynamic resistance coefficient reveals significant (multiple) differences of charge and sintering conditions.

1.6.5 Sinter Machine Performance

Optimization of gas-dynamic operation of sintering machines is to achieve (for a given quality of sinter) the maximum specific productivity.

The performance of the sintering machine is the mass of material (sinter cake), coming down from the tape per unit of time. Thus, productivity can be calculated by the Formula (1.6.9), representing the product of the volume of material per unit of time and its bulk density ρ_{sc} :

$$P = B \cdot h \cdot V_M \cdot \rho_{sc}, \quad (1.6.9)$$

where B —width of the pallet, m ;

h —the height of the sintered charge layer, m ;

V_M —speed of the conveyor belt, m/h .

The speed of the conveyor belt can be expressed in terms of the vertical sintering speed U , taking into account the condition of simultaneous completion of sintering along the layer height h and the length of the sintering machine L :

$$V_M = L \cdot U / h \quad (1.6.10)$$

Substituting (1.6.10) into (1.6.9), we have the following relation for sinter machine productivity:

$$P = B \cdot L \cdot U \cdot \rho_{sc} \quad (1.6.11)$$

In practice, when calculating performance, Formula (1.6.11) is used with correction factors n_1 and n_2 :

n_1 —characterizes the relative yield of the cake from the mixture, depends on the component and chemical composition of the mixture, the type of the obtained sinter, and usually has values of 0.85–0.90;

n_2 —used in assessing the performance of the machine on the yield of suitable (i.e., minus the return), depends on the strength characteristics of the sinter, the order of processing of the cake, normally equal to 0.65–0.70.

The final form of the formula for calculating the performance of the sintering machine can be represented as (1.6.12):

$$P = B \cdot L \cdot U \cdot \rho_{sc} \cdot n_1 \cdot n_2 \quad (1.6.12)$$

Thus, the ratio (1.6.12) clearly demonstrates the factors that determine the productivity of sintering machines: the value of the sintering area ($B \cdot L$), the quality of the sinter (through the yield coefficient N_2), the vertical sintering rate (U), and the structure and composition of the charge (through ρ_{sc} and n_1).

Let us consider some examples of solutions for improving the performance of sintering machines.

1.6.6 Ways to Improve the Performance of Sintering Machines

The desire of sinter producers to increase its production is realized in at least four ways:

- increase in sintering capacities (extensive path);
- an increase in yield (due to the quality of sinter, including in the upper part of the sintered layer and a decrease in the yield of return);
- the intensification of the processes of sintering (intensive way);
- use in blast furnace smelting of substandard sinter (a compromise).

1.6.6.1 Modernization to Increase Sintering Capacities

The increase in sintering capacities at the Shin-Nippon Seitetsu plant in Tobata (sinter machine No. 3) was accompanied by a complete modernization of equipment [48]. The overall scope of the upgrade is shown in Fig. 1.42.

The sintering area was increased from 320 to 480 m² due to the elongation of the tape from the loading side by 27 m, and from the discharge side by 13 m (total length of the tape is 120 m) without increasing the width. To get a bed, they put an independent line, which is able to use various raw materials, such as lump ore, pellets, and a combined charge. Desulfurization equipment was installed in the off-gas system, namely in the system for processing gases with a high SO_x content.

Improvement of equipment for preparation of charge. The capacity of the ore bunker was left unchanged; only the performance of the section of high-speed metering scales was changed. To improve the performance of the mixer, the angle of inclination of its body was changed from 3.0/100 to 3.5/100, and the internal lining of the mixer was made of rubber to reduce sticking of particles.

Improvement of loading equipment. To increase the feed rate of the charge (t/h) at the site of ore loading from the drum feeder, a device for dispersion by granulometric composition was installed (Intensified Sifting Feeder, abbreviated ISF). The main task of the device is a probabilistic screening of material in a three-stage

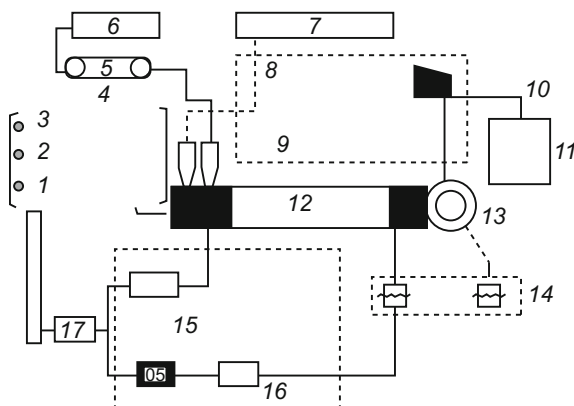


Fig. 1.42 Total modernization of sintering machine No. 3 company “Shin Nippon Seitetsu,” Tobata, Japan [48]. 1—artificial intelligence (system control service), 2—flat flame burner (ignition furnace), 3—screening device at the loading area, 4—changing the angle of the mixer from 3/100 to 3.5/100, 5—mixer, 6 and 7—charge bunkers, 8—line of allocation of bed, 9—line of screening, 10—belt conveyor, 11—blast furnace No. 1, 12—sintering machine (extended length from 80 to 120 m), 13—cooler, 14—equipment for heat recovery, 15—equipment for desulfurization of flue gas (process $Mg(OH)_2$), 16—precipitator, 17—exhauster

grate screen. The device contains 55 rotating bars located along the width. To prevent sticking of the charge, the rods through flexible shafts and gears are rotated by two engines. The spacing between the rods expands as they move to their free end; therefore, in the upper part between them, small pieces selectively slip and fall, in the lower part—large ones.

Modernization of sintering machine. Due to the increase in the sintering area, some changes were made:

Replacing bearings from the wheels of carts with ball bearings on tapered ones; The installation of the damper between the rails and the longitudinal seal.

Modernization of the ignition furnace. In the ignition furnace, surface burners developed by the company were used with preliminary regulation of the ratio in the mixture of coke oven gas—air, made with the possibility of vertical control depending on the layer height. In order to reduce energy consumption, a preheating chamber and a recovery chamber were installed before and after the furnace.

Sinter machine No. 3 in Tobata is equipped with a waste heat recovery boiler: in the system of the main collector of waste gases and in the system of gas removal in the cooling body of the sinter.

After the modernization, the main production characteristics have reached the following values:

- The performance of the machine after the upgrade has risen to 590 t/h.
- The yield after the upgrade has increased from 80 to 84%.

1.6.6.2 Increasing Sinter Yield

Increasing the strength of the upper part of the sinter cake constitutes an important resource for increasing the yield of a usable one. It is believed that the reduced strength of the upper part of the sinter cake is due to a number of factors, including:

- low heat level of the process;
- insufficient formation of the liquid phase;
- low charge density in the layer.

To compensate for the lack of heat in the upper part of the layer and to improve the conditions of slag formation, it is proposed [49] to inject powder into the upper part of the charge layer—a different material—which is a mixture of coke breeze serving as an auxiliary fuel, and flux-activating slag formation. Figure 1.43 shows schematically the system of powder material injection.

It includes a bunker, a plate feeder, a blower, and an umbrella installed after an ignition hood. The powder material comes from the bunker through the plate feeder is transported by the airflow created by the blower, distributed inside the umbrella, and blown into the upper part of the charge layer on the sintering belt. For uniform distribution of the material inside the umbrella in three positions across the width, reflecting plates are installed. The approximate composition of the powder material is listed in Table 1.17.

Fig. 1.43 System of injection of powdered material in the upper part of the layer of sinter charge [49]

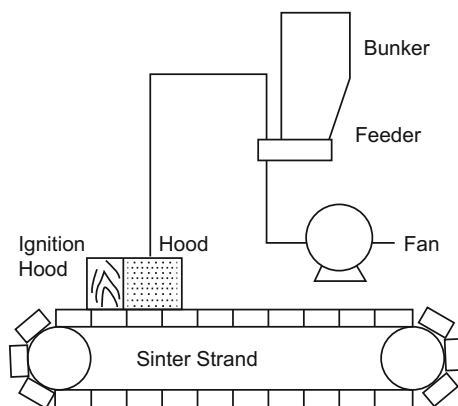


Table 1.17 Composition of powder material for injection

Components	Content (wet basis) (%)
Fe_2O_3	38.6
CaO	17.0
SiO_2	5.7
C	27.5

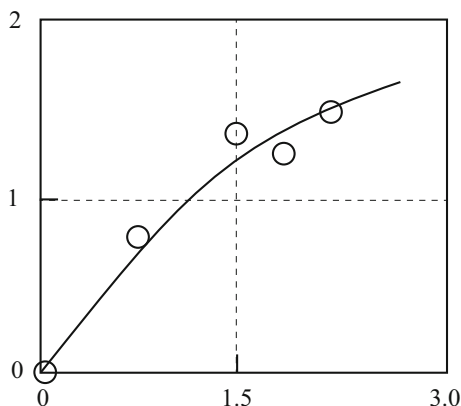


Fig. 1.44 Change in the yield of sinter when blowing flux in the upper part of the layer [49]. The abscissa axis is the flux consumption, kg/t of sinter; ordinate axis—change in the yield of sinter, %

Dust of aspiration systems and gas cleaning of main and auxiliary production can be used as a powder reagent.

The change in the output of the sinter upon injection of the flux increases in proportion to its consumption (Fig. 1.44); in the upper part of the layer, the yield of sinter increased by about 10% as a result of the injection of the flux.

As measures to increase the yield, it is proposed to reduce the return yield due to: [50, 51]:

- optimal use of screens;
- exclusion of secondary crusher;
- reduction of harmful suctions on the sintering machine;
- optimal distribution of thermal resources;
- automatic regulation of the thermal regime.

By introducing a set of measures, the return yield on sintering machine No. 4 in Fukuyama was reduced from 200 to 90 kg/t [51]; at Keihin [50], the return output decreased from 200 to 150 kg/t due to:

- measures to prevent overgrinding of sinter (excluding the secondary crusher and increasing the upper grain size limit of sinter loaded into blast furnaces from 100 to 150 mm, [51]);
- optimal treatment of sinter (two branches in accordance with the size of the product);
- measures to control the state of the grates and sealing units (reduction of harmful suctions on the sintering belt).

At the same time, by improving the classification of lump sinter (vibrating screens), the fraction of fines decreased from 14 to 12%, and the yield of sinter stabilized at the level of 82%.

1.6.6.3 Intensification of the Sintering Process

The development of measures to intensify the sintering process is based on the classical dependence of the vertical sintering rate U on the filtration rate ω :

$$U = \omega \cdot C_g / C_{sc} \cdot (1 - \varepsilon), \quad (1.6.13)$$

where C_g , C_{sc} —apparent heat capacity of gas and charge;
 ε —layer porosity.

Thus, the basis of both traditional and very modern innovations related to the intensification of the sintering process is the management of the gas permeability of the sintered layer due to:

- adjustment of the sintered layer height (in contrast to the previous concept, the new direction [52] is to reduce the sintered layer height to 460 mm);
- the organization of the supporting elements in the sintered layer;
- application of magnetic levitation force to reduce the load on the layer;
- use of new technologies of pelletizing with the use of pseudo-pellets;
- management of the layer structure by organizing the segregation of the sintering mixture when it is loaded on the machine.

With limited forced-draft capacity, it is probably advisable to avoid sintering very high layers (above 600 mm). In order to avoid reducing the strength of the sinter cake and the yield of sinter, and in order to maintain the high productivity of the sintering machine while reducing the height of the sintered layer, a set of measures was taken:

- to increase the efficiency of combustion (strengthening the control of coke size and reducing the charge density of the charge using a reflective plate);
- to ensure the sintering uniformity (improving the uniformity of the bed layer, increasing the sintering uniformity across the width of the sintering belt by increasing regulation of the charge flow during loading, and controlling the gaps of the grates).

With a decrease in the layer height to 460 mm, the specific productivity of the sinter machine was 39 t/day per m^2 at the output of the finished sinter equal to 85%. By introducing voltage and frequency control of the drive motor of the main exhaustor, they achieved 40% energy savings on its drive [52].

In order to achieve high productivity of the sintering process, it is necessary to improve the gas permeability of the melting and waterlogging zones of the sintered layer, which provide the main gas-dynamic resistance to the gas flow filtration.

One of the proposed solutions to this problem is the regulation of the layer structure by organizing vertical slotted holes of different width and height in the sintered layer [53].

The organization of vertical slotted holes in the sintered layer allows:

Table 1.18 Test periods

I	Without racks
II	With racks A (low)
III	With racks B (high)

- reduce head losses in the area of waterlogged sinter charge;
- increase the porosity in the melting zone, which in total provides an increase in the productivity of the sintering process.

A similar effect of increasing productivity is achieved by equipping sintering trolleys with special support racks. On sintering machine No. 1 in Kimitsu, all sintering trolleys were equipped with racks with optimal height [54]. The tests were carried out in different modes, for which all sintering trolleys were equipped with racks of two standard sizes in height (Table 1.18).

The most effective was the design of the trolley with high racks B, during the tests of which, despite the decrease in the share of quicklime in the charge, the vertical sintering speed increased further to ~ 37 mm/min as well as the yield of sinter.

As a measure of regulation of gas-dynamic resistance of the melting zone of the sintering layer [55, 56], the effect of magnetic fields on the sintered layer is proposed.

The magnetic phase contained in the sinter (in the form of magnetite, first of all) determines the behavior of the sinter in the magnetic field [55].

In a magnetic field, an interaction force (Maxwell's force) arises, which causes the effect of the rise (levitation) of the sinter cake.

$$f_y = \left(1 - \frac{1}{\mu_r}\right) \cdot B_y^2 / 2\mu_0 + \mu_0(\mu_r - 1)H_x^2 / 2, \quad (1.6.14)$$

$$B_y = \mu_0\mu_x H_x, \quad (1.6.15)$$

where f_y —Maxwell's force (N);

μ_0 —magnetic permeability in vacuum (–);

μ_r —specific magnetic permeability of magnetic material (–);

H_x —magnetic flux density in the direction of the vertical to the interface between the magnetic material and air (A/m);

B_y —the magnetic field in the interface between the magnetic material and the air (T).

However, when heated, magnetic materials lose their magnetic properties, so the principle of magnetic levitation can be used only at temperatures not exceeding 600 K (~ 400 °C).

Table 1.19 Efficiency indicators of the sintering process using the magnetic levitation force

No.	Sintering conditions		Performance indicators		
	Magnetic force	Height of the layer, mm	Productivity (t/d m ²)	Yield (%)	Vertical rate of sintering (mm/min ^a)
1	Base	600	26.05	85.6	13.0
2	With magnetic levitation	600	35.68	85.1	17.7
3	Base	800	24.66	89.8	11.5
4	With magnetic levitation	800	33.12	88.0	15.8

^aDefined [66]

Experimental equipment mounted on sintering pan with a diameter of 300 mm provided a magnetic evaporation of sinter cake weighing 100 kg at room temperature and a flux density at the magnetic pole of 0.6 T. The pressure force (load) of the sinter cake was determined from the readings of the strain gauge attached under the grate. The efficiency indicators of the sintering process using the magnetic levitation force are given in Table 1.19.

When limiting the sintering process by burning carbon in a layer, it is possible to intensify the sintering process by increasing the oxygen content in the gas that is sucked in. In experiments on sintering pan (diameter 300 mm, layer height 450 mm), the charge of sintering machine No. 4 of the Fukuyama plant was used; together with the intake air, oxygen and nitrogen were supplied at an oxygen concentration in the gas in the range of 16–36%.

The effect of reducing the sintering time was 0.26 min for every 1% increase in the oxygen concentration in the sucked gas. When the oxygen concentration was in the range of 21–36%, no reduction in yield was detected. The parameters of reducibility and strength in the reducing atmosphere remained practically unchanged with the change of oxygen concentration in the gas within the specified limits [57].

Application in blast furnace process off-grade sinter

According to [58], the content of fines (fraction—5 mm) in the sinter can reach 18%. The sinter fines (off-grade sinter) at the same time are a full-fledged charge material, which is advisable to use in the blast furnace process.

Such a solution was tested in [59].

At the Kawasaki Steel Corp plant, in order to reduce production costs by increasing the degree of use of sinter, the blast furnace process in furnace No. 5 is carried out with a large number of sinter fines. Loading of charge components of various sizes was carried out separately. The consumption of sinter fines is about 210 kg/t of hot metal.

Smelting was carried out in four periods.

- (1) the period of consumption of sinter fines at the level of 210 kg/t of hot metal without stabilizing the sinter;

- (2) the period of increasing the consumption of the sinter fines with the stabilization of the sinter (the occurrence of frequent breaks of the charge);
- (3) the period of increase of coke supply;
- (4) the period of reaching the consumption of sinter fines at the level of 260 kg/t of pig iron (with increased coke supply).

The melting of the off-grade sinter (fines) in the blast furnace is accompanied by serious gas-dynamic complications, leading to the suspension and breakage of the charge.

With limited resources of the raw material base of iron ore materials, the use of off-grade sinter (fines) in the blast furnace requires an increase in the consumption of coke.

1.7 Quality of the Sinter in Terms of Influence on the Performance of Blast Furnace Smelting

1.7.1 Sinter Quality Indicators

The quality of iron ore charge and, above all, the quality of the sinter are essential to ensure the high efficiency of blast furnaces. Product quality is a combination of its properties that determine suitability to meet the needs in accordance with the purpose. The quantitative characteristics of these properties are called quality indicators. Of the ten regulated [60] basic groups of quality indicators applied to agglomerated raw materials, it is advisable to distinguish three groups: indicators of manufacturability, transportability, and environmental friendliness.

The technological properties of the sinter are reflected by the following set of indicators [61]:

- (a) General properties:
 - granulometry;
 - chemical composition;
 - mineralogical composition (contents of hematite, magnetite, calcium ferrite, silicates, eutectic, amorphous phase, pores, micro-cracks);
 - physical properties (bulk and specific gravity, porosity, magnetization index).
- (b) Metallurgical properties:
 - mechanical strength (strength and abrasion performance, tumble test);
 - reduction and disintegration during reduction (R_{i60} , V_{40} , abrasion R_{i60});
 - disintegration during reduction (hot strength) RDI (in accordance with ISO and JIS);
 - thermoplastic properties (temperatures of the beginning and end of softening, the temperature range of the viscoplastic state).

A brief description of the equipment and test methods used to determine the sinter quality indicators is given in Table 1.20.

Indicators of the quality of the sinter of some manufacturers are presented in Table 1.21.

The specific consumption of blast furnace coke is influenced not only by the properties of the sinter, but also by the share of the sinter in the blast furnace charge, as well as other parameters of the blast furnace process [4, 10, 12] (Table 1.22).

Table 1.20 Brief description of sinter properties testing methods [61]

Property (quality index)	Equipment, measuring principle	Defined parameters
<i>General properties</i>		
Granulometry	Sieve with cells: 0.5; 5; 10; 25; 31.5; 40; 80 mm	di, % in the sieve, $d_{\min}$, $d_{\max}$
Chemical composition	Analytical equipment	Fe, FeO, Fe ₂ O ₃ , CaO, MgO, SiO ₂ , Al ₂ O ₃ , P, S et al. (if necessary) (%)
Mineralogical composition	Method of ore microscopy in reflected light (microscopes for ore microscopy, including analyzers)	Quantitative assessment of the content of phases: hematite, magnetite, olivine, calcium ferrite, calcium silicates, amorphous ligament; pores, micro-cracks
Physical properties	Pycnometer; measuring capacitance at 1, 3, 5 dm ³	Bulk weight, density (true, apparent), open porosity
	GOST 15165-69 [125]	Apparent density
<i>Metallurgical properties</i>		
Mechanical strength (cold strength)	Test for dropping a sample weighing 10–40 kg on a steel plate from a height of 2 m, followed by sieving and separation of the fraction –5 mm [125]	Only in laboratory tests
	Tumble test according to ISO 3271/75 (drum d 1000 × 500 mm, 2 shelves, rotation speed 25 ± 1 Rev/min, total about 200, loaded sinter of 10–40 mm in the amount of 15 kg)	Tumble +6.3 mm (%) Abrasion –0.5 mm (%)
	Tumble test according to GOST 15137-94 (drum d 1000 × 500 mm, 2 shelves with a width of 50 mm and a sample mass of 15 kg of fraction 5–40 mm, drum speed of 25 Rev/min, duration 8 min)	Shock resistance +5 mm (%) Abrasion –0.5 mm (%)
Reducibility, reducibility rate	Gravimetric assessment at a constant reduction temperature	
	Weight 1 kg with grain sizes 5–8, 11.2–16, 31.5–40 mm; restorative atmosphere 40% CO, 60% N ₂ , 60 min [61]	Reducibility RI, % Reducibility rate V ₄₀ , O ₂ /min, optionally, the fraction –0.5 mm (%)

(continued)

Table 1.20 (continued)

Property (quality index)	Equipment, measuring principle	Defined parameters
	GOST 21707-76 The mass of 300 g of the fraction 10–15 mm is reduced in the hydrogen current at 800 °C for 60 min with continuous mass control [126]	Reducibility R_i (%) Reducibility rate V_{40} (%O ₂ /min)
Reduction disintegration (hot strength)	JIS M8713 (500 g of sinter sample, fraction of 15–20 mm is reduced at 500 °C for 30 min gas composition: 20% CO, 20% CO ₂ , 60% N ₂ , then after cooling in the current N ₂ sample is subjected to dynamic load in the drum d 130 × 200 mm for 30 min)	RDI _{+6.3} (%) RDI _{+3.15} (%) RDI _{–0.5} (%)
	GOST 27446-87 (500 g of sinter sample of 15–20 mm fraction is reduced at 500 °C for 30 min with a gas composition of 20% CO, 20% CO ₂ , 60% N ₂ , and then after cooling in flow of N ₂ , the sample is subjected to dynamic stresses in the drum d 130 × 200 mm for 30 min) [4]	Reduction disintegration index is determined, RDI _{+6.3} (%)
Thermoplastic properties	Heating of a sample of sinter weighing 30 g (fraction 5–8 mm) at a speed of 10 °C/min without air access (in a reducing atmosphere) to 1580 °C under a load of 0.5 kg/cm ²	Temperatures of the beginning and the end of softening, a softening interval are defined
	The sample size of 2–3 mm is placed in a 40-mm layer in a cylindrical glass of heat-resistant steel with a diameter of 20 mm, which is placed in the heater of the electric furnace. The cylinder is covered with a piston rod, which exerts pressure on the sample of 0.2 MPa. Heating of the samples is carried out at a rate of 10 °C/min to a temperature 1400 °C, locking volumetric change of the sample (stem position) [126]	Temperatures of the beginning and the end of softening, a softening interval are defined

1.7.2 Influence of Sinter Quality on Gas-Dynamic Parameters of Blast Furnace Smelting

The main emphasis in the requirements for the quality of the sinter is on its strength properties (tumble test), affecting the gas-dynamic characteristics of the blast furnace shaft and softening indicators that determine the gas dynamics in the zones of cohesion and droplet formation.

Table 1.21 Sinter quality indicators [66]

Quality indicators	Company						
	Severstal ^a	ChMK ^b	CIS ^c	VSMZ ^d	Vitkovice steel ^e	Japan, Germany et al. [4] ^f	Nippon Steel, Muroran, Hokkaido ^g
<i>Chemical composition (%)</i>							
Fe	58.75	55.2	44–58	50.2	49.09	55–59	58.55
FeO	11.8	10.0	7–21	10.72	10.36	4–7	5.20
CaO/basicity	No data/1.49	No data/1.40	No data/0.7–2.1	12.93/1.18	13.61/1.13	No data/1.6–2.2	No data/1.70
MgO				3.06	1.77		0.93
SiO ₂				10.93	12.04		5.21
Al ₂ O ₃				No data	No data		1.88
P/S				1.33/no data	1.14/no data		No data
<i>Mineralogical composition (%)</i>							
Hematite				5.38	9.33		38.7
Magnetite				44.32	40.73		15.3
Calcium ferrite				15.14	13.81		21.7
Calcium silicates				35.16	36.12		24.3 ^h
Fines share –5 mm (%)	11.03	15.5	7.7–19.3	No data	No data	2.5–5.0	No data
<i>Strength TI (%)</i>							
+6.3 mm (+5 mm)	(62.4) ^f			62.04	58.08		73.3
–0.5 mm	7.4 ^f			4.76	4.82		
Reducibility Ri (%)				56.88	55.33		68.2 ⁱ
<i>Hot strength RDI (%)</i>							
+6.3 mm (+5 mm)				69.08	61.18		32.9
–0.5 mm (–3.15 mm)				(14.31)	(16.98)		
<i>Thermoplastic properties (°C)</i>							
– <i>t</i> start softening				No data	No data		1211
– Softening interval				204.8	234.0		204 ^k
– <i>t</i> droplet formation							1415

Notes to Table 1.21

^aSeverstal (Russia, AGC-2); ^bCHMK (Russia); ^cCIS—States of the former USSR (Ukraine, Kazakhstan) [4];^dVSMZ—East Slovak metallurgical plant (Czech Republic); ^eVMMK—Vitkovitsky metallurgical and machine-building plant (Czech Republic) [61]; ^faccording to [27]; ^gto [4]; ^hsinter plant in Muroran, Nippon Steel, Japan [80]; ⁱother (sum of remaining phases); ^jby JIS-RI; ^kdetermined by the author

The influence of the main metallurgical properties of sinter on the specific consumption of blast furnace coke and blast furnace performance is presented in Table 1.22

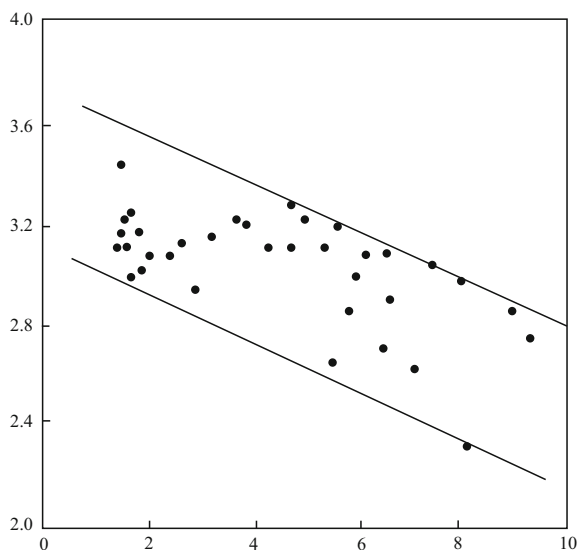
Table 1.22 Impact metallurgical properties of the sinter on the specific consumption of the blast furnace coke and the productivity of a blast furnace

#	Quality indicator of the sinter	Nature and level of influence on the blast furnace process	Notes
1	Granulometric composition	Reduction of coke consumption by 1–2% and increase of blast furnace productivity by 1.5–2.0%	When reducing the fraction-5 mm in the sinter (pellets) by 1% [12]
2	Chemical composition: iron content	Reduction of coke consumption by 0.8–1.3% and increase of blast furnace productivity by 1.5–2.5%	With an increase in the iron content in the sinter (pellets) by 1% [12]
	– Variability of iron content in the sinter (furnace charge)	Reduction of coke consumption by 0.5% and increase of blast furnace productivity	By reducing the variability of iron content from $\pm 0.5\%$ to $\pm 0.2\%$ [126]
	– FeO content	Reduction of coke consumption by 0.03%	When FeO is reduced by 1% [4] for ChMK conditions
	– Basicity	Reduction of coke consumption by 0.74% and increase of blast furnace productivity by 1.67%	With an increase in the basicity of the sinter by 0.1 units [4] for the conditions of ChMK
3	Mineralogical composition	Quantitatively not defined	Influences on reducibility (and strength)
4	Physical properties	Quantitatively not defined	Influences through reducibility
5	Mechanical strength	Reduction of coke consumption by 0.31%	By increasing the cold strength (yield of fraction +5 mm) by 1% [4] for ChMK conditions
6	Reducibility	Reduction of coke consumption by 4 kg/t of hot metal	With an increase in the reducibility of the sinter (or pellets) by 1% [126]
7	Hot strength	Reduction of coke consumption by 2 kg/t of hot metal and increase of blast furnace productivity by 0.6%	With an increase of $RDI_{+3.15}$ by 1% [4]
8	Thermoplastic properties	Quantitatively not defined	The softening interval of the sinter (charge) affects the gas permeability of the cohesion zone in the blast furnace

Ensuring proper gas permeability of the charge materials column is one of the important requirements when switching to coke-saving technologies with the injection of pulverized coal (PCI).

One of the characteristics of sinter quality, indirectly indicating its strength properties, is the fines content (-5 mm), which serves as one of the determining factors for the gas permeability of a column of charge materials in a blast furnace (Fig. 1.45).

Fig. 1.45 Influence of the content of fines in the sinter on the gas permeability of the charge column [123]. The abscissa axis—fraction content—5 mm in the sinter, %; Y-axis—gas permeability index (the ratio of the square of the gas velocity to the pressure drop)



The influence of the composition and properties of the sinter on gas permeability in the cohesion zone of the blast furnace (in terms of KS^6) is illustrated in Fig. 1.46a–d

With an increase in the basicity of the sinter (Fig. 1.46a), the intensity of droplet formation decreases and is especially significant with an increase in the basicity more than 2.1.

With constant basicity, an increase in the Fe content in the sinter is very favorable for increasing the gas permeability (Fig. 1.46b).

Improving the reducibility of sinter is very favorable for improving the gas dynamics of blast furnace (Fig. 1.46c).

The assessment of the significance of sinter quality indicators for gas-dynamic conditions of blast furnace smelting is given in Table 1.23.

The content of silicon dioxide has the strongest effect on the KS index and gas-dynamic resistance in the blast furnace (Fig. 1.46g).

1.7.3 Requirements for Sinter Quality

Chemical composition

There are several general requirements (recommendations) for the chemical composition, but ultimately the recommendations may not be taken into account for

⁶Index KS is an index reflecting the gas-dynamic resistance of the sinter, determined in a special experiment on its softening-reduction, integrated in the temperature range from 1000 to 1600 °C [62].

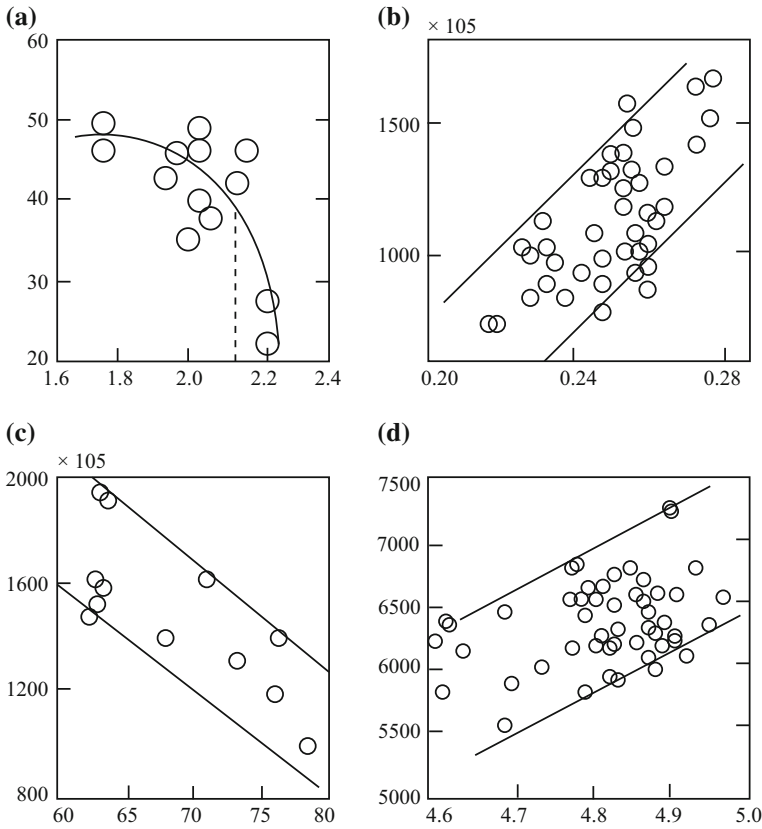


Fig. 1.46 Influence of composition and properties of the sinter on gas permeability in the area of cohesion [124]. **a** The influence of the basicity of the sinter on the relative rate of metal and slag drop formation at a SiO_2 content of 4.5–5.2%; the basicity of $\text{CaO}/\text{SiO}_2 = 1.7\text{--}2.2$; the abscissa axis is the basicity of the sinter; the ordinate axis is the relative rate of metal and slag drop formation, %; **b** the effect of iron content in the sinter, the basicity of $\text{CaO}/\text{SiO}_2 = 1.7\text{--}2.2$; SiO_2 3.8–5.2%; abscissa—ratio $(\text{CaO}/\text{SiO}_2)/\text{Fe}_{\text{total}}$; y-axis—indicator KS, $\times 10^5$; **c** the effect of reducibility of sinter, RI; $\text{CaO}/\text{SiO}_2 = 1.7\text{--}2.2$; $\text{SiO}_2 = 4.5\text{--}5.2\%$; abscissa axis—sinter reducibility according to the standard JIS-RI, %; y-axis—indicator KS, $\times 10^5$; **d** the effect of the content of silicon dioxide in the sinter; abscissa axis—content SiO_2 in sinter, %; ordinate axis—gas-dynamic resistance, $1/\text{m}$

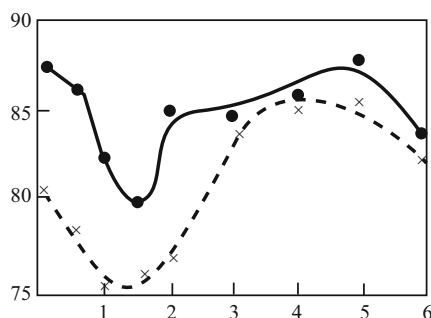
each enterprise due to certain commercial conditions related to the supply of raw materials of sinter charge.

Fe content. An immutable rule is to strive to use charge materials for sintering, which provide the highest possible Fe content in the sinter (when melting in a blast furnace, slag yield and thus coke consumption is reduced). For these purposes, it is advisable, first of all, finely divided concentrates of magnetic separation, as well as secondary products—mill scale, converter production dust, a fine magnetic fraction of wastes of crushing and sorting of steelmaking slag and other iron-containing waste.

Table 1.23 Importance of indicators of quality of sinter

Properties of sinter		Impact on the KS indicator (significance of the factor)
SiO ₂	+1%	+630 × 10
MgO	+1%	−328 × 10
Al ₂ O ₃	+1%	+17 × 10
Reducibility index RI (по JIS)	+1%	−40 × 10

Fig. 1.47 Dependence of sinter strength on basicity [27]. Line (points)—air cooling, line (crosses)—water cooling; abscissa axis—basicity of sinter CaO/SiO₂; ordinate axis—sinter strength (fraction yield +7 mm after dropping, %)



Currently, only fluxed sinter is produced. The task for basicity is determined on the basis of the charge of the blast furnace production base (the ratio of sinter consumption, pellets, raw ore, and other materials), as well as the strength of the sinter. It is known [63] that in the range of basicity values 1.1–1.5, sinter has minimal strength (Fig. 1.47).

The majority of theorists and practitioners of sintering associate the reason for such a significant drop in strength in the specified interval of basicities with polymorphic transformation of dicalcium silicate $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2 \rightarrow \gamma\text{-}2\text{CaO} \cdot \text{SiO}_2$, which occurs with a change in volume of 12% and causing in this connection the occurrence of stresses resulting in the weakening of the structure (and the destruction of the cake) [15]. To prevent silicate decomposition, a series of measures to stabilize dicalcium silicate have been developed [63–65].

The most rational recommendation is the production of fluxed sinter basicity above 1.5, i.e., over the boundary of the critical interval of basicities.

Content of FeO. The connection of this parameter with the strength of the sinter is ambiguous, since depends on sintering conditions (charge conditions, gas permeability, and layer height). The amount of FeO in the sinter is largely determined by the fuel consumption per process.

Stability of chemical composition. It is determined by the conditions of averaging charge components in the ore stockpile, as well as the accuracy of their dosing in the charge compartment. It is set by the deviation parameter from the calculated content (usually, on Fe, basicity) and the probability of falling into a given interval (90, 95, 99%).

Minimum deviations in both iron content and basicity are desirable.

Content of harmful impurities. It is recommended to select charge components with a minimum content of phosphorus, arsenic, non-ferrous metal compounds (zinc, lead, copper, etc.), as well as alkali metal compounds that are not removed during sintering. Such an undesirable component as sulfur is removed in the process of sintering to one degree or another, depending on the type of sulfur compounds.

Strength. Strong sinter—the charge component of the blast furnace smelting, which after sintering, cooling, crushing, and screening, contains the minimum amount of fines in the fraction—5 mm (the recommended level is not higher than 5%).

The strength of the sinter is formed throughout its entire life cycle: during sintering on the belt, cooling of the sinter, and also as a result of dynamic loads during the processing of sinter and its overloads.

The strength of the sintering cake is due to two structural levels:

- the state of the macrostructure (total porosity, pore size and shape, pore size distribution; the presence of certain crystalline phases, their type and distribution, the presence of amorphous phases, fracturing);
- type, composition, and characteristics of the phases that make up the sinter cake.
- Iron ore fluxed sinter consists of a significant number of phases with different physicochemical characteristics, in particular, the strength and reproducibility of the phases are presented in Table 1.24.

The strongest phases are magnetite, hematite, olivines (with $x < 1$), two-calcium ferrite, the least stable phases are olivines, approaching in composition to dicalcium silicate (at $x > 1.5$), amorphous phase (glass).

The study of the mechanism of destruction of real sinter cake by the method of acoustic emission [15] showed that the olivine bond (glass) is the most resistant to nucleation and the development of cracks under loading. On the contrary, the destruction of sinters in the basicity region of 1.1–1.5 is caused not by the low strength of olivine, but by the polymorphic transformation of $\beta\text{-}2\text{CaO} \cdot \text{SiO}_2$.

At the same time, assessing the role of the mineral composition of the sinter in its strength, it is noted that the share of this factor does not exceed 10–15%, and the macrostructure parameters (porosity and pore size distribution, the size of the matrix phase crystals) dominate (90%), the volume of the glass phase and the level of its crystallization, etc.).

The presence of pores and their branched system are the conditions of low strength of sintering cake as a structure (Fig. 1.48a–d).

The presence of stresses also contributes to the destruction of the sintering cake under the action of loads due to its multi-phase character (Fig. 1.49a–d):

- thermal, arising during cooling of the formed cake due to the difference in temperature in separate volumes;
- interfacial due to the multi-phase structure due to differences in the coefficients of thermal expansion of the phases;
- phase, due to polymorphic transformations of some phases (e.g., dicalcium silicate).

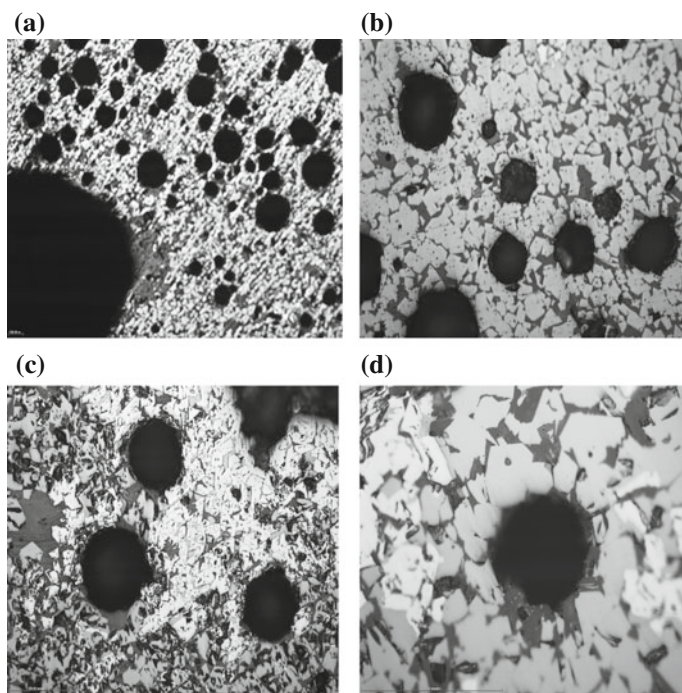


Fig. 1.48 Porous structure of the sinter cake. Sinter (100% fine magnetite concentrate in the mixture, the basicity of 1.1, the Fe content of 59.0%, reflected light): **a** the system of pores in the sinter of various sizes formed on the advantage of filtering the air through the melt, $\times 100$; **b** the set of pores of circular cross section, $\times 200$; **c** the pores with a characteristic zone of oxidation around them, $\times 200$; **d** pore formed around a burning particle of fuel, $\times 500$. Bright white-hematite, white-magnetite, gray-olivine ligament, black-pores

The main components of the macrostructure of the sintering cake are formed in the process of melt crystallization (magnetite, olivines, calcium silicates, calcium ferrites), others in the process of cooling the cake (hematite, glass).

Reducibility. As follows from Table 1.24, hematite and calcium ferrites, which appear separately in the structure of the sinter with sufficiently high basicity (more than 1.5) and can only occur locally with basicity less than 1.5, belong to the easily reduced phases (Fig. 1.49a). The main recipe for increasing the reducibility of sinter is to regulate the content of FeO.

Softening (temperature of the beginning t_b and end of softening t_f). The parameters t_b and t_f are determined by the mineralogical composition of the sinter (which, in turn, depends on the chemical composition of the charge components and fuel consumption), by the FeO content (with priority) and basicity. The adjustment of the technological mode of the sintering process in order to obtain product with the specified softening characteristics is not performed.

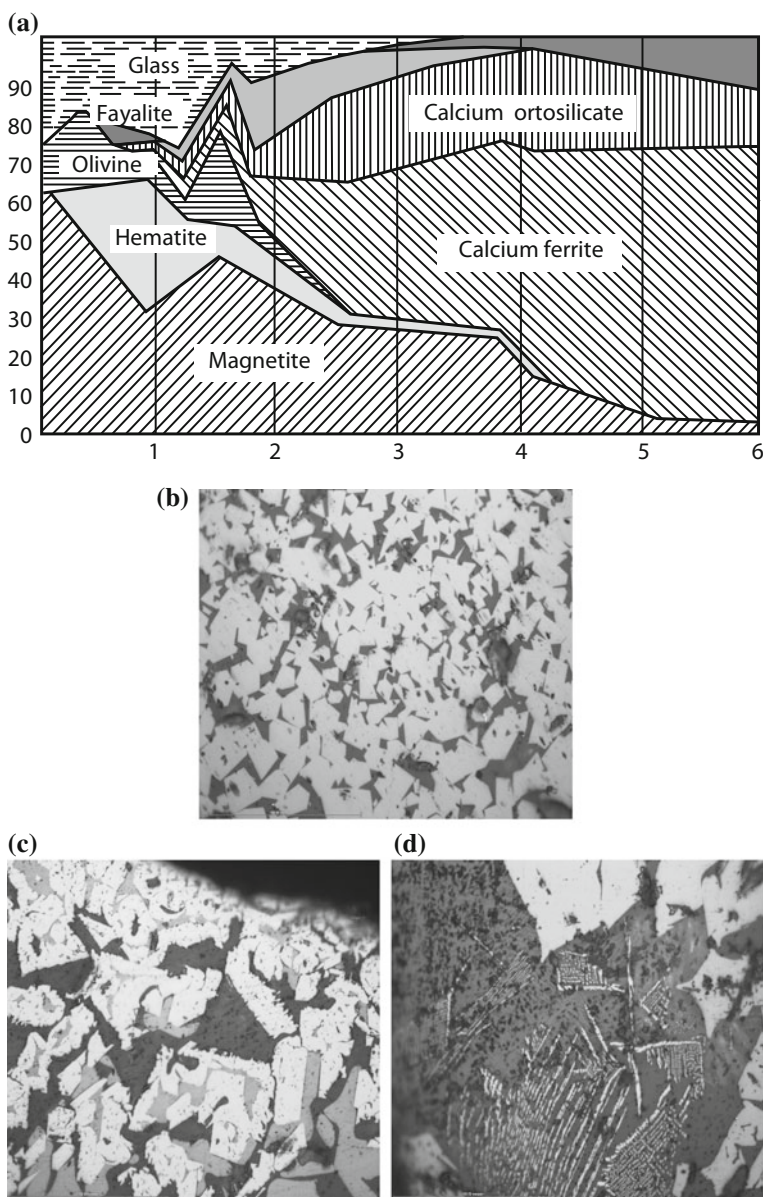


Fig. 1.49 Macrostructure of sinter cake. Sinter (100% fine magnetite concentrate in the mixture, the basicity of 1.1, the Fe content of 59.0%), reflected light): **a** changes in mineralogical composition of fluxed sinters depending on the basicity [27]; **b** crystals of magnetite in the olivine bundle (glass), $\times 200$; **c** hematite, $\times 500$ formed during the oxidation of magnetite crystals; **d** eutectic magnetite—olivines (lower part of the photo), calcium silicates (even selections in the olivine bundle)

Table 1.24 Strength σ and reducibility of the Ri phases included in the iron ore fluxed sinter [27]

Phase composition of the sinter	Strength σ (kN/sm ²)	Reducibility Ri (%)
Hematite Fe ₂ O ₃	26.2	49.9
Magnetite Fe ₃ O ₄	36.2	26.7
Fayalite 2FeO · SiO ₂	19.9	1.0
Olivines CaO _x · FeO _{2-x} · SiO ₂		
$x = 0.25$	26.0	2.1
$x = 0.50$	55.6	2.7
$x = 1.0$	22.9	6.6
$x = 1.0$ (glass)	3.9	3.1
$x = 1.5$	10.0	No data
Calcium ferrites CaO _y · Fe ₂ O ₃		
$y = 1$ (monocalcium)	13.9	40.1
$y = 2$ (dicalcium)	36.3	28.5

In terms of the efficiency of blast furnace smelting, a high-quality sinter should have the following characteristics [66]:

- optimal particle size distribution (size 5–40 mm, recommended size >10 mm);
- high cold strength (strength index TI >92%);
- high reducibility (indicator RI >65%);
- proper hot strength (RDI_{-3,15} not more than 20%);
- softening temperature above 1250 °C (depending on the total composition of the charge);
- narrow softening interval (narrow temperature range in the cohesion zone);
- FeO content stability (reduced level of ~7–8% is recommended);
- stability of the basicity of the sinter corresponding to the optimal conditions of the blast furnace melting [67].

1.7.4 Basic Solutions to Improve Quality of Sinter

The strategy to improve the quality of sinter is associated with the requirements for ensuring the stability and efficiency of blast smelting by regulating:

- silica content (low-silicon sinter), and, accordingly, Fe content;
- iron oxide content in the sinter;
- porosity of sinter (using iron ores of hydrogoethite nature, or limonites);
- viscosity of liquid phases (addition of low-melting additives);
- sintering cake structures (production of hybrid sinter).

1.7.4.1 Production of Low-Silicon Sinter

In the global sintering practice, there is a tendency to reduce the silica content in the sinter: For 10 years, the SiO_2 content decreased from 5.5 to 3.9% due to the use of finely divided concentrates (up to 60%⁷) in the blend, requiring the development of efficient charge agglomeration technologies:

- A method of production of mini-pellets without nucleating centers (method of preliminary pelletizing of dispersed ore), providing for the addition of 1–2% of bentonite, was commissioned in 1987 at the sintering plant in Hirohata (Nippon Steel).
- The method of mini-pellets with the addition of a nucleating component (method of preliminary pelletizing of dispersed ore) provides the introduction of return or oolitic ore as a nucleating material; it was mastered at the sinter plant in Muroran (Nippon Steel) in 1982 and was tested at many plants, including in 1985 in Russia (NTMK) [37]; it works in industrial conditions on the sintering machine number 4 at NLMK, Russia [68].
- The method of separate pelletizing of the nucleating and dispersed fractions (loading of the dispersed material after the pelletization of the fraction +1 mm).
- A method of pelletizing with the addition of a fine-dispersed lump stimulator (converter dust, ultra-fine fraction) was applied in 1985 on sinter machine No. 3 in Tobata (Nippon Steel);
- Hybrid method of sintering of pelletized charge (HPS) was commissioned in November 1988 on the sintering machine No. 5 in Fukuyama (Nippon Kokan).

The HPS method is based on a two-layer pellet model, the core of which consists of a coarse fraction of ore (return) surrounded by a shell of fine iron ore or flux. On the surface of the granules, the shell of coke breeze size is less than 1 mm. The diameter of the granules is not less than 5 mm.

A flowchart of the process for the production of HPP sinter is shown in Fig. 1.50. For granulation, the scheme provides the largest bowl granulator with a diameter of 7.5 m [69].

Favorable factors of HPS production affecting the improvement of sinter quality indicators can be considered [70]:

- reducing the amount and volume of macropores (affects the cold strength of the sinter);
- reducing the content of hematite mineral (affects the destruction of the sinter during reduction);
- an increase in the number and volume of micropores, as well as a decrease in the content of silicates in the structure of the sintering cake (affects the reducibility of sinter);

⁷In Russia, sinter plants work with a very high proportion in the mixture of finely ground concentrates (up to 100%), Fe content in fluxed sinters is 55–59%, SiO_2 —5.5–9%.

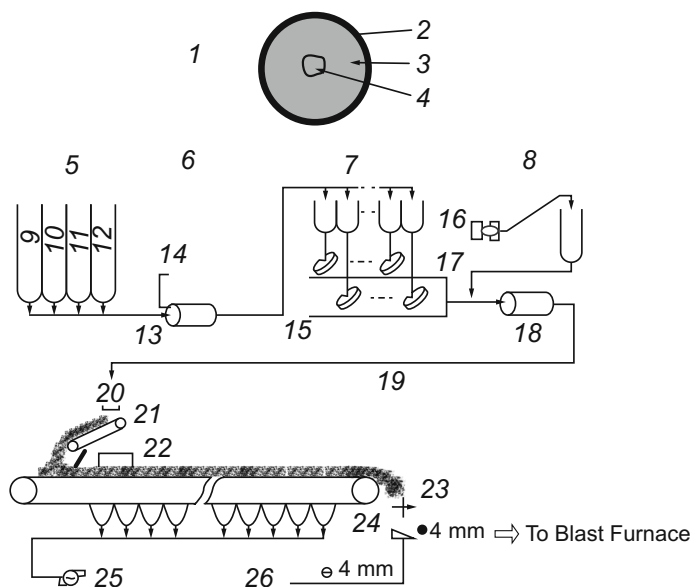


Fig. 1.50 Technological scheme of sintering process of HPS production [69]. 1—structure of the raw pellet; 2—coke breeze, 3—dispersed ore, flux, 4—coarse-grained ore, 5—raw materials 6—mixing, 7—pelletizing 8—rolling shell from coke fines, 9—concentrate for pelletizing, 10—ore fines, 11—returns, 12—flux, 13—mixer, 14—water, 15—disk granulator, 16—rod mill, 17—coke breeze, 18—drum mixer, 19—raw pellets, 20—shuttle distributor, 21—conveyor feeder, 22—ignition hood, 23—sinter crusher, 24—sieve, 25—exhauster, 26—returns

- lowering the concentration of SiO_2 and MgO (affects the gas permeability of the sinter at high temperature).

The preferred measures to improve the quality of sinter in the technologies of sinter production with advanced pelletizing are:

- regulation of pore structure: increase of micropores and decrease of macropores;
- optimization of chemical composition of sinter: an increase in the concentration of magnesium oxide and reduce the concentration of silicon dioxide;
- optimization of the mineralogical composition of the sinter: an increase in the content of magnetite and complex calcium ferrite (SFCA), which in addition to CaO and Fe_2O_3 , as in conventional calcium ferrite, also contains Al_2O_3 and SiO_2 (results [71] confirm that SFCA is the main component in the sinter's binder).

Formation of the macrostructure of granules (pseudo-pellets) in the process of HPS due to the formation and redistribution of the melt is accompanied by the fusion of pores and the formation of a porous structure and a certain mineralogical composition (Fig. 1.51).

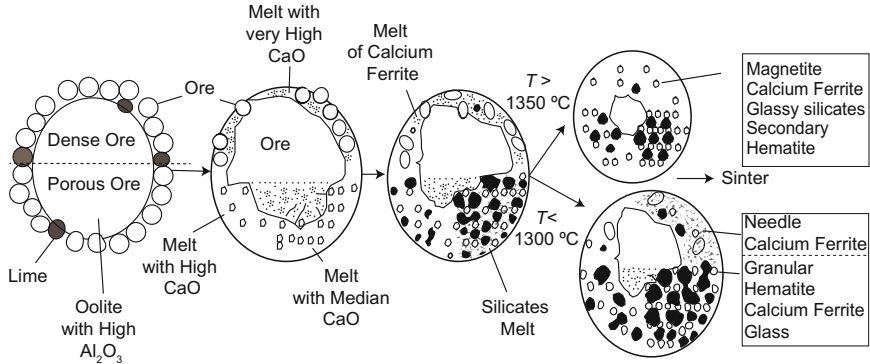


Fig. 1.51 Scheme of formation of macrostructure of granules in the process of HPS [69]

Table 1.25 Concept of porous meso-mosaic structure of the sinter, ensuring the achievement of high quality of the sinter [70]

Name		Favorable trend
Physical properties of sinter	Strength	Macropores↓
	Reduction disintegration	Hematite↓
	Reducibility	Silicates↓, Micropores↑
	Gas permeability at high temperature	SiO ₂ ↓, MgO ↑
Chemical composition		MgO ↑ (CaO, SiO ₂)↓
Good structure		SFCA, magnetite
	Pores	Micropores

Table 1.26 Influence of SiO₂ content^a on sinter quality [72]

Quality indicators	Sinter HPS	Ordinary sinter
TI (+10) (%)	0.5 ↓	0.9 ↓
RDI (%)	0.5 ↑	1.4 ↑
RI (%)	0.9 ↑	1.2 ↑

^aThe change in index in %, by reducing the content of SiO₂ is 0.1%

To identify the factors determining the quality of HPS sinter, the following estimations of favorability are proposed (Table 1.25).

The effectiveness of HPS technology is confirmed by industrial tests on sintering machine No. 5 in Fukuyama [72].

A general pattern of influence of SiO₂ content on the quality of sinter is shown in Table 1.26.

Table 1.27 Properties of industrial sinters

No.	FeO (%)	SiO ₂ (%)	MgO (%)	JIS-RI (%)	ΔT (K)	$P_{\max}$ (kPa)
1	7.99	5.58	1.84	63.9	—	—
2	7.74	5.66	1.44	65.5	—	—
3	7.08	5.17	1.58	66.0	—	—
4	5.15	5.16	1.87	63.1	—	—
5	6.90	5.72	1.67	60.5	244	27.4
6	5.69	5.30	1.48	65.5	241	27.2
7	5.06	5.06	1.78	69.1	288	26.5
8	5.26	5.06	1.66	67.0	—	—
9	5.94	4.93	1.83	66.0	286	35.7

Similar results on the effect of SiO₂ content on the sinter quality with an increase in the share of Brazilian concentrate in the charge were obtained at the Handan Steel plant [73] and were also confirmed in pilot testing [74].

Note that for a sinter production of HPS fuel consumption decreased significantly ($\sim 40\text{--}34$ kg/t).

The study of the reducibility of industrial samples of sinters with a low content of SiO₂ and FeO (Table 1.27), taken from industrial sintering machine No. 2 of the Oita plant (Japan) [75], was carried out in two ways:

- using a vertical probe in a blast furnace (equipped with a stainless steel mesh container) and subsequent research of the extracted materials;
- on the experimental laboratory device BIS, simulating conditions in a blast furnace (softening and reduction under load in the current of the generator gas).

The limiting degree of reduction of sinter with low SiO₂ and FeO content in comparison with conventional sinter (at 1203 K) is quite high (Table 1.27); at the same time, the reducibility in the zone of lump materials of the blast furnace for sinter with low SiO₂ and FeO content is also higher.

The macrostructure of high-quality sinter having high values of cold strength, reducibility, and strength during reduction should be characterized by the following features [76]:

- Only small dense grains of the primary (initial) ore remain inside the micro-needle calcium ferrite; pores of irregular shape are absent.
- Granular hematite is surrounded by fine calcium ferrite (CF) and trace amounts of vitreous silicates; pores have a rounded shape, with a large wall thickness between the pores.

Thus, the use of sinter with reduced SiO₂ content can potentially provide certain advantages in blast furnace smelting:

- increasing the reducibility of the charge;
- reduction of the slag yield;

- reducing the width of the zone of cohesion [77];
- improvement of gas permeability in the lower zones of the blast furnace;
- reduction of silicon content in cast iron.

At the same time, with a decrease in SiO_2 , it is predicted [77]:

- deterioration of RDI;
- lowering the TI drum sample.

1.7.4.2 Control of the Porous Structure of the Sinter

The porous structure of the sinter (pore volume, porosity, and pore size distribution) is formed by several mechanisms:

- filtration of air through the sinter melt during its solidification and subsequent cooling;
- at the outflow of the melt (the formation of shrinkage cavities during solidification of the melt);
- combustion of fuel particles;
- due to the outgassing in the reduction reactions of iron oxides;
- when chemical compounds are dissociated (it is shown, e.g., [78] that the concentration and size of limestone have a significant impact on the structure of the pores of the sinter, increasing their branching and length).

To control the porous structure of the sinter, it is proposed to introduce iron ore components containing crystallization water (brown iron ores) into the mixture.

Initially, the use of limonite and oolitic ores belonging to the group of brown iron ore was caused by restrictions on the production of rich hematite ore [69], and therefore, it was planned to bring the content of limonite ores in the sinter to 20–30%. The introduction of limonite ores due to their high dispersion and poor lumpiness in the sinter charge without special measures is associated with a deterioration of gas permeability.

Oolitic ore has a fish caviar structure with a hematite core and a large amount of goethite surrounding it. As a result, when removing crystallization water, a structure with large cracks is formed, and with a rapidly flowing assimilation by the melt, a large-porous fragile substance appears. In addition, due to the high SiO_2 content, there is a tendency to form a vitreous silicate bond. These features of the ore are the main reasons for the deterioration of the sintering process and reduce the quality of sinter.

It is known that some producers master the industrial process using 50% oolitic ore with a low Al_2O_3 content (BHP, Australia) in the charge; with a 54% share of oolitic ore in fresh raw materials in experiments on an sinter machine in Kobe (Kobe Steel, Japan) and with a 40% share of such ore at a sinter plant in Mizushima (Kawasaki Steel, Japan).

Recently proposed technologies for large-scale involvement of oolitic ores that are acceptable in terms of quality [66] include:

- (a) mixing with high density (and low crystallization water) material (concentrate);
- (b) adding mill scale;
- (c) formation of a protective layer (use of serpentine, converter slag, ore concentrate);
- (d) self-sealing sintering;
- (e) preliminary pelletizing with coke breeze;
- (f) preheating;
- (g) formation of a bed of lump oolitic ore.

Of the presented technical solutions, two methods are introduced into production, three methods are in the stage of industrial testing, and two are at the level of experimental testing.

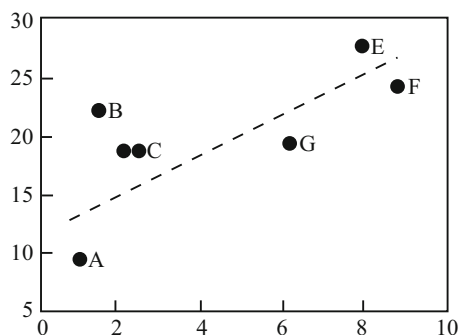
The peculiarity of the method (a) is the mixing of oolitic ore and dense fine-ground material in almost equal parts. In 1989–1990, this technology is applied in Kamaishi on the sintering machine, and sintering machine No. 3 in Nagoya (Nippon Steel) reached the maximum share of oolitic ore in the charge—35%. Technology (b) was tested in 1994 in industrial conditions at the sinter plant in Mizushima (Kawasaki steel). The addition of 8% of mill scale improves the properties of the melt and prevents a decrease in the yield even on the charge with 40% oolitic ore.

Methods (c)–(e) require equipment for selective pelletizing, and their distribution has not yet advanced. Technology (c) provides for selective pelletizing with refractory powder material and the creation of a protective layer on the surface of oolitic ore particles that would prevent a sharp course of assimilation. Selective pelletizing with serpentine was tested at the sinter plant in Kure (Nissin steel) with the effect of increasing the specific productivity. Method (d) involves the delay of contact of coarse-grained oolitic ore with the melt and the use of the ability of goethite in the ore to recrystallization with the compaction of the structure at temperatures of 1200 °C and above.

The effectiveness of selective pelletizing oolitic ore with serpentine and carbon containing material (method (e) tested in 1990 on the sintering machine No. 2 in Sakai (Nippon Steel). In 1992, sintering method with self-compaction and refractory liquid phase (SHS) was introduced on sintering machine No. 1 in Oita (Nippon Steel).

Oolitic ore is subjected to classification with the separation of a class of +3 mm and the subsequent selective pelletizing of a large fraction together with finely ground serpentine, limestone, and coke. A protective layer is formed on the surface of the ore particles, which forms a melt at a temperature not lower than 1350 °C, practically after compaction of the ore. The layer has a low basicity and a high concentration of carbon. The mixture is sintered with a 20% share of oolitic ore, achieving an increase in the yield and a reduction in fuel costs.

Fig. 1.52 Relationship between the content of water of crystallization in ore and sinter porosity [62, 79]. Dots with letters reflect the types of ores, the dotted line—the trend of dependence. The abscissa axis is the content of bound water, %; y-axis—sinter cake porosity, %



Technology (h) tested at the sinter plant in Kokura (Sumimoto metal industries) to obtain a satisfactory quality of sinter with 50% oolitic ore in the charge.

The role of crystallization water in limonite and oolitic ores in the formation of porosity in the sinter is illustrated by the data [62, 79] and Fig. 1.52.

1.7.4.3 Introduction of Low-Melting Additives

With regard to the formation and behavior of the liquid phase (melt) in the sintered layer, it can be argued that the characteristic modes of liquid-phase sintering take place for different horizons of the layer during the formation of the sintering cake [37].

In the upper part of the layer (60–80 mm), when the amount of melt does not exceed 30–40%, the mode of dissolution—secondary separation is preferred. For the central part of the layer (150–250 mm), where the melt mass averages 55–65%, the main contribution to the liquid-phase sintering process is made by the redistribution mode. In the lower part of the layer, when the amount of the liquid phase is more than 70–80% and the redistribution of the material is completed quickly enough, there is a crystallization of heterogeneous ferrous melt.

It is noted that for the formation of the proper strength of the sintering cake (macrostructure), the melt amount should be at least 70% [4, 37].

In order to ensure an adequate amount of melt, light-melting additives are recommended. Low-melting additives, facilitating the formation of the melt, and thereby improving the strength of the sinter, are considered:

- calcium ferrites (solutions aimed at the predominant formation of ferrite–calcium binder are associated with the optimization of the fluxing regime, or with the introduction of ready-made mixtures);
- specially introduced additives (akmit, etc.).

In [4], it is proposed to introduce a mixture of finely ground hematite ore with lime in the ratio corresponding to the $\text{CaO} \cdot \text{Fe}_2\text{O}_3$ compound into the sinter charge in the amount of 10% (the tumble test improved by 30%).

The formation of ferrite of calcium in the structure of the sinter is determined by the type of iron ore material, the degree of fluxing, and physicochemical conditions during sintering of charge.

According to [80], when the basicity of the sinter is 1.83–1.87 with FeO 5.1–8.6%, the content of calcium ferrite (% by mass) varies within 20.8–30.6%.

The results of the analysis of sinter with low content of SiO_2 and MgO produced at the sinter plant in Muroran (Japan) are given in Table 1.21, where the content of calcium ferrite exceeds 20%.

Intensification of the formation of calcium ferrite is due to two main factors:

- the content of the flux component in the sinter (basicity);
- the ability of the flux component to the solid-phase interaction (the activity of the reaction surface and its magnitude) of the flux and iron ore components.

As shown by electron probe micro-analyzer (EPMA) [81], in the presence of gangue, especially of alumina (Al_2O_3 content $\sim 3\%$), calcium ferrite has a complex composition of the aenigmatite type, corresponding to formula $\text{X}_2\text{Y}_6\text{Z}_6\text{O}_{20}$, where

X-ions Ca^{2+} , Na^+ , K^+ ;

Y-ions Ca^{2+} , Mg^{2+} , Fe^{2+} , Fe^{3+} ;

Z-ions Fe^{3+} , Al^{3+} , Si^{4+} .

Lime is an effective reagent for the formation of calcium ferrite. On the sintering machine No. 4 in Chiba Prefecture has installed equipment to obtain quicklime as a by-product. The technological scheme of the equipment for the secondary production of quicklime is shown in Fig. 1.53. The raw material prepared in advance in the mix (85–88% limestone and 12–15% coke) is loaded from the hopper with a second layer on the top of the sinter on the machine belt and distributed there at a width of about 3/5 of the width of the sintering trolleys. Both layers are

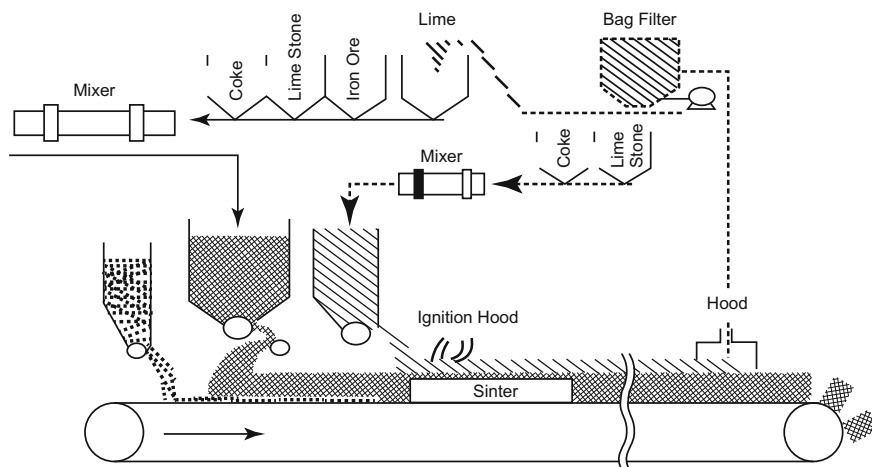


Fig. 1.53 Technological scheme of secondary production of quicklime [82]

Table 1.28 Composition of quicklime

Components	By-product	Purchased lime
CaO	86–88	97
CaCO ₃	6–8	1
Miscellaneous	6	2

simultaneously ignited in the furnace. As the sintering belt moves, the top layer turns into quicklime. The finished lime is sucked from the surface of the sinter through the exhaust nozzle umbrella and returned to the sinter preparation system as a binder.

The quality indicators of the secondary quicklime are presented in Table 1.28. In addition to calcium oxide product contains about 13% impurities. It is a dust-like sinter, as well as limestone and unburned coke. From the point of view of sinter production, these impurities do not pose any problem, and the by-product is quite suitable for use at the sinter plant.

Due to the two-layer loading, the sinter output from the surface layer with a height of 200 mm increased by 14.2%. In terms of the whole sinter, the increase in yield is 2.5% [82].

A method for the production of lime on conveyor machines similar to the sintering process is known [83], when the limestone of the 3–10 mm fraction is loaded onto the firing tape with a layer of 150–200 mm in a mixture with 10–12% coke fines. Such technologies were used at sinter plants in Ukraine.

Another well-known additive in the sintering furnace is a mineral akmit [84], which is introduced by:

- (1) addition of the mixture of water and additives in the entire sinter charge;
- (2) addition of a mixture of water and additives only in the ore material with a high concentration of water of crystallization;
- (3) addition of a mixture of water and additives only in ore material with the usual concentration of crystallization water (i.e., excluding ore material with a high concentration of crystallization water).

A significant increase in the strength of the sintering cake occurs only in the case of 3), i.e., when added to an ore material with a normal concentration of crystallization water.

1.7.4.4 Return Mode

One of the main parameters of sintering process control affecting the strength properties of the sinter is the return mode, which is especially important for charge with a high proportion of fine concentrates.

The return facilitates the start of liquid-phase sintering due to the lower melting rate compared to the rest of the charge, so it can be considered as a fusible additive.

With an increase in the content of the return in the charge, the temperature regime of sintering changes. The presence of a return charge reduces the apparent heat capacity of the charge due to the reduction of heat consumption for moisture evaporation, decomposition of limestone and hydroxides of ore minerals. At the same time, an increase in the return content increases the air filtration rate, resulting in a decrease in the level of maximum temperatures in the layer. Despite the effect of such contradictory processes, the increase in the content of return in the charge leads to an increase in the strength of the sinter.

Each charge corresponds to the optimal amount of return, which ensures the strength of the sinter.

The return content in the charge at sinter plants of the CIS countries lies within 15–40% [4], at foreign factories sintering the charge in a high layer and applying thermal stabilization of the sinter, the return yield of 120–180 kg/t of the sinter has been achieved [51].

From the standpoint of obtaining high strength of the sinter, the lower limit of the share of the return in the charge is 20% [85], with a further increase in the content of the return in the charge, and the strength of the sinter increases and subsequently changes slightly (Fig. 1.54).

Optimal sintering conditions are formed with the proper ratio of fine and coarse fractions, i.e., at a certain return size. With a return size of 0–8 mm, the highest strength of the sinter and the minimum yield of the fines (fraction –5 mm) are achieved (Table 1.29).

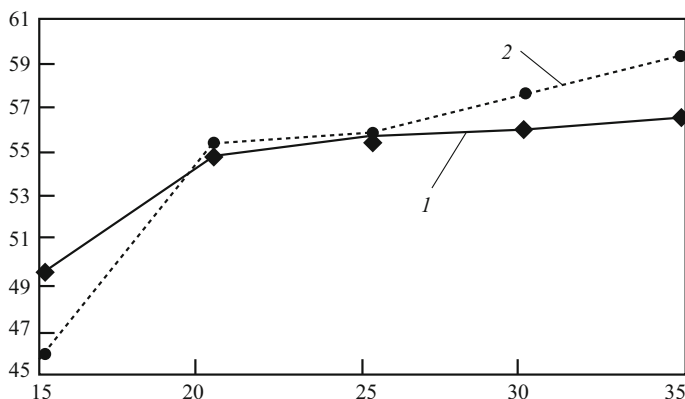


Fig. 1.54 Dependence of the strength of the sinter on the content of return in the charge at the content of concentrate in the ore part of the charge: 1—62.7%, 2—72.9%. The abscissa axis is the content of the return in the charge, %; ordinate axis—sinter impact strength (class yield + 5 mm, %). The yield of fines (fraction—5 mm) from the cake with a proportion of concentrate in the charge of 62.7% is minimal with a return content of 25%, and with a concentrate content of 72.9% in the charge, it continuously decreases from 30.8, 15 to 11.5% (with the content of a return of 35%)

Table 1.29 Effect of particle size of return parameters of sintering process and quality of sinter^a

Indicators	Return size (mm)				
	0–6	0–8	0–10	0–12	0–15
<i>Composition of sinter</i>					
Content in sinter (%)					
Fe	57.4	57.6	57.3	57.5	57.0
FeO	15.9	18.1	16.1	15.0	16.3
S	0.094	0.061	0.066	0.071	0.136
Basicity of sinter	1.48	1.40	1.40	1.49	1.46
<i>Characteristics of the sintering charge</i>					
Moisture of sintering charge (%)	7.6	7.7	7.6	7.7	7.55
The contents of –3 mm in sintering charge (%)	69.6	59.2	55.2	49.4	52.9
The average diameter of granules of sintering charge (mm)	2.99	3.65	4.13	4.76	4.56
Bulk weight of sintering charge (t/m ³)	1.715	1.766	1.786	1.820	1.812
<i>Sintering process parameters</i>					
Sintering rate (mm/min)	19.4	22.04	20.08	19.86	19.08
Specific performance (t/(m ² h) on yield)					
>15 mm	0.999	1.199	1.021	0.966	0.920
>8 mm	1.246	1.550	1.415	1.388	1.313
Yield (%)					
>15 mm	57.8	59.3	54.3	51.9	51.2
>8 mm	72.2	76.6	75.3	72.6	73.2
<i>Sinter strength</i>					
Yield of class –5 mm	20.6	15.0	16.2	17.6	19.4
Sinter strength (%)					
– On strike +5 mm	47.9	55.7	54.3	49.3	51.7
– Abrasion resistance –0.5 mm	6.42	6.16	6.00	6.90	9.80

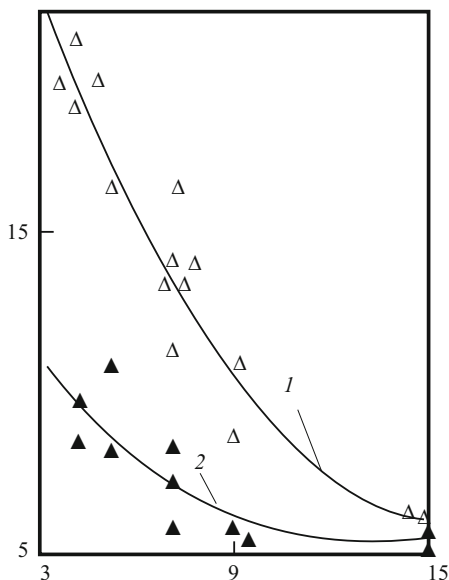
^aComposition of the ore part of the charge (%): concentrate—72.9; sinter ore—12.4; waste—12; lime—2.7; content in the charge (%): return—25; limestone—6.4; fuel—4.7; layer height—260 mm

1.7.4.5 Regulation of the Thermal Level of the Sintering Process

One of the important directions of sinter quality improvement is the regulation of the thermal level of the process due to:

- optimization of fuel consumption for the process;
- providing additional heat input to the layer (including by blowing crushed fuel into the upper part of the layer);
- rational distribution of the fuel layer height;
- high-layer applications.

Fig. 1.55 Effect of carbon consumption during sintering on the strength of the sinter [35, 86] 1—heat-treated sinter; 2—conventional sinter. The abscissa axis is the carbon consumption for sintering, %; ordinate axis—sinter strength (fraction yield minus 5 mm after dropping, %)



From the general laws of sintering [35, 86], it follows that an increase in the heat input to the layer due to the carbon consumption per process contributes to an increase in the strength of the sinter (Fig. 1.55).

At the same time, it should be taken into account that excessive development of the liquid phase (with excess carbon consumption per process) will lead to deterioration of the strength characteristics of the sinter due to the formation of a specific structure (alternation of monolithic melted areas and large pores representing shrinkage shells) [4].

If we consider Fig. 1.56, it is easy to notice that the upper part of the sintered layer (50–100 mm) is experiencing a heat deficit, which actually determines the low strength of this part of the sintering cake.

As a method of covering the heat deficit in the upper layer, the supply of heated air to the sintering layer is proposed (the first industrial plant was introduced in Germany [87]).

There are various options for supplying additional heat to the layer (Fig. 1.57a–c):

- hot air from separate cowper stoves (1.57a),
- flue gases of special fuel-burning devices located behind the ignition hood (1.57b);
- flue gases mixed with heated air coming from the sinter coolers (1.57c).

These options have been called the combined heating of the charge. With undoubted advantages in terms of the quality of the sinter, the combined heating of the charge is associated with a decrease in the vertical sintering speed.

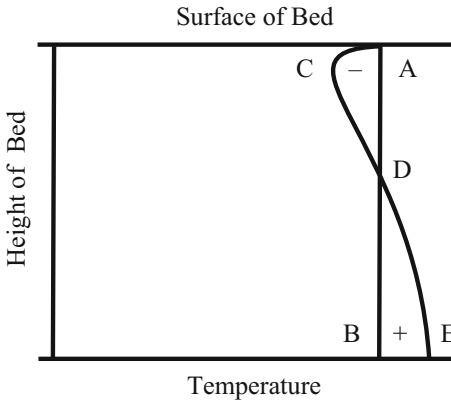


Fig. 1.56 A diagram showing the change of temperature of sintered material on the layer height. ACDE-actual, AB-optimal for maximum yield

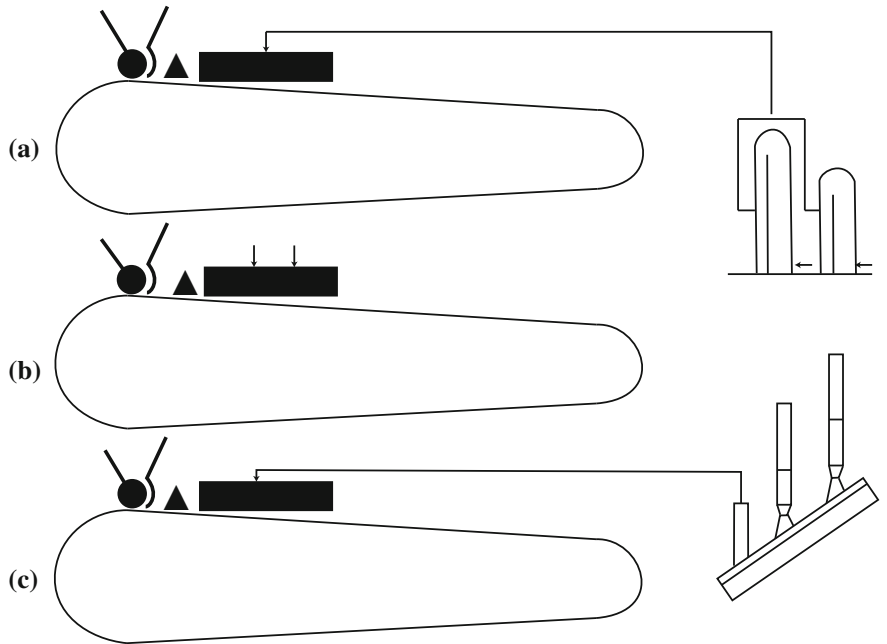


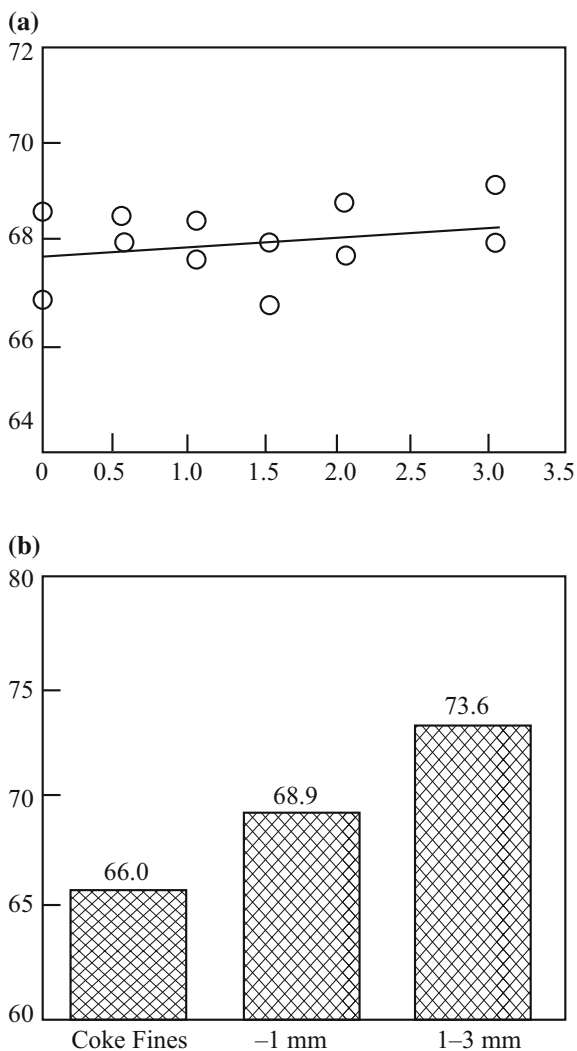
Fig. 1.57 Options for heating the upper part of the sintered layer [27]. **a** Hot air from cowper, **b** due to flue gases of fuel-burning devices; **c** due to a mixture of flue gases and heated air coming from the sinter coolers

It is possible to reduce the lack of heat in the upper layer in [88] by means of injection of coal onto the loading tray by feeding the flow to the edge of the tray or to the middle of the tray.

The carbon content in the layer of 50 mm (from the surface) increased from 5.1 to 6.5% regardless of the method of carbon injection. As a result, the strength indicator of the sinter during the drop test at the exit of the fraction + 5 mm increased from 67.7 (for sintering without blowing carbon) to 70.0% (when blowing carbon into the middle of the tray).

The effect of improving the strength parameters largely depends on the amount of injected carbon (coke breeze) (Fig. 1.58a): With an increase in the amount of

Fig. 1.58 Influence of the characteristics of the injected fuel on the strength of the sinter. **a** The influence of the amount of carbonaceous material; **b** the influence of the size of the injected material (the difference in the carbon content in the upper and lower layers of 1%)



injected carbon-containing material (coke), the strength of the sinter (drop test) increases. The size of the injected fuel 1–3 mm gives the best indicators for the strength of the sinter (Fig. 1.58b).

There are known technical solutions for multi-layer sintering (as a rule, two-layer sintering with different fuel layers is considered to be technically feasible) [35]: Redistribution of fuel to the upper layer allows compensating for the lack of heat in it and, on the contrary, eliminating its excess in the lower layer.

The method of multi-layer sintering was invented by Swedish engineer H. G. Torulf in 1911 (German Patent, CL.18a 1/08 No. 384372, 1911), which just concerned the redistribution of fuel by the height of the sintered layer. Fuel economy in the case of two-layer fuel sintering is about 10–15% regardless of the charge and other sintering conditions.

In the development of two-layer sintering technology, various options have been proposed [35]:

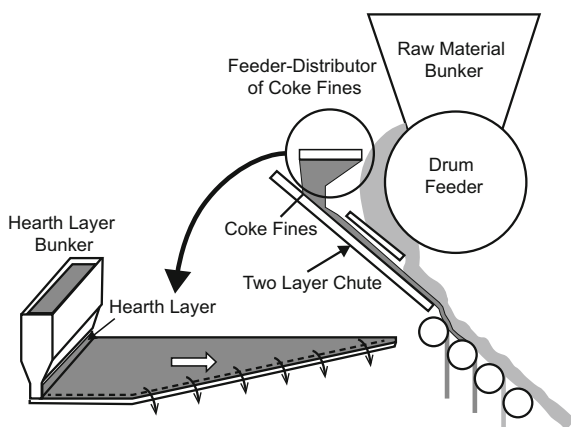
- by sintering ores (the bottom layer is hard-to-creep, the top layer is easily sintered;
- by basicity (lower layer—iron flux, upper layer—sinter with low basicity;
- on return (the lower layer—a larger flow rate, the upper layer—a smaller one);
- by fuel size (lower layer—more than -0.5 mm fraction, less in the upper layer).

An analogue of such a two-layer technology is the proposal for a two-level loading of sinter blend [89].

The loading system with coke feed to the upper part of the layer is shown in Fig. 1.59.

It contains a coke feeder and a two-level tray. A compact horizontal differential feeder was developed for coke breeze loading.

Fig. 1.59 Scheme of coke loading into the upper part of the layer



In order for the coke breeze to arrive only in the upper part of the sintering layer, the loading tray is made two-level, and the coke breeze passes through the lower horizon, and the sintering charge passes through the upper horizon, so that a zone enriched in coke breeze is formed on the sintering belt.

Tests were conducted on an industrial sintering machine in Kakogawa, Japan. The test results showed that in the upper layer with a thickness of 100 mm (total height of the adhesive layer is 600 mm), the carbon concentration is 1.5 times the carbon concentration in the layer. According to the distribution curve of the relative concentration (the ratio of the local concentration to the average concentration over the height of the layer) of coke, about 85% of the loaded coke enters the upper part of the layer with a thickness of 100 mm.

Another option to increase the carbon content in the upper part of the sintered layer is a special loading tray with “slotted grate,” equipped with a purge system. This was tested on sinter plant No. 1 of Nippon Steel in Oita [90]. In this scheme, the concentration of carbon in the surface layer compared with the conditions without blowing increased by 4%, and the tumble test (TI, %) increased from 77.2 to 77.5%.

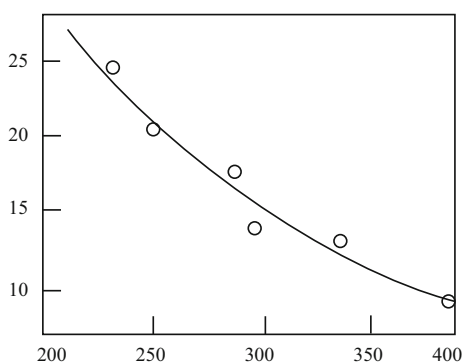
One of the essential resources to increase the strength of the sinter is the increase in the height of the sintered layer, which is clearly shown in Fig. 1.60.

The reason for improving the quality of the sinter with increasing height of the sintered layer is an increase in the amount of melt in the sintered layer [37] Fig. 1.61.

Sintering in the high layer provides greater completeness of chemical and mineralogical transformations due to an increase in the residence time at high temperatures and also helps to relieve thermal stresses during slow cooling of the sintering cake.

At present, with the traditional technology of vacuum agglomeration with a high proportion of finely ground concentrates in the mixture, the layer height at sinter

Fig. 1.60 Dependence of the strength of the sinter on the height of the sintered layer. The ordinate axis is the strength of the sinter (according to the class output — 5 mm, %); ordinate axis — layer height, mm



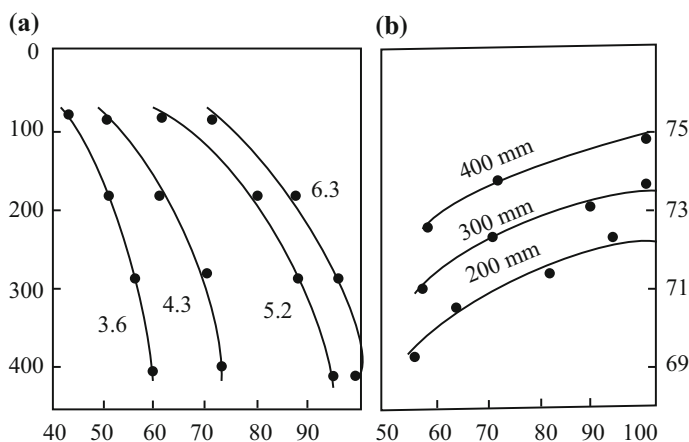


Fig. 1.61 Dependence of the amount of the melt (% of the mass of the charge) on the carbon content in the mixture **a**; the figures for the curves are the carbon content [37], **b** the strength of the sinter versus the amount of melt at different heights of the sintered layer (carbon consumption 6.3%); the figures for the curves—the height of the layer. The abscissa axis **a, b** is the fraction of the melt produced; ordinate axis **a** layer height, mm; ordinate axis **b** strength of the sinter (at the output of the fraction + 5 mm after the drum test, %)

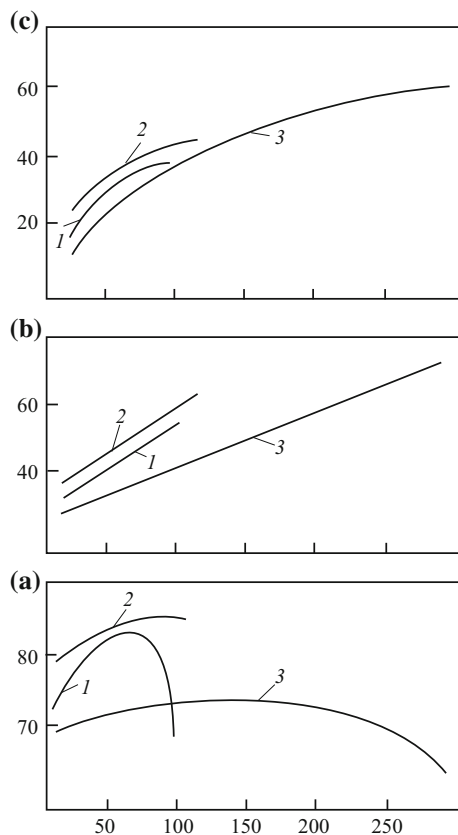
plants in Russia reaches 450 mm (with a bed 50 mm thick). Other possibilities for increasing the height of the sintered layer are opened by the technology of sintering under pressure or with increased pressure above the layer.

1.7.5 Technology of Sintering Under Pressure

The increase in pressure over the sintered layer is accompanied by a change in the main processes taking place in the sintered layer due to an increase in the air filtration rate due to an increase in the pressure drop in the layer and an increase in the absolute pressures over the layer and in the layer, leading to an increase in the density of air and gases (i.e., an increase in the mass of oxygen per unit volume):

- Burning carbon of fuel: With an increase in the filtration rate, the residence time of CO in the high-temperature zone is reduced, the degree of its burning decreases, and the CO/CO₂ ratio increases, the consequence of which is a decrease in the arrival of heat from combustion and a decrease in temperature by 30–50 °C in the combustion zone.
- The amount of regenerated heat transferred with heated air per unit of time increases in comparison with the vacuum mode by 1.7; 3.1; 3.6 times (with an increase in pressure above the layer, respectively, to 100, 200, 300 kPa) due to the intensification of heat transfer in the upper stage.

Fig. 1.62 Pressure sintering parameters of sintering mixture under pressure (Pot) [127], 1—industrial charge No. 1; 2—charge No. 1 with replacement of part of limestone by lime; 3—industrial charge No. 2; **a** yield, **b** vertical sintering rate, **c** specific productivity. The abscissa axis is the pressure above the sintered layer, kPa; y-axis: **a** yield, %; **b** is the vertical sintering rate, mm/min; **c** specific productivity, $t/m^2 h$



During sintering under pressure, there is a real possibility of increasing the height of the sintered layer to 600–1000 mm.

Indicators of sintering of charges under pressure are shown in Fig. 1.62.

The dependence of the yield of sinter (fraction + 8 mm) on the pressure has an extremal character. Note that the specific productivity increases multiply with the pressure increase above the bed.

Further improvement in the efficiency of iron production, due to the quality of sinter, can contribute to:

- increasing the stability of the composition of the sintering mixture (reducing the fluctuation of the Fe content, basicity, particle size distribution), as well as sintering technology, stabilizing the properties of the sinter;
- optimization of the MgO content in the sinter;
- improvement of thermoplastic properties of the sinter;
- mastering the production technology of sinter with high basicity and low FeO content.

1.8 Energy Efficiency of the Sintering Technology

Energy consumption during sintering is determined by technological needs (costs of solid fuel for the sintering process and gaseous or liquid fuel for the ignition of the charge), as well as by the cost of electrical energy to ensure the operation of the equipment. The main costs of electricity in the process of sinter production are caused by the work of crushing, mixing, transporting, and other equipment when receiving, storing, and preparing the charge, the operation of the drives of the main units (sintering and cooling), the service of gas cleaning equipment and smoke exhausters.

Over the past 30 years, the total specific energy consumption for sinter production has decreased from 3333 to 2515 MJ/t; currently, the minimum energy consumption for sinter production is estimated at [91] in 1381 MJ/t.

In the European practice, the heat consumption (data are given in Table 1.30) for the production of sinter (solid fuels, including carbon of furnace dust and liquid or gaseous fuels for heating the furnace) is about 1290–2019 MJ/t of sinter (average 1344 MJ/t of sinter), which is equivalent to 39–64 kg of coke breeze per t of sinter (average 50 kg). There is some difference in fuel consumption between low-basic sinter ($<1.7 \text{ CaO/SiO}_2$) and highly basic sinter ($\geq 1.7 \text{ CaO/SiO}_2$) [91].

Solid fuel consumption (coke breeze, coal) at sinter plants in Russia is in the range of 34.4–59.7 kg/t of sinter depending on the type of sintered concentrates and the basicity of the charge [92].

The total demand for electric energy is in the range of 92–155 MJ/t of sinter with an average value of 105 MJ/t of sinter (or 29 kWh/t); at Russian sinter plants, the consumption of electric energy is within the range of 24–49 kWh/t [92].

Assessment of potential energy savings in the sintering of iron ore materials reveals a set of areas where it is possible to implement measures to reduce energy consumption or its recovery:

- management of the chemical composition of the sintering charge;
- regulation of granulometric composition of the ore part of the charge;
- ensuring optimal sieve composition of coke breeze;

Table 1.30 Energy consumption for the production of sinter (MJ/t sinter) [91]

Energy resource		Consumption		
		Maximum	Minimum	Averaged
Fuel	Solid fuels (anthracite and coke breeze, etc.)	1834	1254	1277
	Gas coke oven/blast/natural	185	35	67
Electric power	To evacuate the gas stream (exhausters)	91	30	39
	Total electric power consumption	155	92	105
Energy resources	Total	2174	1381	1449

- organization of effective technology for the use of fine fraction of coke breeze;
- regulate the height of the sintered layer;
- regulation of gas-dynamic resistance of the sintered layer;
- ensuring the proper gas density of the sintering machine paths;
- waste gas heat recirculation (process heat after sintering machine and hot air from sinter coolers);
- production of secondary energy using waste heat.

Reduction of fuel consumption for sintering by controlling the chemical composition of the sinter

With the exception of a small number of cases, currently, sinter is obtained from rich ores with a SiO_2 content in the sinter of 5.5–6.0%. A decrease in the SiO_2 content in the sinter causes a further reduction in fuel consumption (Fig. 1.63a), while at the same time reducing the amount of slag produced in the blast furnace, which has a positive effect on coke consumption in the blast furnace.

The MgO content in the sinter is currently generally maintained at about 1.5%—the transition from dolomitic to olivine additive allowed to significantly reduce the consumption of coke breeze [93].

Reduction of fuel consumption for sintering by adjusting the particle size distribution of the ore mixture

The granulometric composition of the ore mixture plays a significant role in energy consumption, with larger particles leading to better air permeability, which can reduce the vacuum (and energy consumption) on the exhausters.

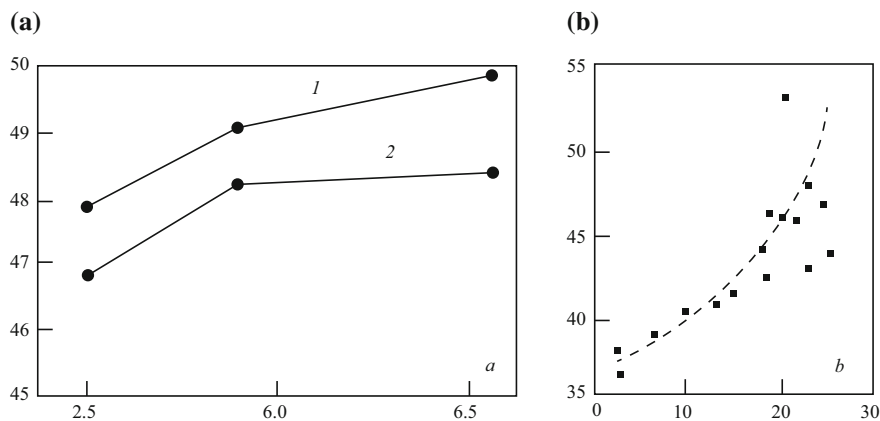
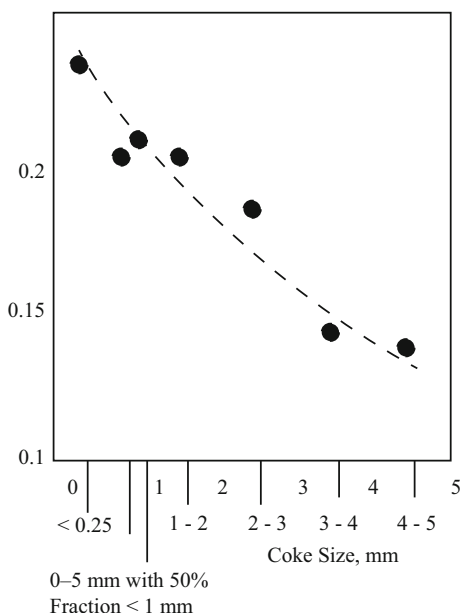


Fig. 1.63 Influence of various technological factors on the consumption of solid fuel during sintering [91]. **a** The effect of content of SiO_2 , 1—dolomite addition, 2—olivine addition; abscissa axis— SiO_2 content in the sinter, %; y-axis—coke consumption, kg/t of sinter; **b** influence of the content of the fraction smaller than 0.1 mm in the ore mixtures; the abscissa axis is the fraction of minus 0.1 mm in the ore mixture, %; ordinate axis—coke consumption, kg/t of sinter; points—experimental values, dashed line—trend of change

Fig. 1.64 Dependence of CO/CO_2 ratio on the size of coke breeze, dotted line—trend of dependence [95]
 abscissa axis: upper line—classes; bottom line—coke breeze fineness, mm; y-axis—ratio CO/CO_2 , shares



It is shown experimentally (Fig. 1.63b) that the FeO content in the sinter, and hence fuel consumption, increases with increasing fraction of -0.1 mm in the ore mixture.

The problem of optimal granulometry today is most successfully solved in the HPS technology, proposed, and introduced by Nippon Kokan.

At the same time, the content of the dispersed fraction of 0.1 – 1 mm in the ore charge affects the process performance and the quality of the sinter.

The reduction of fuel consumption for sintering by control of the grain size distribution of the coke breeze

The particle size of the fuel is extremely important for the level of its consumption. Fine fractions lead to an increased CO content (Fig. 1.64) in the exhaust gases, and excessively large fuel particles do not have time to completely burn in the combustion zone, which provides either a lack of heat or a loss of carbon.

Class 1 (2) mm is considered as the optimum size for coke breeze.

The main problem in the preparation of fuel is:

- the need to organize an effective classification of coke breeze on the boundary limit (0.5 or 1 mm);
- development of technology for utilization of the dispersed component of coke breeze (solved successfully in HPS technology).

Reduction of energy consumption in the process of sintering by utilizing the heat of the exhaust gases of the sinter cooler

To collect the heated air from the coolers, catching umbrellas are installed, through which the heated air is sent to cyclones to remove abrasive dust and then sent through pipelines for recycling.

Hot air from sinter coolers can be used by one of the following methods or their combination [94]:

- production of steam for factory needs (Fig. 1.65);
- obtaining hot water for district heating of the residential area (sintering machine #3, Dunkirk, ArcelorMittal);
- hot air supply for combustion in the ignition hood and in the sintered layer behind the ignition hood (additional heating of the sintered layer (Fig. 1.66) allows to reduce the consumption of solid fuel by 2–5 kg/t of the sinter (sintering machine in Linz, VAI); the same scheme with energy production is presented in Fig. 1.67;
- for heating of the sinter charge;
- supply of hot air to the exhaust gas recirculation system (air with a temperature of $\sim 350^\circ\text{C}$ together with the recirculated gas is used for heat treatment of the sintered charge layer after the ignition hood); there is a saving of up to 10% of solid fuel for the sintering process.

In Japan, heat recovery systems from sinter coolers and heat from the sintering machine cooling zone were used at 64% of sinter plants. On the linear cooler of the

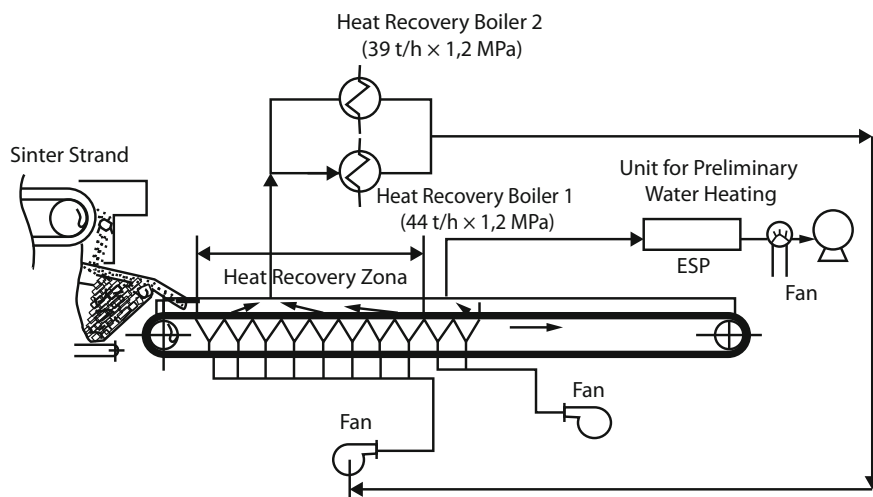


Fig. 1.65 Scheme of heat recovery of exhaust gases cooler of sinter [95]

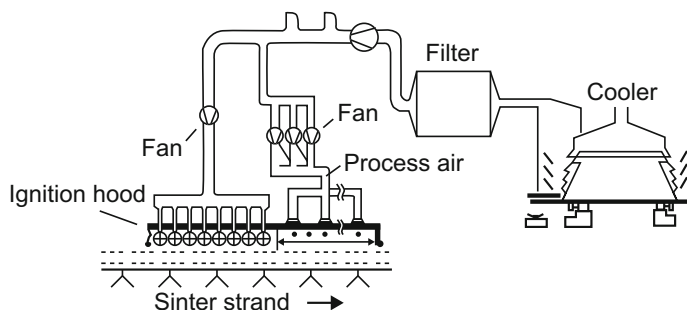


Fig. 1.66 Heat recovery from waste air from sinter cup cooler during sintering [4]

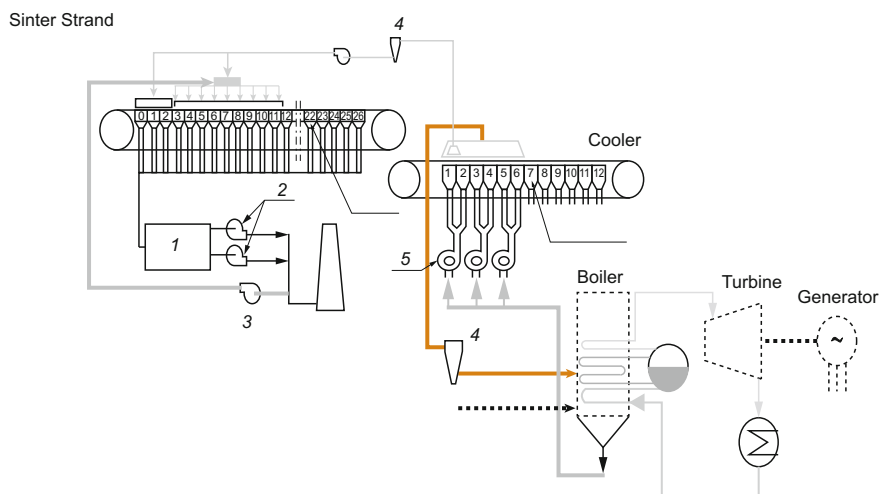


Fig. 1.67 Scheme of recycling the hot air line cooler of sinter for the production of electrical energy [92]

sintering machine of sinter machine number 2 in Kashima [95], a waste heat boiler was installed to recover heat from the exhaust gases of the cooler. The resulting steam is sent to the factory needs.

The scheme of the heat recovery system of the exhaust gases of the sinter cooler is shown in Fig. 1.65.

As a result of the modernization, the following effects were achieved:

- an increase in the capacity of the cooler waste gas utilization system when replacing the sequential arrangement of the waste heat boilers with a parallel one (Table 1.31).
- an increase in the volumetric gas flow rate as a result of a decrease in pressure loss in the recovery boiler (Table 1.31).

Table 1.31 Effectiveness of the modernization

	Before modernization	After modernization
Capacity (t/h (steam))	44	44 + 39
The maximum steam pressure (MPa)	1.2	1.2
Volume gas flow rate (m ³ /h, 10 ³)	444	484
Heat exchange surface area (m ²)	1830	1830 × 2

- prevention of a noticeable decrease in the amount of produced steam when only one waste heat boiler is operating during a planned inspection of the waste heat utilization system.
- prevention of the occurrence of harmful vacuum filtrations (through seals) by mounting an improved type of seals on the cooler.

Heat recovery systems from the sinter cooling zone on the sinter machine are quite common in the EU (the Netherlands, Italy, and Germany). Heat recovery from autonomous sinter coolers is used in France (ArcelorMittal), Great Britain (Corus), and Japan [4, 94].

Energy saving due to heat recovery of waste gases of sintering machine

The principal way to use the heat of the exhaust gases of the sintering machine is their partial recirculation [4], but other options for heat recovery of the exhaust gases are also possible.

For sintering machines with sintering and cooling zones, mixing of hot air from the cooling zone and exhaust gases, feeding the mixture into steam boilers and subsequent return to the sintering machine (sintering machine No. 4, Wakayama, Sumitomo Heavy Industries, Japan), is used. It is also possible to separate the supply of hot airflows from the cooler and exhaust sintering gases for steam production (sintering machine No. 3, Kokura, Sumitomo Heavy Industries, Japan).

In systems with exhaust gas recirculation, hot air from the cooler is used instead of ambient air to increase the oxygen content for sintering. This process is known as Eposint (Environmental Process Optimized Sintering) and was commissioned in 2005 on the sintering machine in Linz, VAI, Austria.

The exhaust gas recirculation systems will be discussed in Sect. 1.9.

1.9 Environmental Aspects of Sinter Production (Best Available Technologies)

In the modern structure of the balance of agglomerated charge materials for blast furnace smelting, the process of sintering is the most preferred method of sintering iron ore fines and concentrates, also due to the possibility of recycling secondary and circulating materials.

The specifics of sinter production, consisting in:

- high sintering process intensity (production scale, high gas filtration rates up to 1 m/s);
- high temperature level (1250–1450 °C);
- dispersion of the charge;
- discreteness of carbon distribution (solid fuel);
- the use of a variety of secondary materials,

predetermine the position of the sinter plant as a powerful source of negative environmental impact in the form of emissions into the atmosphere.

1.9.1 Thermodynamic Modeling of Emissions in the Sintering Process

To describe the thermodynamic system that is adequate to the conditions of the sintering process, we take the following initial conditions:

- composition of the system in the form of $\text{Fe}_3\text{O}_4\text{--CaCO}_3\text{--SiO}_2\text{--O}_2\text{--N}_2\text{--C--S}$ (100% of the concentrate in the iron ore part of the mixture; fluxed sinter);
- temperature level (high-temperature zone) 1200–1500 °C;
- pressure 0.1 MPa;
- consumption of solid fuel in the range of 4–5% wt.;
- airflow 200–2000 m³/t sinter;
- air inflow (for the formation of the final composition of the sinter gas is not taken into account).

The software package IVTANTHERMO [96] served as a tool for thermodynamic modeling.

The simulation results are summarized in Table 1.32.

The formation of carbon monoxide CO in the actual sintering process is a consequence of incomplete combustion of fuel, due to oxygen deficiency because of gas-dynamic constraints (discreteness of fuel distribution, low filtration rate). For this reason, the combustion of solid fuel in the sintering layer does not meet the conditions of thermodynamic equilibrium, and the CO predicted by the thermodynamic model is significantly underestimated (except for the 5% fuel consumption option).

At the same time, the predicted estimates for nitrogen oxide emissions (NO_x , 324 g/t of sinter) coincide with the experimentally measured value [97], equal to 320 g/t of sinter, as well as do not exceed the established key indicators of best available technologies [98] (not more than 550 g/t of sinter). This makes it possible to consider the assumptions made in the thermodynamic modeling of the sintering process acceptable, and in addition, to confirm that the temperature regime during sintering (in the high-temperature zone) lies in the range of 1300–1400 °C

Table 1.32 Composition of gas emissions from the sintering process based on the results of thermodynamic modeling

Solid fuel (% mass.)	Air (m ³ /100 kg of sinter)	T (°C)	Gaseous phase composition (g/100 kg of sinter)					
			NO	NO ₂	N ₂ O	CO	SO ₂	SO ₃
4	50	1200	7.90	0.0078	0.0007	1.18	72.20	0.19
		1300	32.40	0.060	0.0028	1.99	72.06	0.29
		1400	49.14	0.068	0.0041	7.17	72.19	0.19
		1500	71.10	0.079	0.0057	18.96	72.19	0.13
4	20	1300	Unrealizable mode					
	50		32.4	0.0028	0.0028	1.990	72.06	0.29
	100		160.5	0.014	0.014	0.784	71.70	0.74
	200		396.6	2.28	0.035	0.616	71.55	0.92
5	50	1300	0.0159	0	0	3913	72.06	0.00014

The emissions during sintering are determined primarily by the temperature factor: In the range of 1200–1500 °C, with an increase in temperature, the gross emissions increase is almost an order of magnitude.

Emissions of pollutants with sinter gases are a function of the gas-dynamic sintering regime, determined by the air consumption per process, or filtration rate (Fig. 1.68).

The increase in air filtration rate (Fig. 1.68) from 0.3 to 1 m/s is accompanied by an increase in the concentration of nitrogen oxides, especially NO, from 324 g/t sinter to 3966 g/t sinter (value not observed in practice, which indicates the unrealizability of the process at similar air filtration rates).

An increase in the rate of air filtration has a positive effect on carbon monoxide emissions (Table 1.32): The concentration of CO decreases in proportion to the increase in the filtration rate, i.e., about three times.

It is believed [99] that reducing the consumption of solid fuels in the sintering process is accompanied by a decrease in carbon oxide emissions. Thermodynamic modeling confirms this conclusion: An increase in fuel consumption of up to 5% of the same temperature and air consumption leads to an increase in CO emission from 19 g/t of sinter to 39 kg/t of sinter.

Emissions of sulfur compounds, as modeling has shown, are represented mainly by sulfur dioxide (SO₂ yield under thermodynamic equilibrium does not exceed 1%; in sintering practice, they indicate 10% [27]), and its emission is determined only by the arrival (sulfur balance) with materials of sintering mixture.

From an ecological point of view, the effect of fuel saving during sintering is realized not only due to the situation with carbon monoxide, but also due to a decrease in the temperature level of the process while reducing fuel consumption, which allows to reduce the emission of nitrogen oxides.

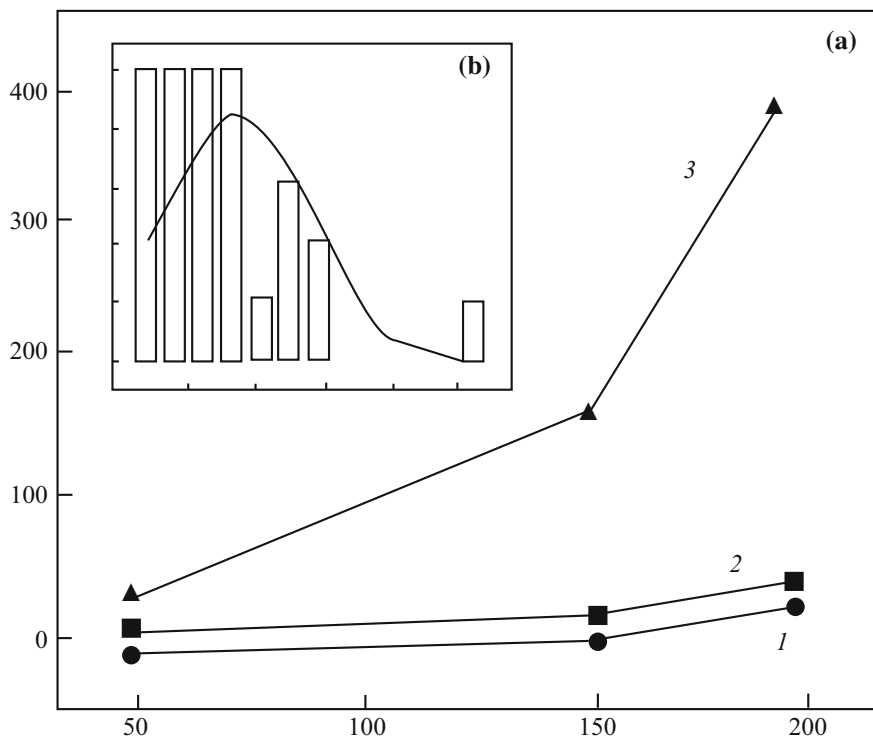


Fig. 1.68 Effect of gas-dynamic factors on the emission of nitrogen oxides during sintering: **a** thermodynamic model (4% coke breeze, $t = 1300\text{ }^{\circ}\text{C}$; 1— $\text{NO}_2 \times 10^2$, 2— $\text{N}_2\text{O} \times 10^3$, 3— NO); abscissa axis—air flow rate, $\text{m}^3/100\text{ kg}$ (compliance of filtration rates to air flow values: 50— $0.3\text{ m}^3/\text{s}$, 100— $0.6\text{ m}^3/\text{s}$, 200— $1.0\text{ m}^3/\text{s}$); ordinate axis—emission, $\text{g}/100\text{ kg}$ sinter; **b** histogram of the distribution of the actual values of total content of nitrogen oxides (in terms of NO_2): abscissa axis—emission NO_x , mg/m^3 ; y-axis—frequency

1.9.2 Characteristics of Emissions from Sinter Production

In real production conditions during the preparation of charge materials, as a result of the physical and chemical processes in the sintering layer, as well as subsequent processing of sintering, emissions of pollutants are formed:

- dust emissions caused by mechanical removal from the layer of fine charge or formed in the process of destruction of the sinter upon descending from the sintering machine, upon cooling, crushing the cake of the sinter after sintering;
- emissions of carbon monoxide caused by incompleteness of combustion due to the peculiarities of the distribution of solid fuel in the sintering layer; are technologically justified;

- emissions of sulfur dioxide SO_2 , depending on the sulfur content in coke breeze or other solid fuels that are used in the composition of the sinter charge, as well as the composition of other charge components (in the presence of calcium oxide (CaO) in the charge, SO_2 emissions are reduced; in other cases, including the use of raw materials containing magnesium oxide (MgO), $\sim 95\text{--}97\%$ of the sulfur content is removed in the gas phase in the form of SO_2); the predominant part of SO_2 emissions occurs in the second third of the sintering belt (closer to the discharge end);
- NO_x emissions due to combustion processes in ignition hood burners, combustion of coke breeze or other fuels, as well as emission of “thermal” nitrogen oxides due to nitrogen content in coke breeze and iron ore part of the charge;
- Emissions of heavy metals (zinc (Zn), lead (Pb), and cadmium (Cd)) appear in specific sintering conditions if the reduction potential of the sintering process increases or chlorides appear in the charge; however, the sublimation processes of heavy metals receive limited development due to the relatively low temperatures of the sintering process and the short duration of the layer stay at these temperatures.
- Emissions of aromatic organic compounds (e.g., polyaromatic hydrocarbons and dioxins) are possible under specific sintering conditions (presence of chlorine-containing substances, including some oils), so the use of dispersed mill scale without appropriate treatment is not recommended.

The volume of exhaust gases depending on process performance, conditions of sintering, blending of components, the quality requirements of sinter, and the condition of the equipment of the sinter machine is in the range $1500\text{--}2500 \text{ nm}^3$ per ton of sinter.

The value of specific emissions in the sintering process according to the European practice is given in Table 1.33 [91].

Thus, gross-specific emissions of sinter production per ton of sinter are in the range of $9.45\text{--}41.3 \text{ kg/t}$ of sinter. Carbon monoxide CO dominates in the gross emission of sinter plants, its share may be as much as $75\text{--}93\%$, and the proportion of sulfur dioxide (depending on the composition of the charge materials and sintering conditions, the presence of desulfurization treatment facilities) can reach up to 18% ; dust emissions—up to 10% , as much as the proportion of nitrogen oxides [24].

Sources of emissions into the atmospheric air during the production of sinter are combined into two large categories: *aspiration systems*, which evacuate exclusively dust emissions resulting from crushing, grinding, removal, dispersion during handling and processing of materials; and *chimneys* discharging process waste gases from sintering machines containing both the dust component and chemical compounds in gaseous form.

Table 1.33 Main emissions in sintering production [91]

Parameter	Units	Maximum value	Minimum value	Statistical representativeness ^a
<i>Emission into the atmospheric air</i>				
Dust	g/t sinter	559.4	40.7	94,321
Fine dust (<10 µm)		177.13	66.30	60,385
CO		37,000	8783	81,284
NO _x (by NO ₂)		1031.2	302.1	94,321
SO ₂		973.3	219.9	94,321
HCl		847.6	1.4	63,579
CH ₄		412.5	35.5	48,835
NVOC ^a		260.9	1.5	56,901
HF		8.2	0.4	59,129
Pb	mg/t sinter	5661.2	26.1	69,140
Zn		1931.3	2.1	75,197
Benzopyrene		41.5	0.1	41,243
Cu		600.5	1.9	69,140
Polycyclic aromatic hydrocarbons		591.7	0.2	40,441
Mn		539.4	3.4	56,612
Cd		276.7	0.2	77,731
Hg		207.0	0.1	72,693
Ni		175.6	1.3	65,492
V		158.5	0.6	47,156
Cr		125.1	3.6	69,140
Se		120.5	21.8	40,598
Tl		86.6	0.5	56,612
As		15.0	0.6	66,358
<i>Production residues (waste and by-products)</i>				
Sludge	g/t sinter	4492.18	472.73	11,341
Dust		3641.29	171.05	23,021
<i>Wastewater</i>				
Wastewater	m ³ /t sinter	0.06	0.03	7028

^aNon-methane volatile organic compounds^bSinter production capacity, K_t (kilotons)

1.9.3 Influence of Technological Factors on the Emission of Pollutants During Sintering

Development of measures to reduce emissions of pollutants with sinter gases is impossible without analyzing their dependence on the indicators of the technological process of sintering. At the same time, this task is quite complicated for a

number of reasons: due to the complexity of physical, physicochemical, and chemical processes in the sintered layer, which was discussed in the previous chapters, due to the relationship and interdependence of the registered technological parameters, and the lack of information on the emissions of pollutants associated with technological parameters.

To identify the priority technological factors in work [24], statistical material was used (the scope of technological factors for each sample is given in Table 1.34 using the example of a sinter plant of one of the metallurgical enterprises); response functions were residual concentrations (mg/m^3) in waste sinter gases of dust, nitrogen oxides (total), carbon monoxide, and sulfur dioxide. Evaluation of the influence of factors was carried out using statistical models with computer simulation [100].

A multiple regression model for the response function in general can be represented by the following equation:

$$Y = C + K_1 \cdot X_1 + K_2 \cdot X_2 + K_3 \cdot X_3 + K_4 \cdot X_4 + K_5 \cdot X_5 + K_6 \cdot X_6 + K_7 \cdot X_7 + K_8 \cdot X_8 + K_9 \cdot X_9 + K_{10} \cdot X_{10} + K_{11} \cdot X_{11} + K_{12} \cdot X_{12} + K_{13} \cdot X_{13} \quad (1.9.1)$$

where Y —response function (residual concentrations of dust, nitrogen oxides (total), carbon monoxide, sulfur dioxide);

C —constant;

$K_1, K_2, K_3 \dots K_{13}$ —model coefficients;

$X_1, X_2, X_3 \dots X_{13}$ —technological factors (Table 1.34).

To determine the structure of the model (factors determining a particular response function), the influence (significance) of each technological factor was estimated for each response function for each factor by the method of pair regression. Further, on the basis of significant factors, a basic version of the statistical model was formed, which was sequentially supplemented by enumerative technique method to obtain the maximum correlation coefficient.

Thus, the model (1.9.1) included following number of factors for various response functions:

- for the residual dust content 11 factors (except for X_3, X_7); correlation coefficient of 0.74;
- for carbon monoxide—10 factors (except X_3, X_7, X_9); correlation coefficient of 0.55;
- for nitrogen oxides—13 factors; correlation coefficient of 0.71;
- for sulfur dioxide—13 factors; correlation coefficient of 0.81.

Table 1.34 Intervals of values of technological factors for the construction of statistical models

Response function	Technological factors ^a												
	Fe _{sint} (%)	Conc. (%)	W (%)	K (%)	B	Lime (%)	Sc (%)	P (τ/t ₄)	V (m/min)	h (mm)	Pressure (mm H ₂ O)	FeO _s (%)	σFeO _s (%)
	X ₁	X ₂	X ₃	X ₄	X ₅	X ₆	X ₇	X ₈	X ₉	X ₁₀	X ₁₁	X ₁₂	X ₁₃
Dust (g/m ³)													
Maxim. 0.23	53.9	60	—	10	2.04	42.9	—	92.2	2.4	340	970	20.4	0.86
Minim. 0.034	46.6	10	—	3.5	1.21	0	—	70.15	1.2	230	600	8.8	0.01
NO _x (mg/m ³)													
Maxim. 241	58.3	60	8.55	7.5	1.82	50	0.33	85.5	3.0	340	800	16.7	1.0
Minim. 0.004	49.2	10	6.10	2.4	1.08	0	0.16	64.7	1.1	220	500	10.3	0.03
CO (mg/m ³)													
Maxim. 7500	58.3	60	—	7.5	1.82	50	—	85.5	3.0	340	800	16.7	0.93
Minim. 208	49.2	10	—	2.4	1.08	0	—	64.7	1.4	220	500	10.3	0.03
SO ₂ (g/m ³)													
Maxim. 1.83	58.3	60	8.55	7.5	1.82	50	0.71	85.5	3.0	340	800	16.7	0.96
Minim. 0.062	50.3	10	6.10	2.4	1.08	0	0.18	64.7	1.1	200	500	10.3	0.02

Notes

^aFe_s—total iron content in the sinter (% wt.) Conc.—the share of fine concentrate in the iron ore part of the charge, %; W—moisture content of pelletized charge (%); K—consumption of coke fines in the charge (% by weight.); B—the basicity of the sinter; lime—the proportion of lime in the flux part of the charge (%); Sc—sulfur content in the charge (% mass); P—the performance of the sintering machine (t/h); V—the speed of the sintering belt (m/min); h—the height of the sintered layer (mm); underpressure in the collector (mm of water column); FeOs—content of FeO in sinter (% mass.); σFeOs—dispersion of FeO content in sinter (%)

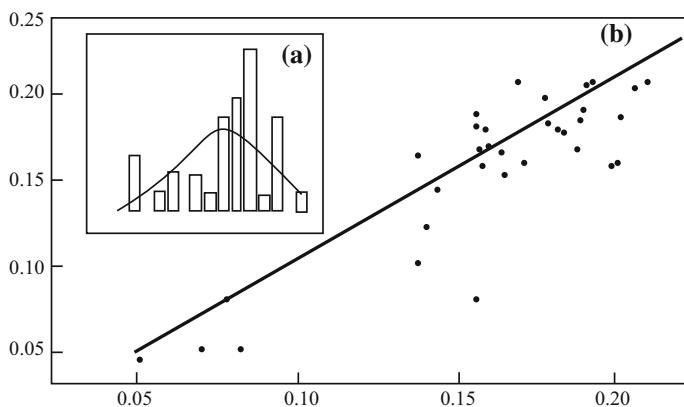


Fig. 1.69 Statistical model of dust removal during sintering. **a** Histogram of the distribution of the actual values of dust removal; abscissa axis—emission of dust g/m^3 ; y-axis—frequency; **b** the ratio of the actual values of dust removal and predicted by the model; abscissa axis—dust emission (forecast), g/m^3 ; ordinate axis—dust emission (actual), g/m^3

Significant model correlation coefficients for the response functions indicate the adequacy of the models, which is illustrated by an example for the residual dust response function (Fig. 1.69), where the sample data are plotted and predicted by the model.

Analysis of the influence of technological factors by regression analysis can be recommended as an approach; but for a detailed quantitative assessment, despite the confirmed adequacy of statistical models, it is not very suitable, or at least will require larger samples.

The contribution of each factor to the variation of the response function was estimated from the coefficients of the generalized sample (the transformation of the physical sample into the generalized correlation coefficient of the model remains unchanged). The values of contribution are presented in Table 1.35.

The critical parameter, which determines the dust emission by 45.7% (Table 1.35), is the Fe content in sinter, apparently due to the introduction of fine concentrate into the mixture and, accordingly, the content of dispersed fractions in it. The relationship between the amount of fines in the charge and dust removal was established experimentally [99]. Slightly less impact (16.4%) has the basicity of the sinter and the belt speed (12.4%), the latter factor changing dust removal in a positive direction. The role of sinter quality is manifested through FeO (the share of this factor is 12.2%).

These results allow us to recommend directions for technological measures to reduce emissions of dust particles:

- improvement of the granulometric composition of the pelletized charge (with the exception of dispersed fractions in it);
- improving the quality (strength) of sinter by optimizing the content of FeO in it.

Table 1.35 Contribution of technological factors to the variation of response functions

Name	Factors ^a	Contribution of the factor in the variation of the response function ^b , %			
		Dust	CO	NO _x	SO ₂
X1	Fe _s (% mass)	45.7	(4.6)	17.9	16.7
X2	Concentrate share (%)	1.8	(4.6)	(1.1)	2.0
X3	Moisture (% mass)	–	–	4.9	3.0
X4	Coke nut consumption (%)	(1.4)	(3.0)	(5.1)	5.5
X5	Basicity of sinter	16.4	(0.9)	(1.7)	(25.0)
X6	Lime share (%)	0.3	4.8	(3.6)	(2.5)
X7	Content of Sc (% mass)	–	–	(1.6)	4.6
X8	Capacity (t/h)	(4.7)	35.1	2.6	12.2
X9	Belt speed (m/min)	(12.8)	–	24.6	(3.9)
X10	Layer height (mm)	2.0	8.6	16.7	11.1
X11	Underpressure (mm H ₂ O)	(1.0)	14.2	(0.6)	1.5
X12	FeO _s (% mass)	12.2	(13.2)	(8.5)	(8.9)
X13	Dispersion Fe _s (%)	(1.3)	10.8	(11.1)	(3.3)

^aDetailed explanation of the factors is given in the notes to Table 1.34

^bFigures in parentheses reflect the negative influence of a factor on the response function

The value of nitrogen oxide emissions (Table 1.35) is determined by the factors reflecting the gas permeability of the layer: 24.6% of the variations in the volume of nitrogen oxide emissions are caused by changes in the belt speed.⁸ The priority role of gas-dynamic factors in the formation of nitrogen oxides is also predicted by a thermodynamic model (Sect. 1.9.1). An increase in the height of the sintered layer as a temperature factor contributes to an increase in the formation of nitrogen oxides (a contribution of 16, 7%). At the same time, the model does not reveal a positive dependence on the consumption of coke (it is possible that under conditions of gas-dynamic constraints, there is competition for free oxygen).

The carbon monoxide emission volumes (Table 1.35) are primarily due to the scale of production; therefore, a 35.1% contribution of such a factor as productivity to the amount of emission is natural. The share of the “thermal” reserve due to excessive fuel consumption due to the instability of the composition of the mixture in terms of Fe is quite large (10.8%). As in the case of emissions of nitrogen oxides, gas-dynamic factors play a significant role in the amount of carbon monoxide emissions (the contribution of the factor—the underpressure in the collector is 14.2%). The effect of the dependence of the carbon monoxide yield on the gas-dynamic conditions of fuel combustion was discovered quite a long time [97] and manifested itself in the existence of a close correlation relationship between the

⁸From the general considerations of the sintering theory, we have a relation for the speeds of the belt movement v and the filtration rate ω : $v = (L/h) \cdot K \cdot (C_g/C_p) \cdot \omega$, where C_g , C_p is the heat capacities of the filtered gas and charge; K —coefficient.

CO content in the exhaust gases and the air excess factor (but not by the fuel consumption to the charge).

Solutions to reduce carbon monoxide emissions are based on ensuring optimal combustion conditions:

- improvement of fuel supply in the oxygen layer [101];
- humidification with steam of sucked air [99];
- pulsating air supply [102].

In the absence of gas-dynamic restrictions (with the optimal granulometric composition of the pelletized charge and the strength of the granules), the reduction of carbon monoxide emissions can be achieved with fuel economy [99, 103].

Technological factors in accordance with the value that they have on sulfur dioxide emissions (Table 1.35) can be divided into charge (Fe content in the sinter with a contribution of 16.7%; basicity with a contribution of 25%; consumption of coke breeze with a contribution of 5.5%; the S content in the charge is 4.6%) and temperature (the contribution of the layer height is 11.1%).

The increase in sulfur dioxide emission with an increase in the consumption of coke and the sulfur content in the charge reflects the balance mechanism of the formation of sulfur emissions with sufficient oxygen in the gas phase. The decrease in sulfur dioxide emissions with an increase in the basicity of the sinter, revealed from statistical observations, is evidence of the occurrence of the reactions of absorption of the formed sulfur dioxide in the layer of sintering mixture.

As measures to limit sulfur emissions, it is advisable to sinter the high-base charge, control the sulfur content in the charge materials, reduce the consumption of coke breeze, or organize special sintering conditions (filter-absorbers) [104].

1.9.4 Environmental Requirements as the Main Priority of Production Modernization

Environmental constraints are becoming an important factor in the development of sinter production due to the fact that the sinter plant is a large-scale factor affecting the environment autonomously and as part of a metallurgical enterprise. Indeed, in the gross emissions of the integrated metallurgical enterprise, the share of emissions from sinter production exceeds 50%.

In world practice, the decisive direction of development and improvement of technological processes in general, and sinter production in particular, is the introduction of the best available technologies.

The best available technology (BAT) is the technology of production of products (goods), performance of works, rendering services, determined on the basis of modern achievements of science and technology and the best combination of criteria for achieving environmental protection goals subject to the technical feasibility of its application [98].

The transition to BAT involves not only the equipping of sintering equipment with modern dust- and gas cleaning devices (i.e., the use of “end-of-pipe” technologies), but also the modernization of the main production, improvement of technological processes and operations, optimization of logistics schemes of raw material flows, organizational interactions, etc., in order to reduce the negative impact on the environment and improve resource efficiency.

The key objectives for the best available technologies in sintering in the Russian Federation in relation to atmospheric air impact indicators are defined in [98], kg/t of the sinter:

- nitrogen dioxide (NO_2) ≤ 0.4 ;
- nitrogen oxide (NO) ≤ 0.15 ;
- carbon monoxide (CO) ≤ 14.0 ;
- sulfur dioxide (SO_2) ≤ 4.0 ;
- dust overall ≤ 1.2 .

In the sections above, technological solutions aimed at improving the resource efficiency of the sinter production process and reducing the impact on the environment are considered. Below are the existing and projected technical solutions for the main characteristic emissions of the sinter production process, mainly in the status “at the end of the pipe.”

Dedusting of waste gases of sintering machines

Cyclones, battery cyclones, electrostatic precipitators, and bag filters are used as apparatus for cleaning dust from process gases of sintering machines; devices for wet gas cleaning are rarely used. Schematic diagrams of the gas cleaning apparatus are shown in Fig. 1.70.

The choice of apparatus for the gas cleaning is determined by a number of factors, the main of which are the dimensions of the particles to be collected and the desired degree of purification of gases [105] with an appropriate level of technological development (Table 1.36).

Cyclones separate solid particles from gas due to the action of centrifugal forces (Fig. 1.70a). With a decrease in the diameter of the cyclone, the centrifugal force increases, and on the basis of this dependence, the designs of the battery cyclones are created. A number of sinter plants in the world use cyclones and battery cyclones as dust cleansing steps, for example, Hoogovens IJmuiden, the Netherlands or Wakamatsu, Yawata, Japan [105]. Autonomous cyclones and battery cyclones are not used for cleaning sinter gas from dust in foreign factories.

There is a positive operating experience of battery cyclones at the sintering plant of NLMK, Russia [106]: At a flow rate of gas out of one sinter machine of the type AKM-312 at ~ 940 thousand nm^3/h and dust concentration at the inlet $\sim 2300 \text{ mg}/\text{nm}^3$, dust concentration at the outlet (after battery cyclones) was about $140 \text{ mg}/\text{Nm}^3$, and the cleaning efficiency was 94%.

From the point of view of reducing the cost of subsequent disposal of the captured product, in terms of dedusting, preference should be given to dry methods

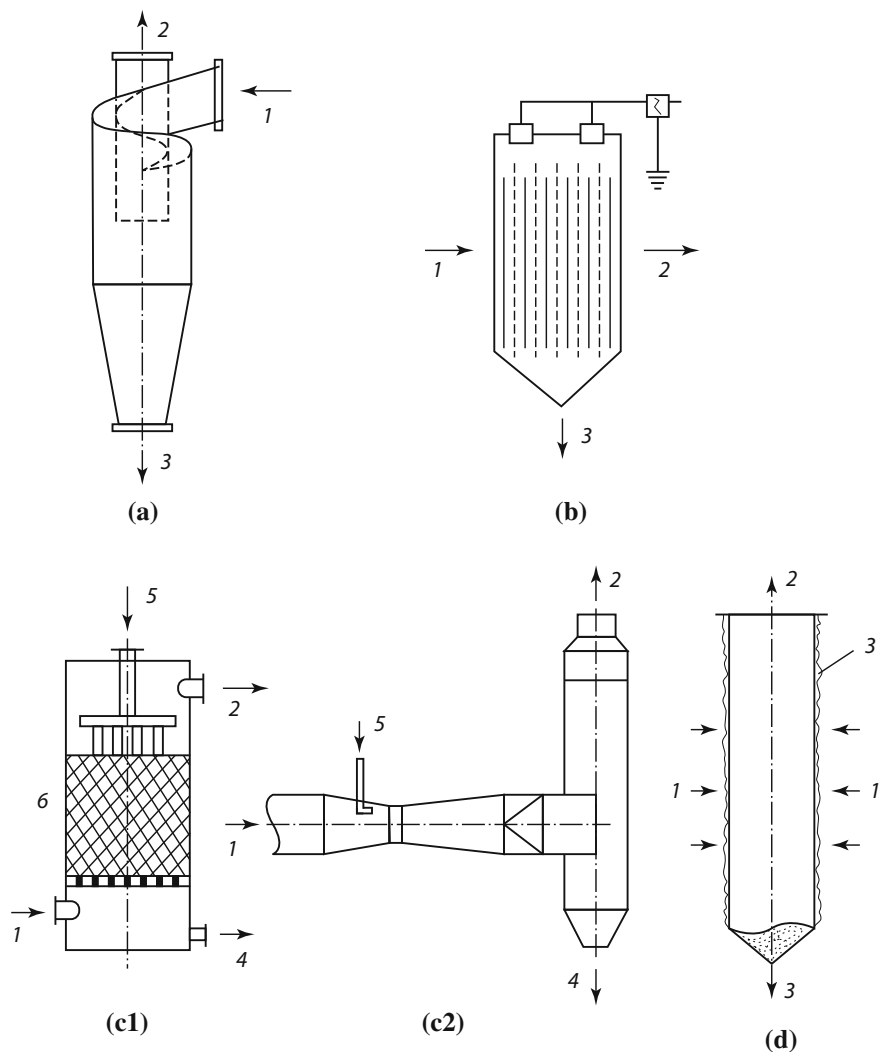


Fig. 1.70 Schematic diagrams of gas cleaning devices. **a** Cyclone, **b** electrostatic precipitators, **c** wet gas cleaning (c_1 —nozzle scrubber and c_2 —Venturi scrubber); **d** bag filter; 1—dusty gas; 2—purified gas; 3—collected dust; 4—sludge; 5—water supply

of cleaning sinter gases; in foreign practice, universal multi-stage precipitators have received general recognition [107, 108].

The operation of an electrostatic precipitator is based on the process of deposition of charged dust particles in electric fields. The particles are electrically charged in the field of a corona discharge arising between the corona-forming (high-voltage) and precipitation (grounded) electrodes (Fig. 1.70b).

Table 1.36 Options for the choice of dust-collecting devices

No.	Type of dust-collecting device	Size of the entrained particles (microns)	Degree of purification (%)
1	Dust-collecting chambers	5–20,000	40–70
2	Centrifugal dust precipitators	3–100	45–85
3	Electrofilters	0.005–10	85–99
4	Hydraulic dust collectors and fabric filters	0.01–10	85–99

In foreign factories, dry electrostatic precipitators with three or four (and even five) fields are used; in the Russian Federation, an example of such technology is the sinter plant of the Chelyabinsk Metallurgical Plant, Mechel, Russia. The performance of this three-field electrostatic precipitator is presented below: [45]

- Productivity—740 thousand m³/h;
- dust concentration at the inlet (max.) 1.095 g/Nm³;
- dust concentration at the outlet (min.) 38 mg/Nm³;
- efficiency (degree of gas cleaning from dust) of the filter—96.3%.

The efficiency of the electric filter depends primarily on the specific resistance of the deposited particles; as a rule, it must meet the range 10^4 – 10^9 Ω . In the presence of particles with higher resistance (calcium oxides, for example), the efficiency of the electric filter decreases. The presence of alkalis is also undesirable: So on the sintering machine in voestalpine Stahl (Linz, Austria), equipped with an electrostatic precipitator, the arrival of alkalis with the charge is limited to 2.5 kg/t sinter [45].

Other factors contributing to the efficiency of the electrostatic precipitator (dust cleaning performance, corrosion resistance, electrical filter overhaul interval) are electric field strength, input dust concentration and its qualitative composition, shape and area of electrodes; gas flow rate, acid gas content (NO_x, SO₂, etc.), moisture content.

In order to increase the efficiency of dust cleaning, different designs of electro filters have been developed: with increased voltage, with pulsating voltage, with moving electrodes, etc.

The electrostatic precipitator Electrostatic Space Cleaner Super (ESCS) works with an increased voltage of 70–200 kV, which is possible with a greater distance between the electrodes and was installed at the sinter plant of Nippon Steel Corporation, Yawata, Japan.

In a pulsating voltage electric filter, high-voltage pulses can be repeated up to 200 times per second. The increased peak voltage at pulsating excitation ensures better charging of the particles and their distribution in the electric filter, which guarantees the removal of dust particles with high electrical resistance. It is used at four sinter plants of Gwangyang plant (POSCO, South Korea); on two sinter machines of Thyssen Krupp Stahl (Duisburg, Germany); on two sinter machines of ArcelorMittal (Gent, Belgium).

The electrostatic precipitator with moving electrodes (Moving Electrode Electrostatic Precipitator, or MEEP) has several groups of electrode plates that move on tracked drive. The rotating brushes continuously clean the plates, removing the adhered dust and thereby eliminating the insulating effect of the dust layer. Such filters are installed at two sinter plants in Japan; on two sintering machines in Riva (Taranto, Italy); at the sinter plant of ArcelorMittal (Eisenhüttenstadt, Germany).

The efficiency of the electric filter lies in the range of 95–99%. The output dust concentration after the electric filter is reached at the level of 20–50 mg/Nm³.

However, the precipitators do not represent the only alternative in view of the development of technology of bag filters.

The action of the bag filter is based on the capture of dust particles during deposition on the fabric of the sleeve (Fig. 1.70d). During the flow of gas through the fabric of the sleeves, dust is retained on the surface of the sleeve, increasing its gas-dynamic resistance. As the resistance of the sleeves reaches a predetermined value (from 100 to 200 Pa), the chamber is disconnected from the system for cleaning using a reverse compressed air pulse. The removed dust is collected in the bunker in the lower part of the chamber and is removed to the collecting bin by a screw (or chain) conveyor.

An essential element of the filter, affecting the performance of its work, is the actual filter fabric. Studies on a pilot installation of a bag filter with a pulsed blowing with a capacity of 5000 m³/h [107] to determine effective filtration parameters and operating conditions (pressure drop, choice of filter material, its working order) showed that fiberglass or felt, almost complete dedusting was achieved (dust concentration was <5 mg/m³), and aerosols of acids and organic compounds were partially captured. However, this high filtration efficiency caused significant pressure losses (about 300 mm of H₂O).

Due to the pre-coating of the filter elements with slaked lime, the operating conditions of the filter have improved significantly, and the pressure losses have reached less than 200 mm of H₂O without deterioration of filtration efficiency; at the same time, the frequency of cleaning cycles of the bag filter became comparable with that which is characteristic for industrial conditions.

Industrial bag filters used in sinter plants can operate as stand-alone devices, but, as a rule, to improve the efficiency of cleaning, they are installed either behind battery cyclones or behind electric filters.

The combination of cleaning devices in addition to effective dust collection provides the possibility of cleaning from other pollutants by introducing certain reagents⁹:

⁹European enterprises [54] practice supplying reagents (activated carbons, coke, coal, specially prepared carbon materials) to the gas pipeline of waste gas before the electrostatic precipitator with a flow rate that provides 80 mg/m³ of carbon in the gas flow and 200 mg/m³ inert additive (limestone).

- the introduction of adsorbents (powdered activated carbon, lignite coke, coke, and/or zeolites) against the flow of gases in a bag filter to remove organic pollutants, dioxins;
- introduction of sodium bicarbonate or hydrated lime into the flue before the filter to remove acid gases (SO_2 , HCl , and HF) in combination with flue gas treatment by humidifying them and adjusting the temperature (90–100 °C);
- recirculation of part of the collected dust by feeding into the gas stream at the inlet of the bag filter (in order to reduce the consumption of reagents and effectively remove heavy metals and dioxins).

An example of combined gas cleaning technology using a bag filter is the Maximized Emission Reduction of Sintering (MEROS) process. It is operated on sintering machine 222 m² of Voestalpine Stahl (Linz, Austria). The MEROS process diagram is shown in Fig. 1.71.

In European factories using bag filters, the concentration of dust at the outlet reaches 1–10 mg/Nm³, including periods of peak load. Lime and activated carbon additives reduce dioxin emissions to 0.1 ng I-TEQ/Nm³. SO_2 emissions can be reduced by 30–80% with the introduction of hydrated lime and by 90% with the use of sodium bicarbonate, which provides a residual concentration in the range of 100–500 mg/Nm³, depending on the type and consumption of the reagent. With the addition of lime, a HF concentration of 0.2–1.0 mg/Nm^{3 and HCl of 1–10 mg/Nm³ can be achieved.}

The system of wet cleaning (Fig. 1.70c) of waste sinter gases Air-Fine was developed by the Austrian company VAI and was first introduced in 1993 at the sinter plant in Linz [109]. The scheme of the Air-Fine gas cleaning unit is shown in Fig. 1.72). Gas cleaning at this facility involves trapping solid and gaseous impurities in series in the cooling scrubber (4) and the fine scrubber (5). At the

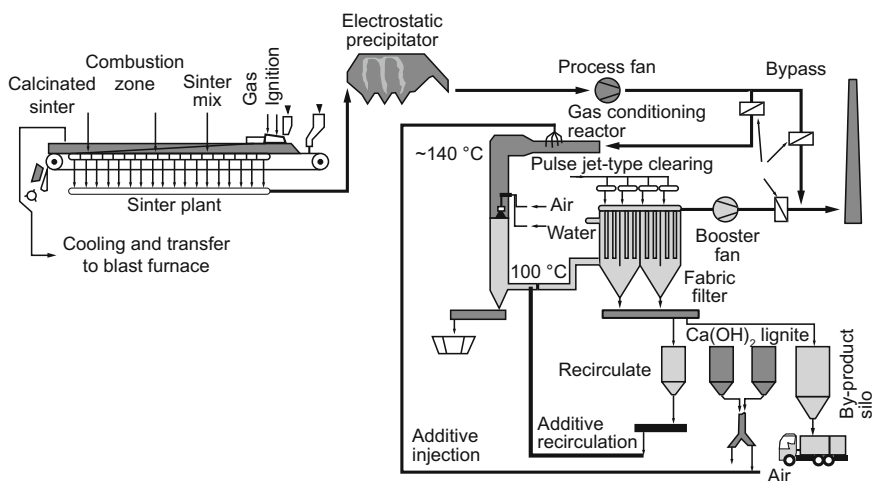


Fig. 1.71 Process flow diagram of combined gas purification technology MEROS

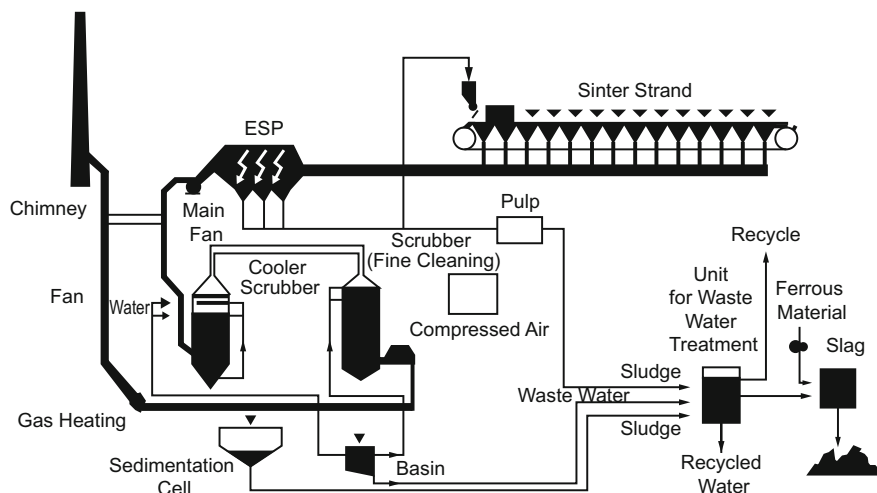


Fig. 1.72 Diagram of air-fine gas treatment plant [109]

cooling stage, larger particles of more than ten microns are removed as a result of the injection of circulating water into the counterflow of gas, to which sodium hydroxide NaOH , magnesium $\text{Mg}(\text{OH})_2$, or lime milk of $\text{Ca}(\text{OH})_2$ is added to trap SO_2 . The required desulfurization efficiency (above 95%) is achieved by adjusting the pH in the circulating water. The circulating water cycle consists of two closed circuits; the water consumption in each circuit is $2500 \text{ m}^3/\text{h}$.

At the stage of fine cleaning, the separation of the smallest particles of dust and harmful components, including heavy metals and dioxins/furans, occurs due to the injection of a water–air jet under high pressure. The compressed air consumption is $40,000 \text{ m}^3/\text{h}$, and the circulating water flow rate is $800 \text{ m}^3/\text{h}$ for each of the two circuits. High gas purification efficiency, unattainable with typical systems, is provided by a combination of several mechanisms: inertial impact, molecular and turbulent diffusion, as well as the formation of nuclei during steam condensation as a result of local supersaturation. With initial dust content in the exhaust gas of $450\text{--}1000 \text{ mg}/\text{m}^3$, a concentration of $50 \text{ mg}/\text{m}^3$ can be obtained at the outlet.

Wastewater treatment takes place in three stages. At the first stage, suspended solids are separated in the settling pool (mainly iron components), dehydrated, and returned to the sinter plant. The second stage involves the removal of heavy metals by sulfide deposition. The separated solids are dehydrated and stored for further processing. At the third stage, the wastewater is treated with hydrochloric acid and additional removal of suspended solids by means of a gravel filter. The volume of wastewater should not exceed $50 \text{ m}^3/\text{h}$.

The Air-Fine process allows:

- to ensure maximum permissible standards for emissions of dust, hydrogen chloride, hydrogen fluoride, heavy metals, dioxins, and furans; and if necessary, additional purification of waste gases from sulfur dioxide.
- to evacuate heavy metals (in the form of chemical compounds) for deposition;
- return to the process (recycle) captured iron-containing components.
- The main disadvantage of the Air-Fine process is the presence of the water cycle and the need for its operation.

Reduction of sulfur emissions during sintering

Sulfur dioxide during sintering is formed from iron sulfides (or other elements) contained in iron ore or fuels and organic sulfur fuels [110].

Due to the fact that sulfur compounds in the form of sulfide and organic sulfur are almost completely removed during the sintering process (95–97%), when using sulfurous materials, there is an urgent need to reduce sulfur emissions in the composition of sinter gases.

For cleaning waste gases from sulfur emissions, wet scrubbers are used in which the irrigation of a stream of gases containing SO_2 is carried out with solutions containing oxides (hydroxides) of calcium or magnesium:

- slaked lime $\text{Ca}(\text{OH})_2$;
- magnesium hydroxide $\text{Mg}(\text{OH})_2$;
- chalk CaCO_3 mixed with $\text{Ca}(\text{OH})_2$;
- steelmaking slag (up to 55% CaO) mixed with $\text{Ca}(\text{OH})_2$.

The consumption of the reagent depends on its type, the volume of waste gases for the removal of sulfur emissions, the content of sulfur components in them, and the required degree of purification. It is known that the consumption of, for example, hydrated lime in flue gases is 3–4 kg/m^3 of SO_2 at the sintering plant of Wakamatsu (NSC, Japan, [45]). In the Russian Federation, this method is used in sinter plants No. 3 and No. 4 of MMK (Magnitogorsk).

As a result of such treatment, sulfate (CaSO_4 or MgSO_4) is formed depending on the reagent used, which is removed after dehydration.

The degree of desulfurization of waste gases can reach 95% (in practice—85 to 90%). The residual concentration of SO_2 in the exhaust gases after such a setup reaches less than 200 mg/Nm^3 with an input concentration of 1.5 mg/Nm^3 [45].

From the point of view of control of charge materials, well-known trivial solutions are recommended as a measure to guarantee the reduction of sulfur emissions during sintering:

- the use of fuel and other charge components with reduced sulfur content;
- increase of charge basicity;
- sintering with limestone bed.

The positive role of the flux in limiting sulfur emissions is realized in the undoubtedly original way of preparing fuel for sintering [109], which provides a

significant reduction in emissions of sulfur compounds. For granulation of coke breeze, lime milk and slaked lime are used as a binder, and the solidification of the granules is provided by the absorption of carbon dioxide (the authors call the obtained granules “white coke”). The use of granulated coke breeze provides the following benefits:

- coke saving of about 8–10% (depending on the size distribution of the granules);
- improvement of combustion conditions and, for this reason, reduction of carbon oxide emissions due to the formation of a coke and lime porous framework during the reaction of ash;
- decrease due to reduction of coke consumption and improvement of its burning conditions, emission of carbon monoxide, sulfur dioxide, nitrogen oxides.

In addition to “white coke,” the use of lime milk treatment to produce a “white bed” reduced SO_2 emissions by about 60%.

To improve the efficiency of gas cleaning, including sulfur components, at the sintering plant of Nippon Steel (Nagoya, Japan), electrostatic precipitators [111] have been replaced by a new exhaust gas cleaning system. The dust that is contained in the waste gas is collected by a filtering layer formed of activated carbon. Figure 1.73 shows a layout of the waste gas cleaning system at the sintering plant in Nagoya.

To prevent the “clogging” of the layer of activated carbon by sorbed dust, this layer has a certain mobility. In order to avoid excessive grinding of activated carbon, the moving layer of activated carbon was divided in the direction of gas

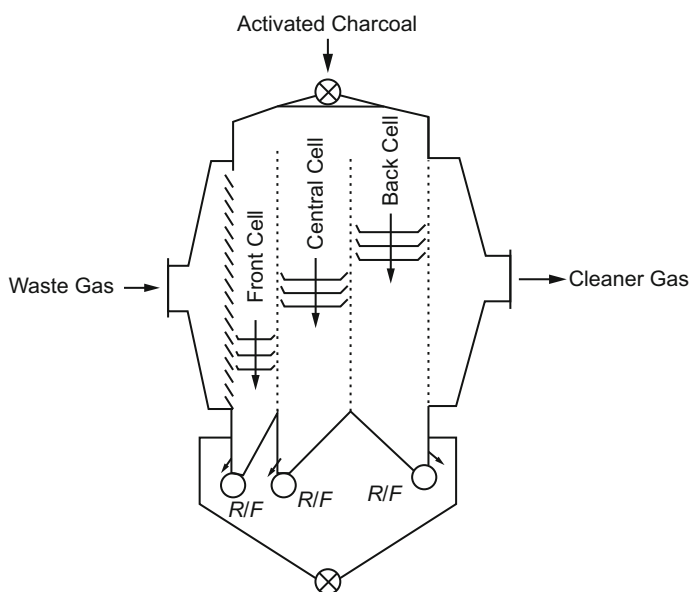
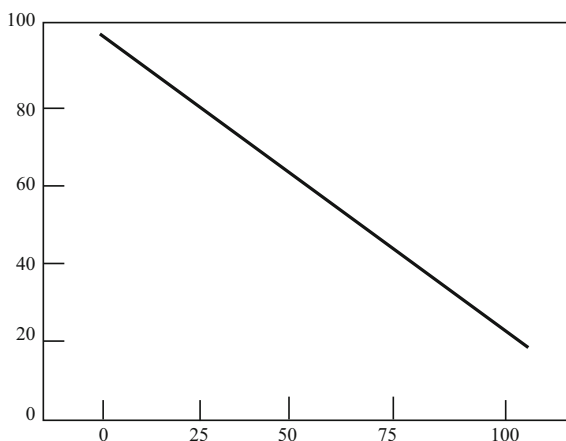


Fig. 1.73 Exhaust gas treatment system at Nippon Steel sinter plant, (Nagoya, Japan) [111]

Fig. 1.74 Effect of urea consumption in the sinter charge to reduce sulfur dioxide emissions [108]. The abscissa axis is the urea consumption, kg/h; Y-axis— SO_x level in emissions, %



flow into zones in which the rate of penetration of particles of activated carbon is different [112].

The efficiency of dust collection from 70 to 80% increased to 95% and higher, the degree of desulfurization was 96–98% [111].

To reduce the SO_2 content in the waste gases [108], the technology of urea addition to the sinter charge is proposed. The concentration of SO_2 in the off-gases is a linear function of urea flow (Fig. 1.74) and decreases with increasing of the latter.

Dioxin formation during sinter production and waste gas disposal measures

The term “dioxins” is used to refer to two groups of compounds known as polychloro-dibenzo-para-dioxins (PCDDs) and polychloro-dibenzo-furans (PCDFs), abbreviated to PCDD/F (dioxins/furans). These products are two groups of tricyclic aromatic esters. Structural formulas of dioxins/furans are shown in Fig. 1.75.

There are 75 possible dioxin structures (PCDD) and 135 possible furan structures (PCDF [66]). Each structure differs in the number and position of chlorine atoms. The chemical toxicity of dioxins/furans is also a function of chlorine atoms in such structures.

Only structures or structural isomers that contain substituted chlorine atoms in positions 2, 3, 7, and 8 (chemical products with chlorine atoms that are farthest from the bond connecting the two benzene rings) have significant toxicological importance (Fig. 1.75; Table 1.37).

The calculation of the total toxicity equivalent (I-TEQ) is carried out on the basis of structural chemical analysis data by multiplying the individual mass concentration of each PCD/F (C_x) isomer by the individual toxicity weight index (I-TEF_x) and then summing the results.

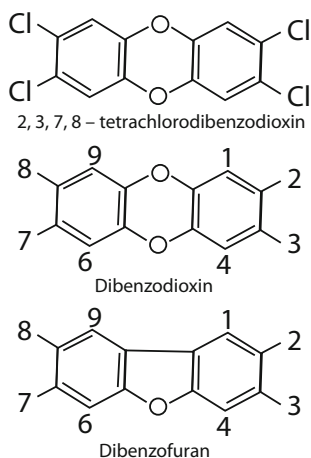


Fig. 1.75 Structural formulas of dioxins/furans [66]

Table 1.37 Toxicity of dioxin/furan structural isomers (international toxicity index, I-TEF^a)

Substituted chlorine atoms	Dioxins	Furans
2, 3, 7, 8—tetrachloro-	1	0.1
2, 3, 4, 7, 8—pentachloro-	No data	0.5
1, 2, 3, 7, 8—pentachloro-	0.5	0.05
1, 2, 3, 4, 7, 8—hexachloro-	0.1	0.1
1, 2, 3, 7, 8, 9—hexachloro-	0.1	0.1
1, 2, 3, 6, 7, 8—hexachloro-	0.1	0.1
2, 3, 4, 6, 7, 8—heptachloro-	No data	0.1
1, 2, 3, 4, 6, 7, 8—heptachloro	0.01	0.01
1, 2, 3, 4, 7, 8, 9—heptachloro-	No data	0.01
Octachloro-	0.001	0.001

^aI-TEF-International toxicity equivalence factors. I-TEF uses the toxicity of isomer 2, 3, 7, 8 TCDD (highest toxicity) as a reference for comparison

$$I - TEQ = \sum(C_x \cdot I - TEF_x) \quad (1.9.2)$$

For the first time [113], dioxins in waste sinter gases were detected in 1989.

Emissions from sinter plants are characterized by a low concentration of dioxins [108], while the mass emissions of dioxins and their isomeric composition are about the same for different sinter plants, although they were built according to different projects and have a different service life and work on different technological conditions for different raw materials.

For sinter plants, the preferred mechanism for the formation of dioxins is the interaction of coke breeze carbon with oxygen and inorganic chlorides in the

presence of copper (or other dispersed metal phases) as catalysts for the formation of organochlorine compounds (de novo synthesis).

In simulating the formation of dioxins during the sintering process, polyvinyl chloride (PVC), sodium chloride NaCl, and a roll lubricant were added to the usual base sinter mix. As the “real” charge, we chose the base charge with the additions of recycled dust A and B, mill scale and anthracite [114].

The concentration of chlorine in the model charge was 1000 ppm (which is ten times higher than the concentration of chlorine in the charge of the industrial sinter machine) and 500 ppm.

Sodium chloride (NaCl) and polyvinyl chloride (PVC) in any case (with high and low chlorine concentrations) have a significant impact on the release of dioxins.

At lower concentrations (500 ppm), the state of chlorine (inorganic chlorine and organic chlorine) was not found to affect the relative amount of dioxins produced, although at chlorine concentrations of 1000 ppm, organic chlorine produced a greater amount of dioxins.

Experiments using four types of “real” sinter (Fig. 1.76) have established that circulating dust A has the greatest effect on dioxin formation, as well as any compositions that include circulating dust A (with rolling oxide, circulating dust B, even with anthracite).

The formation of dioxins during the sintering of iron ores is associated with the presence of chlorine in the initial charge.

It is believed [115] that the formation of dioxins in the process of sintering is carried out in several stages, in which chlorobenzenes (CBs) and chlorophenol (CPs) are intermediate products. The experiments were carried out in sintering pan, in which various special additives of dioxins and chlorophenol (Table 1.38) were introduced into the baseline mixture and the concentration of dioxins in the exhaust gases formed during sintering was analyzed.

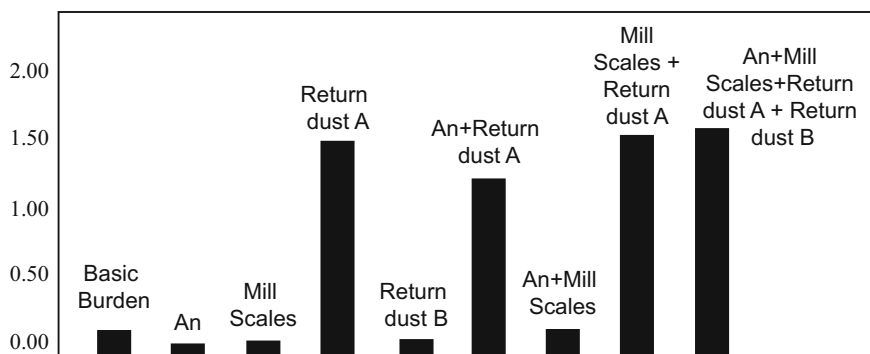


Fig. 1.76 Sources of dioxin formation in sintering [114]. The abscissa axis is the materials added to the sintering mixture; ordinate axis—relative amount of dioxins produced

Table 1.38 Removal of dioxins and furans during sintering

No.	Additive	Original quantity	Dimension	Result	
				Amount of additives in waste gas	Degree of removal in waste gas (%)
(i)	The basic charge (without additive)	<0.8	ng/kg of charge	–	–
(ii)	Circulating dust	46 T4CDFs ^a	ng/kg of charge	14.4	4
(iii)	¹³ C-08CDD	142	ng/kg of charge	0.19	0.1
(iv)	¹³ C-2378-T4CDF	200	ng/kg of charge	5.2	3
(v)	¹³ C-246-T3CP (chlorophenol)	20	mg/kg of charge	8	40

^aT4CDFs-furan homologue with four chlorine atoms in the molecule

In experiments (iii–v), dioxins and chlorophenol, containing ¹³C carbon isotope, were added to the initial baseline charge, and then the percentage fraction of the transition of these substances to flue gases during sintering was analyzed.

The results of determining the concentration of dioxins in the exhaust gases and the degree of their removal are presented in Table 1.38.

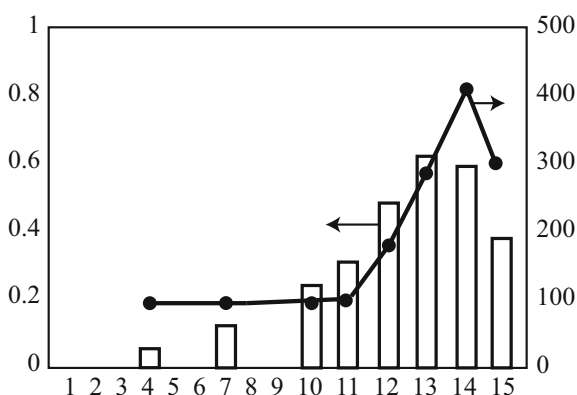
The degree of transition of dioxins in the waste sinter gas is small [(ii), (iii), and (iv) in Table 1.38]. The probability of circulation of dioxins when used in a mixture of captured dust from gas cleaning systems is small. Obviously, the possibility of the concentration of dioxins in the sinter during repeated processes of transition to the lower layer from the upper part of the sintered layer is also small [115].

Isotopic analysis (at 13 °C) shows that in each case (iii–v), no dioxins, except those added to the mixture, were detected. This confirms that there is no transition to dioxins and furans with a reduced number of chlorine atoms in the molecule, which is usually accomplished by the cleavage of the chlorine.

When chlorophenol (v) was introduced into the mixture, no dioxins were detected in the exhaust gases. Based on the fact that the amount of chlorophenol added in experiments in sintering pane is ten times the total amount of chlorobenzene in the exhaust gases during sintering of the basic sinter, it can be assumed that chlorophenol added to the initial sinter is not the immediately preceding product in the multi-step reaction of dioxin formation PCDD/Fs.

According to [115], waste gases that are formed during the sintering of iron ores contain dioxins (PCDD/Fs). According to independent measurements of the Japanese Society of Ferrous Metals, 100 g of I-TEQ/year is emitted from all Japanese sintering machines. This corresponds to approximately 3% of the total amount of dioxins entering the air in Japan.

Fig. 1.77 Change in the concentration of dioxins (diagram) in the exhaust gases along the length of the sintering machine [115] curve—flue gas temperature, °C; the abscissa axis—numbers of vacuum chambers; ordinate axis (left)—dioxin concentration index PCDD/F; ordinate axis (right)—temperature, °C



To study the nature of dioxin emissions on an industrial sintering machine, exhaust gas was taken from eight sites from fifteen vacuum chambers, and dioxins with a number of chlorine atoms in a molecule more than four were analyzed.

Exhaust gas sampling and the quantitative analysis of dioxins were carried out on the basis of Japanese Industrial Standard JIS K 0311. In addition, for comparison with other components of the exhaust gas, CO, CO₂, O₂, NO_x, SO_x, etc., were simultaneously measured.

Figure 1.77 shows a scheme for dioxin release by vacuum chambers of sintering machine. The maximum formation of dioxins occurs at the end of sintering with an increase in the temperature of the exhaust gases. These experimental data are supported by research by Corus (sinter plant l'en-Verne) [108].

Comparing changes in emissions of dioxins, NO_x and SO_x, we can conclude that the process of evacuation of dioxins is more similar to the removal of SO_x than NO_x.

This fact suggests that the dioxins formed in the first half of the sinter machine, as well as SO_x, can be absorbed by the underlying layers of the sinter charge. This conclusion contradicts the conclusions [108] about the absence of concentration of dioxins by the charge layer.

The reduction of dioxin/furan emissions during sintering can be achieved by two fundamentally different methods or their combination:

- sinter blend composition control;
- providing a system (method and device) for capturing from waste gases. Regulation (optimization) of the component composition of the sinter charge includes the following measures:
 - limiting the sinter plant load on oils and chlorides (for chlorides—the exclusion of ores with high or variable levels of chlorine);
 - monitoring of chlorine in circulating products;
 - restriction of the use of circulating materials containing chlorine (without the use of circulating materials, the emissions of dioxins were 1.5 ng/m³, with the introduction of circulating materials, the average emissions increased to 5.6 ng/m³).

A relatively simple and cost-effective technology for reducing emissions of dioxins/furans was developed by Corus on the basis of tests on the sinter machine “B” in l’en-Verne [66].

Sintering machine “B” was built in 1962 and produces about 5000 tons of sinter per day. The sintering area is 180 m^3 , the belt width is 3 m, the layer height is 47 cm, and machine is equipped with 15 vacuum chambers.

The exhaust gas in the amount of 500 thousand m^3/h is cleaned in a dry electrostatic precipitator; the dust concentration is $65 \text{ mg}/\text{m}^3$.

As an optimal solution to reduce dioxin/furan emissions, it was proposed to add ammonia as close as possible to the combustion zone (to the charge, [108]). Urea (NH_2)₂CO was chosen as the source of ammonia, since this compound is stable in air, easily transported, and quite affordable as an inexpensive, stable solid (granular) material.

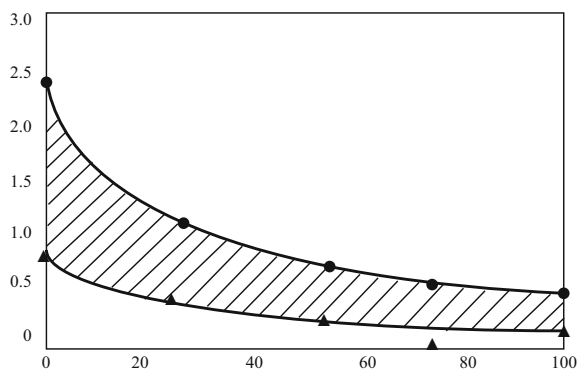
Urea granules were added to the charge near the weight feeders for hydrated lime and in front of the drum mixer. When heated in the combustion zone, urea decomposes, releasing ammonia near the area where de novo synthesis can occur.

The total values of dioxin levels in the chimney (Fig. 1.78) show a decrease in the concentration of dioxins/furans from an average of $1.4 \text{ ng}/\text{m}^3$ I-TEQ under standard conditions without urea additive to $0.6 \text{ ng}/\text{m}^3$ I-TEQ at a consumption of the added urea in the range of 50–70 kg/h. A significant decrease in the concentration of dioxins/furans is achieved with a relatively low consumption of added urea in the range of 25–50 kg/h. An increase in urea consumption in excess of 50 kg/h gives a slight further reduction in dioxins/furans in emissions.

One of the possible mechanisms to reduce dioxin/furan emissions from the addition of urea is to reduce the formation of HCl, since this substance may be involved in the product of the preceding reaction stage, and in the mechanisms of the synthesis of dioxins de novo.

With low and medium consumption of urea additives, the existing electrostatic precipitator successfully copes with the additional load and effectively removes these additional solid particles, but with increasing urea consumption, it is necessary to take measures to improve the performance of the electrostatic precipitator.

Fig. 1.78 Change in the concentration of dioxins/furans in the off-gases depending on the urea consumption in the charge [108]. The abscissa axis is the urea consumption, kg/h; ordinate axis—concentration of dioxins/furans in emissions, ng/m^3



1.9.5 Waste Gas Recirculation Concept

A fundamental solution to the problem of emissions of suspended solids, sulfur compounds, nitrogen oxides, and dioxins may be an approach implemented by the Emission Optimized Sintering System (EOS) [113, 116, 117], which is based on the principle of recycling of waste sinter gases.

Similar systems are equipped with sinter plant in Eumenden (Netherlands) [113] and sinter plant No. 3 in Tobata (Japan) [116].

Prerequisites for the implementation of recycling technology were:

- tightening environmental requirements;
- the need to reduce the volume of exhaust gas (and subsequent capital and operating costs for its purification);
- energy efficiency requirements;
- reduction of energy consumption and greenhouse gas emissions (CO_2);
- requirements of competitiveness (maximum reduction of production costs).

Justification for the use of gas recirculation

Qualitatively, the change in the characteristics of the waste sinter gas according to the oxygen content, humidity, and temperature along the length of the machine can be illustrated by Fig. 1.79.

The exhaust gas from the middle of the sintering belt has a relatively low temperature, low oxygen content, and high humidity, and therefore, from the point of view of the prospects for improving the performance of the sintering process, such gas is considered unsuitable for reuse.

For this reason, the following three conditions were taken into account in determining whether the off-gas should be recycled:

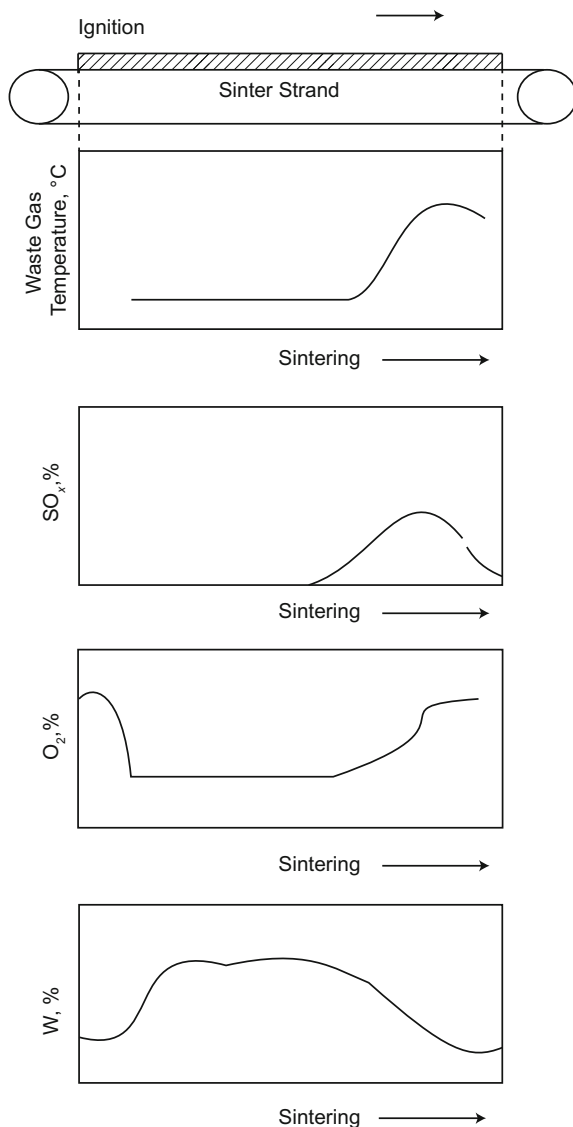
- oxygen content in the recirculated gas;
- humidity of recirculated gas;
- temperature limiting to prevent acid corrosion of electrostatic precipitators (industrial tests at the sintering plant No. 3 in Tobat [116] determined that the maximum gas temperature at the entrance to the electrostatic precipitator for a stream with a low content of SO_2 should be about 100 °C; for a stream with a high content of SO_2 —about 120 °C).

The influence of oxygen content (in the range of 13–21%) and humidity (within 3–16%) was studied [116, 118] experimentally in laboratory conditions, and the results are given in Fig. 1.80.

The productivity of the process (Fig. 1.80a), estimated by the sintering time, varies little if the oxygen content in the exhaust gas exceeds 18%, and the gas humidity, on the contrary, does not exceed 10% [116, 119].

It is noteworthy that the use of air heated to 250 °C (regardless of the content of oxygen and humidity in it) is accompanied by a decrease in the performance of the process (Fig. 1.80b).

Fig. 1.79 Characteristics of the exhaust gas along the length of the sintering strand



When the humidity of the sucked air is 13%, even when the oxygen concentration in it is 21%, sintering is impossible due to the decrease in the residence time of the material at temperatures above 900 °C and the decrease in the maximum temperature level. In the course of water vapor sucking, there was a tendency for the temperature of the moisture condensation zone in the middle and lower layers of the sinter to increase by 10–20 °C (and an increase in the amount of condensed moisture). It is obvious in this case that one of the reasons for the increase in the

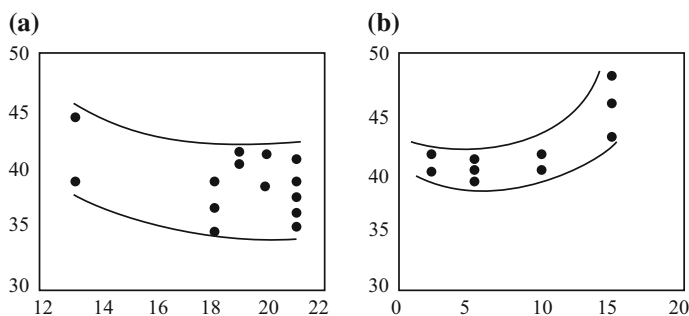


Fig. 1.80 Conditions for recirculation of exhaust sinter gas on the criterion of constancy of performance of the unit [116–118]. **a** Waste gas oxygen content; gas temperature 140 °C; abscissa axis—oxygen content in recirculated gas, %; Y-axis—duration of sintering, min.; **b** waste gas humidity; gas temperature 140 °C, oxygen content 21%; abscissa axis—the humidity of the recirculated gas, %; Y-axis—duration of sintering, min

duration of sintering is also the growth of gas-dynamic resistance in the lower horizons of the sintered layer [118].

Thus, when recirculating exhaust gases with low oxygen content and high humidity, it is necessary to regulate:

- waste gas extraction zone for recycling;
- volume of recycled gas;
- composition (according to oxygen content and humidity) of recirculated gases.

Model tests have shown that 5 and 20% of the waste gas can be recycled at the loading and unloading ends of the sintering machine, respectively, due to the maximum utilization of unused oxygen and low humidity waste gas at the loading end of the sintering machine and at the unloading end of the sintering belt. As a result, the oxygen content of the recirculated gas will be 19.8%, and the humidity of the recirculated gas will vary from 3.6% in winter to 4.4% in summer. The temperature of the exhaust gas entering the electrostatic precipitator is in the range of 105–125 °C and is equivalent to the critical temperature for the acid corrosion of the electrostatic precipitator. This temperature range determined the degree of waste gas recirculation at a level of 25% [116].

Waste gas recirculation

There are various options for partial recycling of waste gases [4], presented in Fig. 1.81:

- recycling part of the waste gas volume of the sintering machine and its supply to the largest possible sintering area (EOS process, or Emission Optimized Sintering, Corus, Ijmuiden, the Netherlands); more detailed—in Fig. 1.82a.
- recirculation of flue gases from the most distant vacuum chambers and supply to the entire area of sintering beyond the ignition hood (LEEP process, Low

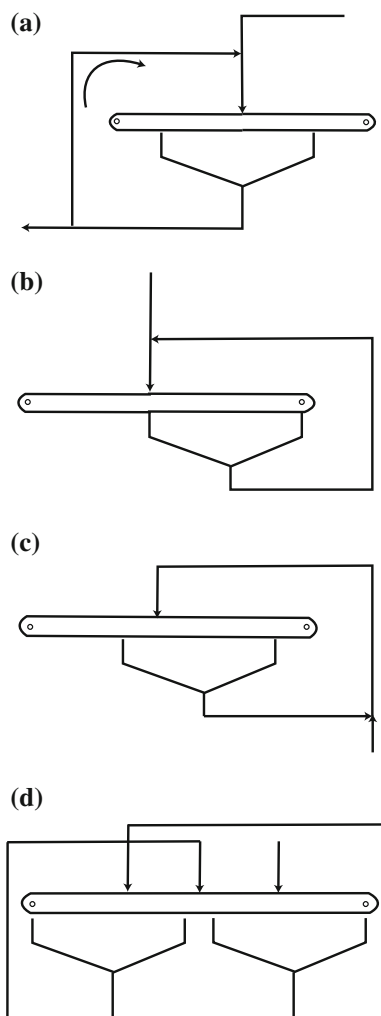


Fig. 1.81 Options for partial recirculation of waste sinter gases [4]. **a** EOS process, **b** LEEP process, **c** EPOSINT process, **d** selective recirculation

Emission and Energy optimized Process, HKM, Germany); more detailed—in Fig. 1.82b.

- off-gas recirculation jointly utilizing air heat from a sinter coolant or combined recirculation (EPOSINT, VAI, Linz, Austria process), more detailed—in Fig. 1.82c.
- selective off-gas recirculation, which is a combined recirculation (NSC, Tobata, Japan), more detailed—in Fig. 1.82d.

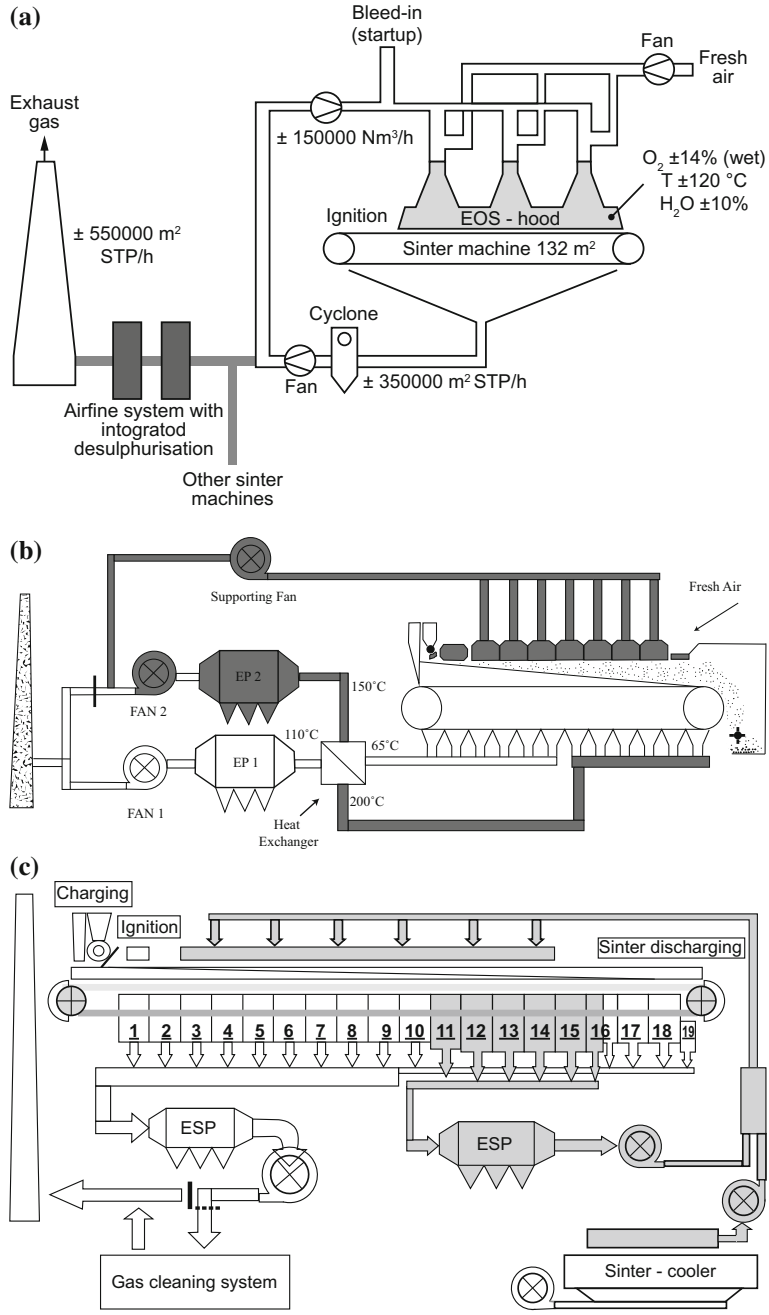


Fig. 1.82 Exhaust gas recirculation systems [4]. **a** EOS process, **b** LEEP process, **c** EPOSINT process, **d** selective recycling

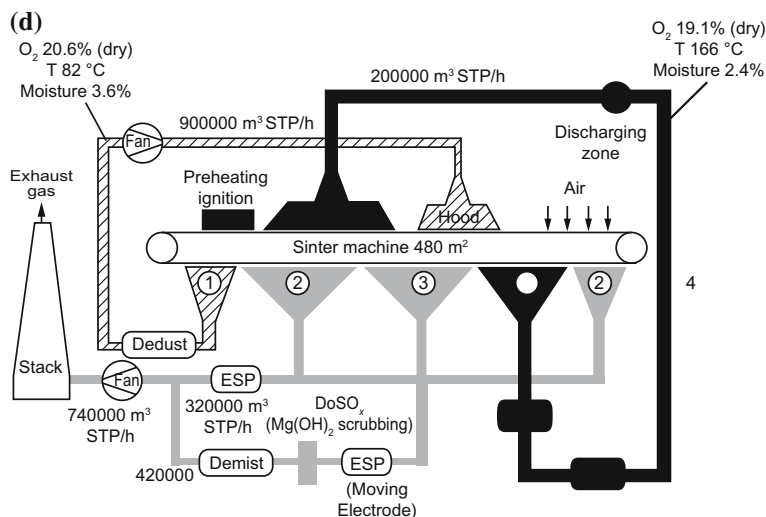


Fig. 1.82 (continued)

The recirculation of exhaust gases from the cooling zone of the sinter to the blast machine supply them to the layer after the ignition hood of sinter plant is introduced at the sinter plant of ChMK (MECHEL, Russia). Sinter plant has four machines with a total area of 240 m² each, with the sintering area of 138 m², the cooling area of 102 m². The exhaust gas is withdrawn from the pipe of the chimney of the sintering zone. From a variable cross-sectional collector, the recirculated gas is supplied to two shelters of the sintering machine. The volume of recycled gas is equal to 28% of the total. The performance of the machine with a recirculation system in comparison with the mode of air supply is given in Table 1.39 [4].

Gross emissions of CO (and dust) decreased by $\sim 30\%$, i.e., practically proportional to the consumption of recycled gas, emissions of nitrogen oxides, and sulfur decreased slightly.

As an example of an industrially implemented system of zonal recirculation of exhaust gases, Fig. 1.82d shows the scheme of the technological line of exhaust gas recirculation on sintering machine No. 3 in Tobat, the sintering area of 480 m². It includes exhaust gas evacuation systems in four positions along the length of the sintering machine.

The exhaust gas recirculation line from the charging end B1 of the sintering machine was equipped with a recirculation blower with a capacity of about 90 thousand m³/h and a dust collector, whose performance and operating modes are consistent with the blower capacity and dust properties.

The exhaust gas recirculation line from the discharge end of the B2 sintering machine was equipped with a recirculation blower with a capacity of about 200 thousand m³/h and a dust collector. The exhaust gas from the discharge end of

Table 1.39 Comparative characteristics of the machine during air supply and recirculation

No.	Indicator	Feeding conditions	
		Air	Recycle
1	<i>Parameters of the gas suction blower</i>		
	– Temperature (°C)	189	174
	– Flow rate (nm ³ /s)	104.9	97.5
	– Content O ₂ (%)	17.2	15.2
2	<i>Parameters of the gas at the exhauster</i>		
	– Temperature (°C)	32	180
	– Flow rate (nm ³ /s)	39.8	27.5
	– Content O ₂ (%)	20.6	15.2
3	The volume of gas released into the atmosphere (m ³ /s)	104.9	70.0
4	<i>Gross air emissions (kg/h)</i>		
	– CO	2663	1772
	– NO _x	46.2	45.9
	– SO ₂	124.3	119.4

the sintering belt was removed to the head of the belt, so that its heat content could be used to ignite the sinter mixture.

After preheating the charge, the exhaust gas from the low-temperature charging end of the sintering machine was discharged through the middle part of the sintering belt. A recirculation exhaust hood was installed to distribute the exhaust gas over the sintering belt. In order to maintain the load in the process line when evacuating high-temperature off-gas with high SO_x content (at the level of 400 thousand m³/h), and also to change the load in the process line to evacuate low-temperature off-gas with low SO_x content (from 600 to 300 thousand m³/h), the position of the separation plates in the main gas ducts has been changed.

Since the volume of exhaust gas to be processed decreased, the capacity of the main blower was reduced from 1000 to 740 thousand m³/h, and the EP (B) electric filter with a capacity of 300 thousand m³/h was decommissioned [116].

The temperature of the exhaust gas in each vacuum chamber along the length of the machine after the introduction of exhaust gas recirculation technology increased with increasing duration of sinter cake stay in the zone of high temperatures.

Exhaust gas recirculation has helped move the location of the onset of SO_x emissions by 3–5 vacuum chambers to the charging end of the sintering belt. In this case, the maximum concentration of SO_x increases, and there is a tendency to concentrate SO_x emissions. As a result, the exhaust gas evacuated from vacuum chambers No. 26–31 to line B2 has a reduced SO_x content. The exhaust gas discharged through the last vacuum chamber (No. 32) by the main blower to maintain the desired temperature of the exhaust gas also has a reduced SO_x content, which results in a reduction in SO_x emissions in the chimney.

Table 1.40 Comparison of operational data before and after the introduction of exhaust gas recirculation technology

Indicators			Actual characteristics		Coeff-t of improvement (%)
			Before recirculation	After recirculation	
Gas characteristics, output from the chimney	Rate of emissions with exhaust gas (m ³ /h)		925 × 10 ³	665 × 10 ³	↓28
	Dust	Concentration (mg/m ³)	50	30	↓56
		Rate of emissions (kg/h)	46	20	
	SO _x	Concentration, 1 × 10 ⁻⁴ (%)	9	5	↓63
		Rate of emissions (m ³ /h)	8	3	
	NO _x	Concentration, 1 × 10 ⁻⁴ , %	199 (at O ₂ = 15%)	199 (at O ₂ = 15%)	↓3
		Rate of emissions (m ³ /h)	179 (at O ₂ = actual)	173 (at O ₂ = actual)	
Energy saving (MJ/tsinter)	Power consumption for sintering		1498	1400	↓7
	The total power consumption		1662	1570	↓6

Table 1.40 summarizes the changes in the performance of the sinter before and after the introduction of the exhaust gas recirculation technology.

The total energy consumption (including electricity consumption and steam production energy due to the recovery of the energy of the exhaust gas) decreased from 1662 to 1570 MJ/ton of sinter.

Flue gas recirculation technology ensures a significant environmental impact:

- reduction of dust emission (by 56%);
- reduction of SO_x emissions (by 63%);
- reduction of NO_x emissions (by 3%);
- reduction of dioxin emissions.

A scheme for reducing the formation of dioxins is discussed in [120]. Gas with a high concentration of dioxins is taken from the middle part of the sintering belt and is fed into the sinter layer in the last third of the length of the machine. Passing through the region of high temperatures (>1200 °C), dioxins undergo complete destruction.

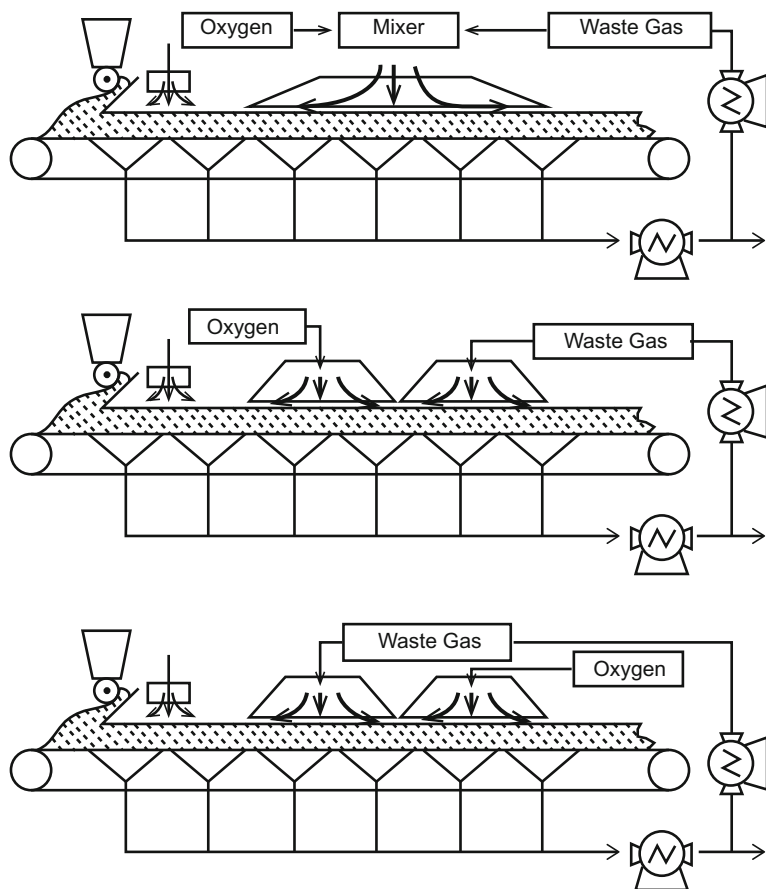


Fig. 1.83 Schemes of oxygen supply to the sintering layer during exhaust gases recirculation [117, 121]

Combined exhaust gas recirculation system. The lack of oxygen in the recirculated exhaust gas can be compensated in the combined recirculation system of the exhaust gas and/or supplemented with oxygen enrichment of the sucked gas [117, 121].

There are three fundamentally different schemes of supplying oxygen in sintering layer (Fig. 1.83):

- (1) Oxygen is enriched in recycled waste gas, and the concentration of oxygen in the gas being sucked in coincides with the concentration of oxygen in the atmosphere. This method is similar to the EOS method in that the injection is carried out uniformly throughout the entire area of the sintered layer while regulating the oxygen concentration in the recycled exhaust gas.

- (2) The recycled exhaust gas and the oxygen enrichment of the drawn in air are carried out independently of each other. A process is proposed in which the enrichment of the sucked gas is carried out in the first half of the sinter machine (after the ignition hood), and the exhaust gases are recycled in the second half of the sintering machine.
- (3) A process is proposed in which the exhaust gases are recirculated in the first half of the sintering machine, while in the second half of the sintering machine, the enrichment of the sucked gas by oxygen takes place.

The evaluation of the variants of the combined system of exhaust gas recirculation was carried out by the method of simulation under the following initial conditions:

Thickness of a layer of sinter	500 mm
Underpressure	14.7 kPa
Temperature/time of ignition	1200 °C/90 s
The diameter of the pelletized charge	2.5 mm
Amount of coke breeze added	3% mass
The amount of limestone in sinter charge (CaO)	9% mass
Initial, ultimate, and equilibrium moisture content	6.0; 1.0; 0% mass
Oxygen enrichment of sucked gas and oxygen concentration in flue gases	26; 16%
The gas injection time	The beginning of the injection after 400 s after the temperature in the layer began to rise
Oxygen concentration in sucked ambient air	21%

There is no significant difference between the three variants of the sintering process in terms of the layer heating modes. Compared with option (1), the burning of coke breeze in option (2) is completed up to the bottom layer during the oxygen enrichment period, equal to 400 s. Therefore, even when flue gases with a low oxygen concentration are blown in the second half of the sinter machine, the combustion of coke breeze does not slow down.

On the contrary, in the third variant, as a result of the enrichment of the sucked gas in oxygen in the second half of the sinter machine, the rate of burning of the coke in the lower layer is accelerated compared to options (1) and (2). However, as a result of the injection of exhaust gas with a low oxygen concentration in the first half of the sinter machine, the burning of coke breeze in the middle layer slows down while simultaneously slowing down the burning of coke breeze in the whole layer.

Despite the fact that the total amount of oxygen supplied in variant (3) is higher, variant (2) seems to be more preferable under the conditions of fuel combustion.

To determine the mode of oxygen supply (degree of enrichment and duration of supply), laboratory studies were conducted in [117].

The typical sinter charge used at the sintering machine No. 4 of sinter plant in Fukuyama was used as an experimental charge.

The components of the sinter (on the basis of ore fines, dosed according the basicity of 2.05) were mixed in a drum mixer (internal diameter of 600 mm, the speed of rotation of 30 rpm), and for each mode, pelletizing was carried out for 3 min. After pelletizing, the moisture content of the sinter was usually 7% by weight.

The sintering was carried out under the following conditions: The thickness of the sinter layer is 450 mm; the mass of the charge is 50 kg; bed layer thickness—50 mm; underpressure (constant)—9.8 kPa. The oxygen concentration was varied by supplying specified volumes of oxygen (50–200 l/min) and nitrogen (340,600 l/min). The temperature was measured at three points inside the layer and the exhaust gases directly under the grate. To determine the composition of the exhaust gases, an infrared gas analyzer of continuous action (CO, CO₂) and a magnetic analyzer (O₂) were used.

The duration of sintering decreases in direct proportion to the increase in oxygen concentration in the sucked gas with the equal increase in the productivity of the sinter of the fraction +5 mm and +10 mm. When the oxygen concentration is lower than 21%, there is a tendency to decrease the yield of the sinter and the cold strength of the sinter (SI). On the other hand, even if the oxygen concentration is above 21%, there is no change in the yield of the sinter and in its drop strength.

The effect of oxygen in the sucked gas on reducibility (JIS-RI) and hot strength (RDI) do not manifest itself. However, the content of FeO in the sinter with increasing oxygen concentration shows a tendency to decrease.

Preferred from the point of view of productivity and sintering time are oxygen enrichment modes, which assume the oxygen supply is focused on the region located in the first half of the sinter machine and corresponding to 1/8–1/4 of its length.

The optimal variant of the combined method of enrichment of sucked air with oxygen and recirculation of exhaust gases is:

- enrichment of sucked air in the first half of the sintering belt, in the second half —supply of recycled gas;
- oxygen is supplied focused right behind the incendiary mountain;
- oxygen content is 28–30%, feed time is 2–3 min.

1.9.6 Recommendations on the Best Available Technologies (BAT) in Sintering

Based on a detailed analysis of the operation of existing sinter plants, assessment of the state of technique and technology, environmental impact characteristics, requirements of the Pollution Control and Prevention Directive, as well as regulatory requirements regarding the quality of environmental components, the European IPPC Bureau formulated a set of indicators regarding environmental impacts and technologies that provide similar indicators.

As best practices, these measures on metallurgical technologies are grouped in [91]; the best available technologies and their indicators are given in [122] and are given below.

The best available dedusting technologies for exhaust gases and aspiration air of sinter plants are as follows:

No.	Impact factor	Event (cleaning devices)	Indicator ^a	Note
1	Storage, transport, processing of disperse materials	Moisture management of materials or water spray when dealing with materials to prevent dusting	—	Unorganized sources (diffuse emissions)
2	Waste sinter gas (technologies “at the end of the pipe”)	Bag filters	1–15 mg/nm ³	
		New-generation electric filters	20–40 mg/nm ³	If bag filters are not applicable
		Combination of devices: cyclone and bag filter	1–15 mg/nm ³	
		Combination of devices: electrostatic precipitator and bag filter	1–15 mg/nm ³	
3	Aspiration emissions (charge compartment, cooling and sinter processing)	Combination of devices: shelters and/or fencing and bag filter	<10 mg/nm ³	
		Combination of devices: shelters and/or fencing and electrostatic precipitator	<30 mg/nm ³	If bag filters are not applicable

^aDetermined as daily average

The best available technologies for reducing the content of sulfur compounds in the waste sinter gas (used separately or in combination with the measures) are as follows:

No.	Impact factor	Event (cleaning devices)	Indicator ^a (mg/nm ³)	Note
1	Sulfur-containing charge components	Reduction of sulfur in the mixture by the use of low-sulfur solid fuel	500	If applicable
		Reducing sulfur intake by minimizing solid fuel consumption	500	
		Reduction of sulfur in the charge due to the use of iron ore materials with low sulfur content	500	
2	Processes in the sintered layer	Injection of adsorbents into waste sinter gases before bag filter	350	
3	Waste sinter gas (technologies “at the end of the pipe”)	Desulfurization in a wet scrubber	<100	
		Regenerative Activated Carbon (RAC) process	<100	

^aExpressed in terms of SO₂, defined as daily average

The best available technologies to reduce emissions of nitrogen oxides with sinter gases (used separately or in combination of measures):

No.	Impact factor	Event (cleaning machine)	Indicator ^a (mg/nm ³)	Note
1	Processes in the sintered layer	Recycling waste sinter gas	<500	If applicable (strict control of CO is necessary to avoid personnel poisoning)
		Other preliminary methods (the use of anthracite; the use of burners with a low formation of nitrogen oxides in the incendiary furnace)	<500	
2	Waste sinter gas (technologies “at the end of the pipe”)	Regenerative Activated Carbon (RAC) process	<250	
		Selective Catalytic Reduction (SCR)	<120	Requires pre-treatment of gas, including its desulfurization. The temperature of the exhaust gas should not be below 300 °C

^aExpressed in terms of NO₂, referred to the content of 15% O₂, defined as the daily average

The best available technologies for the removal of polyaromatic hydrocarbons, including dioxins and furans (used separately or in combination of measures) are as follows:

No.	Impact factor	Event (cleaning devices)	Indicator ^a	Note
1	Charge components	Exclusion of receipt of raw materials containing dioxins and furans, or components from which they can be synthesized, to the mixture	<0.5 ng I-TEQ/nm ³	
2	Processes in the sintered layer	Introduction of nitrogen compounds to suppress the formation of dioxins and furans		
3	Waste sinter gas (technologies “at the end of the pipe”)	Waste gas recirculation		
		Injection of appropriate adsorbents into the flue gas duct before the bag filter	<0.05–0.2 ng I-TEQ/nm ³	For bag filter
		Injection of proper adsorbents into the flue gas duct before the electrostatic precipitator	<0.2–0.4 ng I-TEQ/nm ³	For electrostatic precipitator

It should be noted that the technical solutions considered as the best available technologies are advisory in nature.

1.9.7 Sinter Plant Without Chimney

Reducing emissions of pollutants in the production of sinter by these or other technological measures does not solve the problem of environmental impact radically. However, an ecologically flawless sinter production scheme seems quite feasible.

The concept of sustainable development in relation to metallurgy involves the complete elimination of emissions of pollutants into the atmosphere with waste gases from sintering machines [24]. It is based on the technical idea of using waste process gases as blast for blast furnaces. To this end, the sinter gases are cleaned of dust and moisture and fed to the suction of the blower machine. In this case, the blast furnace performs the functions of a deactivator of toxic components in the composition of the waste sintering gases:

- oxides of nitrogen in the furnace oxidize carbon, reducing to nitrogen.
- Sulfur of sulfur oxides is distributed between iron and slag with a coefficient depending on the temperature of smelting products in the furnace’s hearth, slag basicity, slag degree of oxidation, etc., with partial removal to the gas phase.

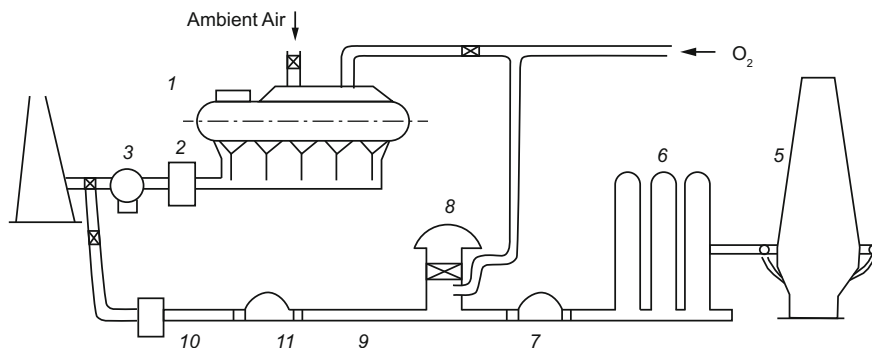


Fig. 1.84 Concept of the complex “sinter plant—blast furnace”

- Carbon monoxide is oxidized to CO_2 already when the blast is heated and then participates in the gasification of coke carbon in the blast furnace (despite the low (no more than 1.5% by volume) carbon monoxide content in the waste sinter gases, additional CO_2 will be accompanied by increased coke consumption).
- etc.

In the framework of the proposed concept, a technical and economic assessment of the blast furnace smelting parameters was carried out as part of the sinter–blast furnace complex (Fig. 1.84):

- sinter machine (1) (area 312 m^2) with gas cleaning system (2), exhaustor (3), chimney (4);
- blast furnace (5) (volume 2700 m^3) with a blower machine (7), air heaters (6), and an air intake device (8);
- between the exhaustor (3) and the intake of the blower machine (7), interconnected by a gas pipeline (9), a moisture separator (10), and a fan (11) are provided to overcome the gas-dynamic resistance in the path of the sinter gas to the blower machine.

An important technical problem in the operation of such a complex is the cleaning of sinter gas from dust. To ensure the normal operation of the blower machine, the concentration of dust in the air (sinter gas) entering it should not exceed 2 mg/m^3 . Such a level of dedusting can be provided only by a multi-stage cleaning system, which includes, in addition to traditional apparatuses (battery cyclone or electrostatic precipitator) bag filter, louvered or rolled devices, or other equipment.

The performance of the blast furnace was calculated using a mathematical model of the blast furnace process, which allows an adequate assessment of the furnace performance, fuel consumption, the composition of the pig iron and slag, and the composition of the top gas in any conditions of the blast furnace smelting. The actual operating conditions of the blast furnace were used to tune the model:

Table 1.41 Composition and yield of sinter gases with different oxygen content in the sucked air

No.	O ₂ in the air (%)	Composition of sinter gas (% vol.)				Yield (m ³ /t)
		N ₂	O ₂	CO ₂	CO	
1	21.0	78.34	12.22	7.77	1.67	890
2	35.6	70.99	15.87	10.91	2.33	639
3	43.2	67.18	17.32	12.96	2.54	542
4	50.1	63.82	18.73	14.79	2.66	481
5	58.4	59.72	20.26	17.22	2.80	420
6	73.1	52.54	23.12	21.23	3.02	345
7	95.2	41.84	26.92	27.79	3.45	269

capacity 6116 tons/day; coke consumption 425 kg/t of pig iron; consumption of natural gas 123 m³/t of pig iron; the oxygen content in the blast is 28%; blowing temperature 113 °C; sinter consumption 1 t/t of pig iron. Possible modeling error does not exceed 2% for fuel consumption and 5% for furnace performance.

In modeling, two variants of the operation of the complex are evaluated: with the usual sinter production mode and with the enrichment of the sucked air with oxygen (oxygen sintering). The composition of the waste sinter gases was determined by the results of oxygen sintering in the sinter pan [35], as well as by means of computational modeling under the assumption that the inflows are 50% and the consumption of solid fuels is 5% (Table 1.41).

At the first stage of the simulation, the boundary conditions of the temperature-stable criteria for the operation of the blast furnace were established when the waste sinter gases are supplied as blast, assuming that such work is possible within the limits of the theoretical burning temperature of 1800–2300 °C. The temperature of the blast (sinter gases enriched to the required level with oxygen) varied from 900 to 1300 °C. As a technological factor of the indicated boundary conditions, we took the ratio of the amount of oxygen entering the furnace with blast (the amount of oxygen that went to enrich the sinter gases and the enrichment of the blast) to the amount of carbon oxides coming into the furnace with the sintering gases (the sum of CO and CO₂ in the sinter gas) or $V_{O_2}^Z/V_{CO_x}$.

The simulation results showed that in the investigated range of blast temperatures, the theoretical temperature of fuel combustion in a blast furnace does not exceed the interval of 1800–2300 °C, if the amount of oxygen entering the furnace per 1 m³ of carbon dioxide of sinter gases falls within 3.5–4.3 m³/m³. The lower limit relates to a blast temperature of 1300 °C, the upper limit to a blast temperature of 900 °C.

At the second stage of modeling, as a criterion for optimizing the technological parameters of the “sinter–blast furnace” complex, the consumption of reference fuel for the smelting of cast iron (Q) was determined taking into account the calorific value and the top gas outlet from the ratio:

$$Q = (K \cdot q_K + NG \cdot q_{NG} - V_{OF} \cdot q_{OF})/29,300 \quad (1.9.3)$$

where K , NG , V_{OF} —coke consumption, kg/t of pig iron; natural gas, m³/t pig iron; blast furnace gas output, m³/t of pig iron, respectively;

q_K , q_{NG} , q_{OF} —coke caloric content, kJ/kg, caloric value of natural gas, kJ/m³; caloric content of top gas, kJ/m³, respectively;

29,300—calorific value of reference fuel, kJ/kg t.

The flow rate of the injected natural gas and the temperature of the blast were maintained at the level of the base case (123 m³/t of pig iron, 1130 °C, respectively). The amount of oxygen for the enrichment of the blast was taken so that the theoretical combustion temperature corresponded to the basic variant.

The simulation results are summarized in Table 1.42.

The first option (basic) corresponds to the operation of the furnace on a conventional blast without injection of sinter gases. The second variant describes the operation of the furnace with injection of sinter gases, but with an oxygen concentration in the blast equal to the concentration in the base variant (28%). Options 3–9 correspond to the operation of the “sinter–blast furnace” complex with the required degree of oxygen enrichment from the point of view of maintaining the theoretical combustion temperature.

Table 1.42 Performance indicators of the “sintering machine–blast furnace” complex^a

No.	Sintering indicators			Blast furnace indicators					
	O ₂ , %	V _{SG}	V _{O₂} ^S	V _{SG} ^{BF}	V _{O₂} ^{BF}	V _{O₂} ^t	V _{O₂} ^S /V _{O₂} ^t	T _{theor} °C	Q, kg e.f./t
1	21.0	890	0	0	297	76	0	2050	483.2
2	21.0	890	0	451	303	34	0	1800	489.3
3	21.0	890	0	890	305	196	0	1914	485.6
4	35.6	639	57.7	639	307	205	0.28	2040	482.9
5	43.2	542	74.2	542	307	213	0.34	2050	483.0
6	50.1	481	86.2	481	308	218	0.39	2050	483.0
7	58.4	420	96.5	420	309	224	0.43	2050	484.3
8	73.1	345	110.4	345	311	230	0.48	2050	485.1
9	95.2	269	121.9	269	311	239	0.51	2050	485.7

Notes ^aV_{SG}—rate of sinter gas (m³/t of iron);

V_{O₂}^S—oxygen consumption for enrichment of air during sintering, m³/t of iron;

V_{SG}—rate of sinter gas, m³/t of iron;

V_{SG}^{BF}—the consumption of sinter gas in the blast furnace, m³/t of pig iron;

V_{O₂}^{BF}—oxygen consumption for enrichment of blast furnace blast, m³/t of pig iron;

V_{O₂}^t—the total amount of oxygen consumed for enrichment (air during sintering and blast), m³/t of pig iron;

T_{theor}—theoretical temperature of carbonaceous materials;

Q—the consumption of equivalent fuel for blast furnace process, kg e.f./t of hot metal

Bold values are reflected the optimal significance of indicators

As can be seen from Table 1.42, in terms of energy, the proposed method of operating the “sintering plant—blast furnace” complex is not more expensive compared to the traditional blast smelting technology. The consumption of equivalent fuel at the optimum parameters of the technological mode of sintering does not exceed the cost of fuel in the base case, when no sinter gases enter the furnace. Minimal energy costs occur when the supply for the enrichment of sintering air 0.28–0.39 of all oxygen consumed for the enrichment of sintering air and blast furnace blast.

As for the consumption of coke, it increases as the amount of carbon oxides flowing into the furnace with blast (as part of the supplied sinter gases) and the degree of enrichment of the blast with oxygen increases and amounts to: in variant 1 (base)—425 kg/t of pig iron, in option 2—448.5 kg/t of pig iron, in options 3 to 9—463 to 464 kg/t of iron.

In order to avoid coke consumption growth in blast furnace smelting using sinter gases as the blast, it is necessary either to compensate for the increase in heat consumption by additional consumption of blown fuel or to clean the sinter gas from CO₂ before blowing them into the furnace. Such purification is possible (industrially developed methods of CO₂ absorption exist); however, for the case of utilization of sinter gases, the main criterion of this technology should be the minimum impact on the environment.

Summarizing the above, we can conclude that the concept of environmentally flawless sinter–blast furnace technology has certain prospects for further development as a whole and according to the technological stages that make up its essence.

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Chapter 2

Pellet Production



2.1 General Information About Pellet Production

2.1.1 Technological Scheme of the Production of Pellets

Pellets are spherical solid bodies obtained by the granulation of finely divided iron ore materials with the addition of binder and fluxing components (or without them), followed by strengthening [1].

Production of pellets (pelletizing¹) is the process of converting dispersed iron ore components (particle size less than 0.1 mm) into agglomerated product through the production of raw granules with their subsequent strengthening by means of roasting, autoclaving, or cementation.

Pellet production is a relatively young branch of the mining industry. The world's first pellet factory was built at Silver Bay (USA) in 1955 [2]. In Russia (former USSR), the first pilot industrial pelletizing plant was built at the Southern Mining and Processing Plant (now PJSC YuGOK, Ukraine) in 1958. Industrial pellet production was organized at Sokolovsko-Sarbaisky GOK (now the Eurasian Resources Group, Kazakhstan) in 1964. In 2017, the production of pellets in Russia amounted to more than 40 million tons [3], in the world—398 million tons.

The main reasons for the intensive development of pellet production in the world in the middle of the twentieth century were [4]:

- an increase in the production of poor ores that require deep beneficiation, and the emergence of a new type of iron ore raw material (fine concentrate);
- low productivity of sintering machines during sintering finely ground concentrates, especially when producing non-fluxed sinter and without using various sintering process intensifiers;

¹The terms “pellet,” “pelletizing” originated in the USA in the 40s of the twentieth century; the synonym “okatysh,” established in metallurgical practice, was proposed in Russia in 1952 [5].

- high transportability of pellets, especially non-fluxed, in comparison with sinter;
- high-quality indicators (iron content, cold strength, low fines content (fraction—5 mm), uniform lumpiness of pellets).

Pellets differ in the degree of fluxing, estimated by the value of basicity (CaO/SiO_2):

- non-fluxed pellets (produced without the addition of flux, but may have a natural basicity inherent in iron ore concentrate, not higher than 0.15);
- partially fluxed with basicity up to 1.0 (produced with the addition of flux);
- fluxed pellets with a basicity higher than 1.0.

Depending on the presence of fuel in its composition, iron ore pellets (without the addition of solid fuels) and ore–coal (with the introduction of solid fuels) are distinguished.

The pellets can be made single layer, when the entire volume of the pellet has a uniform composition, or double-layered, when the inner part of the pellet is represented by a material of the same composition, and the outer shell is made of a material of a different composition (Fig. 2.1).

In addition to non-fluxed and flux pellets, metallized pellets are produced (using appropriate metallurgical technologies other than blast furnace production and therefore are not covered in this book).

Production of pellets is carried out in the pelletizing factories, usually confined to the ore-dressing enterprises.

The technological scheme of production of pellets is shown in Fig. 2.2 [4].

The technological scheme of the pelletizing plant is a graphic representation of the sequence of technological operations with an indication of the type of materials, their size and consumption (the latter refers only to a specific pelletizing plant).

Concentrate coming from the processing plant with a moisture content of 8–10% and a particle size of 95–97% of the fraction—0.05 mm (after averaging at a

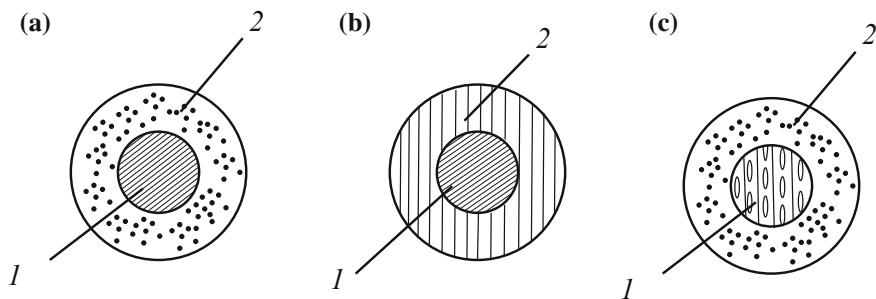


Fig. 2.1 Diagram of the formation of a two-layer pellet. **a** 1—iron ore concentrate + bentonite + limestone, basicity 1.2; 2—iron ore concentrate + bentonite; **b** 1—iron ore concentrate + bentonite + limestone, basicity 1.2; 2—iron ore concentrate + bentonite + limestone, basicity 0.4; **c** 1—iron ore concentrate + bentonite + coke breeze; 2—iron ore concentrate + bentonite

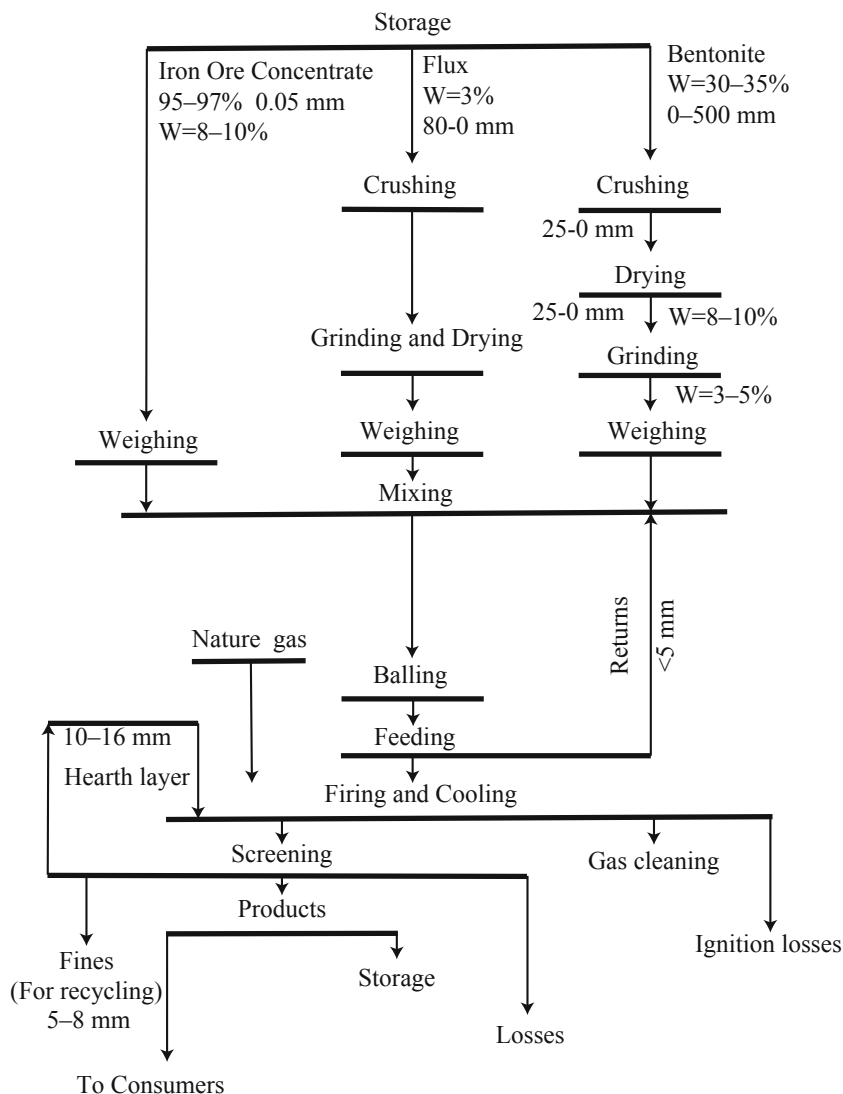


Fig. 2.2 Technological scheme of the production of pellets [4]

warehouse of wet concentrate) is dosed into the charge from feed bins. Binder (bentonite) with a moisture content of ~ 30 to 35% and a particle size of 0–500 mm after unloading (as a rule, from railway cars) is fed to crushing to a particle size of 0–25 mm (and then to the warehouse, from where it is taken into the process). Bentonite with a particle size of 0–25 mm is dried to a moisture content of 8–10% in a drying drum by treating with heat transfer gas with a temperature of 600–800 °C and is directed to grinding with simultaneous drying with hot gases with a

temperature of 200–250 °C to a moisture content of 3–5%; size of ground bentonite is not less than 95–97% of fraction—0.050 mm.

In the case of the production of fluxed pellets, preliminary (prior to dosing) flux components, for example, limestone, also undergo preparation. Limestone with a particle size of 0–80 mm is crushed to a particle size of 0–25 mm and then is pulverized (with simultaneous drying); size of crushed limestone 90–95% fraction—0.05 mm.

After the dosing operation, the components of the charge (binder and flux) together with the concentrate are fed to the mixing, which is carried out either in special units or directly on modular conveyors using special devices.

Mixed charge enters the pelletizing, where in special units (drum pelletizers or disk granulators) raw pellets are formed, the sizes of which are determined by the specific raw materials and technological conditions of the pelletizing factory, but usually lie in the range of 5–25 mm (92–95%).

Raw pellets are stacked on a conveyor roasting machine (with a screening of fines from the fraction—5 mm and its return to the mixing operation) and are subjected to strengthening roasting. Before loading the conveyor machine, the bed is fed to its grate (in Russia burned pellets of a 10–16 mm fraction, isolated during the screening of burned pellets).

Ready fired pellets are screened with the release of fractions: acceptable quality pellets (8–10 mm, +16 mm), bed (10–16 mm), and return (–8 mm).

Thus, in the general case, the production of pellets includes two distinct stages that distinguish different laws:

- production of raw pellets;
- strengthening processing of raw pellets.

2.1.2 Formation of Raw Pellets

The tendency to reduce energy when pelletizing is inherent to the system “dispersed iron ore material—water”:

- by reducing the magnitude of the surface tension at the interface when the iron ore material interacts with water (wetting phenomenon);
- as a result of coarsening of particles (with their adhesion).

The mechanism of aggregation of finely divided iron ore materials can be described by a combination of a complex of processes (phenomena): wetting, capillary interaction (discussed in Sect. 1.3) and by swelling, surface dispersion, dissolution, etc. (specific for interaction in the pellets due to the presence of a binder component).

In general, the adhesion force F in the pelletized aggregate (pellet) due to capillary forces according to [6] can be described by the relation (2.1.1):

$$F = k \cdot S \cdot \rho \cdot (1 - \varepsilon) / \varepsilon, \quad (2.1.1)$$

where

k —coefficient taking into account the shape of particles, the nature of their packaging in the pelletized aggregate, the hydrophilicity of the material;

S is the specific surface of the dispersed material;

ρ is the density of iron ore material;

ε is the porosity of the pelletized unit.

The priority factor determining the adhesion strength of wetted particles of iron ore materials (and ultimately the strength of the pelletized unit) according to (2.1.1) is the specific surface area (Fig. 2.3).

The role of capillary pressure forces in strengthening, arising from the distribution of water in the pelletized aggregate, can be estimated from [4] from (2.1.2):

$$F = 8 \cdot (\sigma/d) \cdot (1 - \varepsilon) / \varepsilon, \quad (2.1.2)$$

where

σ is the surface tension of the moisturizing fluid;

d —diameter of the pellet.

For fine-granulated concentrate conditions, adsorption- and capillary-bound water contributes to the strengthening of the raw pellets. The cohesive forces of the particles are proportional to the maximum molecular moisture capacity² ($W_{m.m.m.c.}$), which characterizes the energy state of the concentrate. The structural state of the concentrate depends on the maximum capillary moisture capacity³ ($W_{m.c.m.c.}$). The combination of these indicators determines the ability of dispersed materials to pelletizing or crumpling ability K [7]:

$$K = W_{m.m.m.c.} / (W_{m.c.m.c.} - W_{m.m.m.c.}) \quad (2.1.3)$$

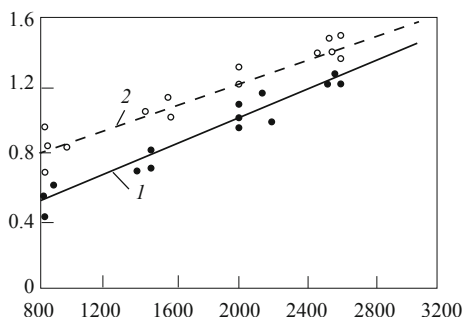
The crumpling ability K varies from 0 to 1. By crumpling ability, all materials can be divided into the following categories [8]:

- up to 0.2—the material is not crumpled;
- 0.2 to 0.35—weakly crumpled material;
- 0.35 to 0.5—average lumps;
- 0.5 to 0.8—well-crumpled material;
- more than 0.8—very well-crumpled material.

²Maximum molecular moisture capacity ($W_{m.m.m.c.}$)—for industrial concentrates with a specific surface area of 1600–2000 cm²/g—varies from 7.0 to 8.0% [8].

³Maximum capillary moisture capacity ($W_{m.c.m.c.}$)—for industrial concentrates with a specific surface of 1600–2000 cm²/g—varies in the range of 18–20% [8].

Fig. 2.3 Dependence of the strength of raw pellets from the specific surface of the concentrate [8].
 1—non-fluxed pellets,
 2—fluxed to basicity 0.8–1.0.
 X-axis—specific surface of concentrate, sm^2/g ; Y-axis—compressive strength of raw pellets, kg/pellet



Practice shows that the more crumpling ability of the charge, the higher the strength of the raw pellets.

The process of obtaining raw pellets in the granulator consists of three stages: core formation, lump growth, mass transfer between the formed lumps. The primary nucleus is formed when a drop of water falls into the volume of the dry material; the over-wetted primary lumps have high plasticity. An increase in the size of the granules occurs as a result of repeated strikes of the nucleus against a fixed layer of material during movement in the pelletizer.

Under the action of dynamic loads, the lump is compacted, while excess moisture is squeezed to the surface, which ensures that new particles of the material are adhered to the lump, i.e., its growth. As the particles in the lump come closer, the thickness of the water film decreases and the strength particle adhesion grows, while for the emerging dynamic loads (determined by the type and design of the granulator), there is a corresponding minimum thickness of water films. Upon reaching this value, the pellet stops increasing in size.

The process of pelletizing of iron ore concentrate should ensure that the optimal structure of raw pellets (porosity) is obtained, which upon further processing will create the proper properties of the pellets during drying and roasting.

2.1.3 Strengthening of Raw Pellets

2.1.3.1 Pellet Drying

In the technological cycle of pellet production, the drying operation precedes the roasting of the pellets. Raw iron ore pellets are a capillary-porous body, the water content of which is about 8–11% with a total porosity in the range of 28–36% [9].

It is believed [10] that when drying, moisture is removed from the pellets as a steam-water mixture. During the formation of bubbles, the size of which is smaller than the diameter of the capillary, the movement of the steam-water mixture can occur without the formation of a pressure zone in the capillary. If a large number of bubbles are formed, the size of which is commensurate with or exceeding the

diameter of the capillary, an overpressure in the places of vaporization can form and the resulting pressure gradient can cause the destruction of the pellets.

The influence of the porosity of the pellets on the amount of excess pressure developed in the body of the pellet, according to [11], is shown in Fig. 2.4.

The appearance of a pressure gradient during drying of the pellets is caused not only by the porous structure of the pellets, but also by their thermal properties, in particular, thermal conductivity. There are two mechanisms for drying the pellets:

- If the thermal conductivity of a material is much higher than the thermal conductivity of water ($\lambda_M > \lambda_\beta$), then a “piston mode of moisture removal” is possible with the appearance of excessive pressures (high-intensity drying).
- If the values of thermal conductivity of the material and water are the same ($\lambda_M = \lambda_\beta$), in this case the mechanism of liquid removal is close to the laws of evaporation of water from the free surface.

The study of the relationship between the indicators of the structure of the pellets after drying and the strength of the roasted pellets showed that an increase in the initial density of pellets (decrease in porosity), accompanied by an increase in the contact surface between the particles, leads to an increase in the strength of the roasted pellets (Table 2.1). At the same time, along with a decrease in the total

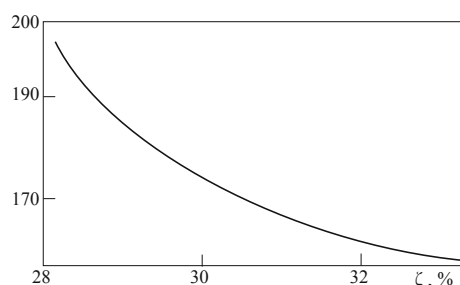


Fig. 2.4 Effect of porosity of raw pellets on the amount of excess pressure during drying [11]. Abscissa axis—porosity of raw pellets, %; Y-axis— P_{exc} , kPa

Table 2.1 Effect of initial porosity on the parameters of the microstructure of the roasted pellets^a

Initial porosity ^b (%)	The parameters of the microstructure of the roasted pellets		
	Total porosity (%)	The average pore size (μm)	The average distance between the pores (μm)
38.4	28.1	18.0	47.0
35.5	26.2	16.0	45.0
33.4	25.2	14.0	42.0
31.0	23.3	12.9	39.0
28.5	22.1	10.0	36.0
27.0	21.1	9.0	34.0

^aPellets—concentrate with Fe content of 71.4%, roasting temperature 1300 °C, roasting time 10 min

^bInitial porosity = porosity of the pellets after drying

porosity of roasted pellets, both the average pore size and the distance between the pores are reduced.

The strength of the pellets during drying (in case of proper drying mode) increases several times compared with the strength of raw pellets: the strength of raw pellets in the range of 4–15 N/pellet, at the same time, the strength of dried pellets 20–50 N/pellet.

2.1.3.2 Roasting of Pellets

Roasting is a finishing operation for the thermal treatment of pellets. In industrial conditions, the maximum roasting temperature is 1200–1350 °C; the duration of high-temperature treatment is up to 20 min depending on the composition of the pellet, requirements for its quality, technology features.

Strengthening of pellets from the charge of different basicity is shown in Fig. 2.5.

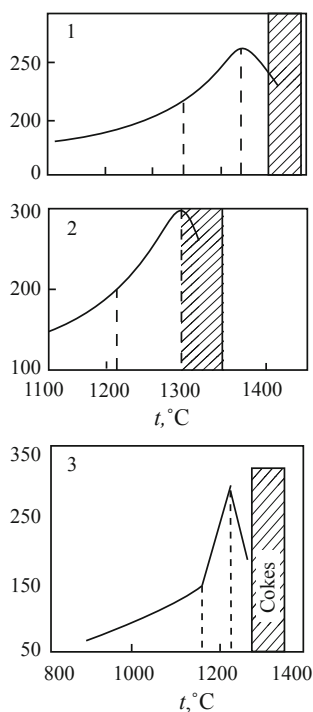


Fig. 2.5 Crushing strength of the pellets depending on the heat treatment temperature. Pellets from LebGOK concentrate, Russia [11]. 1—basicity 0.13 (the amount of $\text{CaO} + \text{SiO}_2 = 3.5\%$); 2—basicity of 0.69 (the sum of $\text{CaO} + \text{SiO}_2 = 5.0\%$); 3—basicity of 1.25 (the amount of $\text{CaO} + \text{SiO}_2 = 12.0\%$). X-axis—roasting temperature, $^\circ\text{C}$; Y-axis—crush strength of pellets after roasting, kg/pellet

With an increase in the basicity of the pellets (and the amount of slag-forming oxides), the temperature level, which guarantees the greatest strength, decreases. The growth of the amount of slag-forming oxides creates the danger of cake formation.

2.2 Charge Components for the Production of Pellets

In the composition of the charge for the production of pellets there are three groups (parts) of components:

- iron ore portion of the mixture (fine concentrate);
- binder;
- flux part of the charge (in the production of fluxed pellets).

The structure of the charge for the production of pellets and the requirements for its components, ensuring the subsequent properties of the pellets, are illustrated by the scheme of Fig. 2.6.

The determining indicator of iron ore concentrate used for the production of pellets is the chemical composition. The composition of iron ore concentrate depends on the type of ore minerals, the type of the main iron ore component, and the beneficiation technology. If the main mineral in the concentrate is hematite Fe_2O_3 , the maximum possible content of Fe in the concentrate does not exceed 70%. If the main mineral in the concentrate is magnetite Fe_3O_4 , then the maximum achievable iron content of Fe in the concentrate is 72.4% [8].

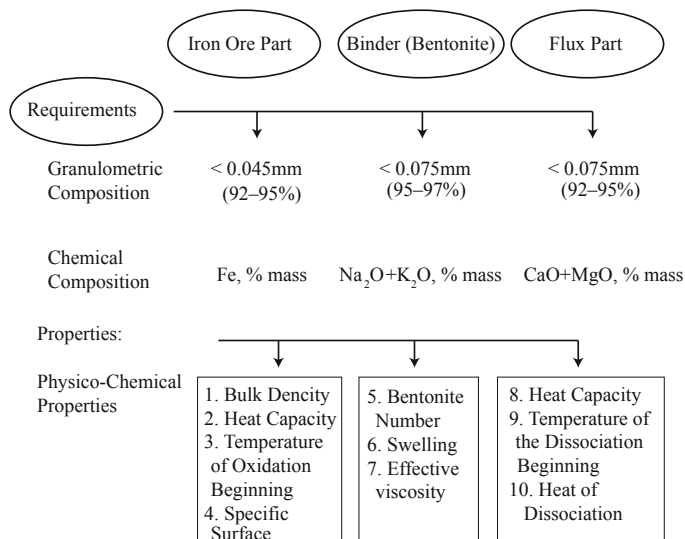


Fig. 2.6 Requirements for batch components for the production of pellets

Concentrates containing more than 60% iron are commonly used in the production of pellets.

Gangue (not containing the basic mineral, in this case, Fe) iron ore concentrate may contain quartz, silicates (feldspars, chlorites), complex silicates, and aluminosilicates (micas, amphiboles), rarely carbonates, and ultrabasic rocks. The mineralogy of gangue is extremely important for pellets, since the totality of the minerals of the waste rock determines the characteristics of the liquid phase (melt) and the indicators of liquid-phase hardening, especially in the production of non-fluxed pellets.

High demands are placed on the granulometric composition of iron ore concentrates for the production of pellets. This is due to the fact that the most important factor affecting the mechanical strength of the pellets is the particle size, the specific surface area of the concentrate: The strength of the raw pellets is the higher, the more contacts between individual particles. With modern technologies of enrichment, the achievable grain size of the concentrate is estimated by the fraction—0.044 mm (content 92–95%).

Chemical and granulometric compositions of common concentrates of the main Russian suppliers of raw materials are presented in Table 1.1 (Sect. 1.2).

For the production of raw pellets, the moisture content of iron ore concentrates, depending on the ore-dressing technology, is important. It is believed that the optimal moisture content is the moisture content in the charge, which provides the maximum yield of raw pellets of a given size. Moisture content of iron ore concentrates used for the production of pellets is 8.5–10%. Fluctuations in the moisture content of the concentrates are preferably not more than 0.20–0.25%.

Various types of binders are used to give the raw pellets (as well as pellets after drying) sufficient strength (see Sect. 2.3).

In modern practice, bentonite is most often used as a binder. The consumption of bentonite per ton of pellets, depending on the quality of bentonite, lies in the range of 2–10 kg [12].

Bentonite is a clay mineral; its mineral composition is shown in the diagram (Fig. 2.7).

Bentonite clays are characterized by a high content of oxides of silicon and aluminum (48–75% and 10–22%, respectively).

Bentonite clays have good dispersibility when wetted with water. Water molecules penetrate through the capillaries to the particles and then into the interlayer gaps. Due to the action of the disjoining pressure, the water layers thicken, and the particles move away from each other up to complete separation. There is a spontaneous grinding of clay or dispersion.

The ability of bentonite clays to disperse and form spatial coagulation structures is characterized by a bentonite number, which is about 80–99 for alkaline bentonites, 10–60 for alkaline-earth bentonites and clays (see Sect. 2.3).

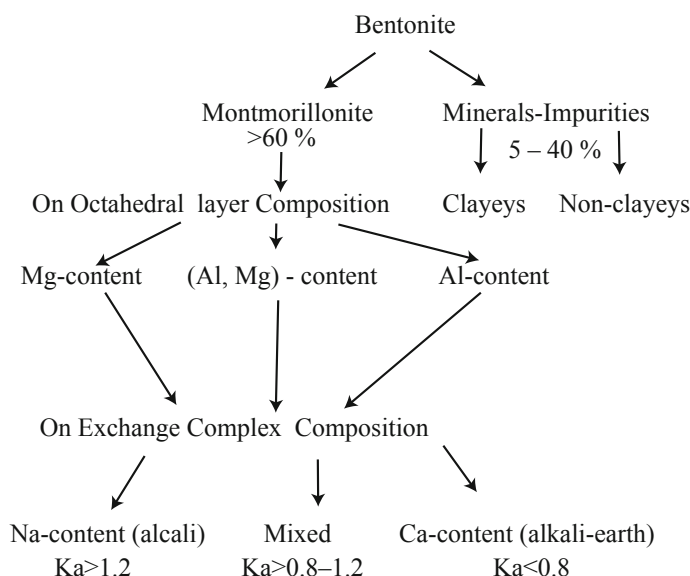


Fig. 2.7 Mineral composition of bentonite

Swelling is a property of bentonite clays to increase significantly in volume when water is absorbed.

The chemical composition (as well as the characteristics of swelling and bentonite number) of known bentonites,⁴ which have been used in pelletizing iron ore concentrates, is presented in Table 2.2.

In the production of fluxed pellets, flux additives are added to the charge of iron ore pellets. The main purpose of these additives is the formation of the required metallurgical properties of the pellets, such as “hot” strength, reducibility, shrinkage in the reduction process [15].

Due to the fact that waste rock concentrates are primarily acidic, carbonate components (limestone, dolomite, dolomitic limestone) are used as flux additives. The requirements for the chemical composition of the flux components are reflected in Sect. 1.2.

⁴Suppliers of quality bentonites are Greece, India, Bulgaria, Azerbaijan [14]; the composition is given in Table 2.3.

Table 2.2 Chemical composition and properties of some bentonites known on the world market, used in the pelletizing of iron ore concentrates [13]

Field (Country)	Chemical composition (% mass)										Properties			
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	SO ₂	LOI ^a	w	S _B ^b , times	B ^c
Sarigyu (Armenia)	60.67	–	14.70	5.30	–	3.78	2.36	–	–	–	7.12	–	13.3	83.5
Askan (Georgia)	60.11	–	15.23	3.0	–	3.35	1.47	1.94	1.90	–	14.9	–	18.2	99
Oglandinsky (Turkmenistan)	69.3	–	12.7	2.80	–	1.88	2.51	–	–	–	7.24	–	12.0	99
Cherkassy (Ukraine)	54.9	0.24	18.13	3.22	0.43	3.72	1.84	2.34	0.77	0.15	–	–	9.6	20.0
Wyoming (USA)	55.44	0.10	20.14	3.67	0.30	2.43	0.50	2.75	0.60	–	7.99	4.81	–	–
Fort Steele (USA)	49.20	0.10	17.60	1.60	–	5.08	1.52	–	–	–	–	25.52	–	–

^aLOI—loss on ignition

^bS_B—swelling of bentonite ratio

^cB—bentonite number

w—moisture content

Table 2.3 Chemical composition and effective viscosity (*E*) of bentonites known in the world market [13]

Country of origin	Chemical composition (% mass)										<i>E</i> ^b (mPa s)	
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	<i>S</i>	<i>P</i>	LOI ^a
Dash-Salakhly (Azerbaijan)	54.03	0.40	18.4	4.74	1.46	2.90	5.25	1.32	0.58	0.164	0.095	9.78
Dash-Salakhly (Azerbaijan)	57.89	0.41	19.5	5.62	0.09	3.19	2.10	2.21	0.7	0.051	0.081	6.55
Bulgaria	53.68	0.44	18.8	4.22	0.78	3.15	4.24	3.15	1.61	0.06	0.138	9.46
Bulgaria	55.0	0.46	19.9	4.86	0.48	3.24	4.11	0.95	1.58	0.027	0.142	8.79
Greece	49.71	0.37	18.2	6.76	1.10	2.73	8.1	2.43	0.97	0.9	0.07	11.33
Greece	50.38	0.36	20.2	4.80	0.73	2.99	5.07	1.43	0.57	0.836	0.073	9.98
India	51.09	1.01	18.7	13.21	0.34	3.04	2.02	2.72	0.45	0.085	0.076	8.24
India	52.34	0.87	20.8	12.65	0.56	2.68	1.15	0.95	0.17	0.026	0.062	8.38

^aLOI—loss on ignition
^b*E*—effective viscosity (see Sect. 2.3)

2.3 Formation of Raw Pellets

2.3.1 *Interaction Between Wetted Particles During the Formation of a Raw Pellet*

Raw granules (pellets) are formed when the wet iron ore material or charge composition, which is based on dispersed iron ore material, is pelleted in special devices. The moisture content of the raw granule is 7–9%.

The formation of a raw granule can be provided by a set of acting forces [2, 16–19]: capillary, colloidal, molecular (van der Waals, electrostatic, mechanical, and magnetic). From various experimental estimates, it was noted [20] that the priority interaction in the raw granule, preserving its structure, due to the smallness of other types of active forces, is the forces of capillary interaction.

The main provisions of the theory of capillary interaction in relation to the work of iron ore materials are laid down by works [21].

The structure of the granules is considered as a porous body, which represents a system of capillaries emerging on the surface of the granules. The adhesion of the particles forming the walls of such a capillary is ensured by the presence of menisci at the ends of the capillary.

When assessing the aggregate interaction of particles in the granules, the influence of the electrokinetic properties of the surface should be taken into account. Upon contact of the surface of particles of dispersed iron ore with water, adsorption of ions takes place, both initially contained in the moisturizing water, and those formed as a result of the hydration of the material upon contact with water. This creates an excess charge on the particle surface, which is compensated (partially or completely) by the opposite charge of the ions of the liquid phase in the layer adjacent to the surface. The potential jump between the surface and the adsorption layer is called the electrokinetic potential or ζ -potential. According to Ken's rule [20], the surface of the ore particles, when wetted with water, acquires a negative charge and has a rather high electrokinetic potential. The reduction of the ζ -potential in the case of a negatively charged surface is facilitated by cations: Li, Na, K, Rb, as well as Cs, Mg, Ca, Sr, Ba; and in the case of positively charged—anions.

The effect of capillary interaction forces on the wetting perimeter on the strength of the granule formed by the dispersed iron ore material is shown in detail in Chap. 1 (Sect. 1.3).

To analyze the forces of capillary interaction of particles through a liquid cuff of spherical aggregates with respect to pellets^{5,6} a simplified model was proposed [20]. The model is based on the assumption of the uniformity of the mechanism of the drop separation from the capillary and the separation of particles connected by a liquid cuff.

⁵Characterized by the degree of dispersion $D = 1/d$, where d is the particle size, cm.

⁶The model is also suitable for the sintering of sinter charges.

The actual weight of the drop P , detached from the capillary of radius r , is determined from the expression:

$$P = 2 \cdot \pi \cdot r \cdot \sigma, \quad (2.3.1)$$

where

σ is the surface tension of the fluid.

Separation of the drop occurs over the smallest section of the liquid cuff; in this case, the equilibrium condition (the weight of the drop and the surface tension force) can be written as follows:

$$2 \cdot \sigma / r = P / \pi \cdot r_1^2, \quad (2.3.2)$$

where

r_1 —radius of the section of the drop separation.

The approximation of the experimental data [22] on the separation of water droplets revealed an empirical relationship between the capillary radius r and the radius of the cross section for the separation of the drop r_1 :

$$r_1 = 0.7937 \cdot r \quad (2.3.3)$$

Substituting (2.3.3) into (2.3.2), we obtain the relation for P , which characterizes the maximum adhesion force that occurs when a liquid is separated from a capillary of a given size:

$$P = 2 \cdot \pi \cdot \sigma \cdot 0.63 \cdot r = 1.26 \cdot \pi \cdot \sigma \cdot r \quad (2.3.4)$$

Taking into account the model of the drop from the capillaries, we calculate the adhesion forces of spherical particles connected by a liquid cuff (Fig. 2.8).

The maximum pullout force at a given particle radius r and angle φ can be calculated by replacing the bottom particle with a drop of liquid, assuming that the smallest section of the cuff corresponds to the accepted equilibrium condition (2.3.2). By (2.3.4), we calculate the maximum value of the holding force ($F_{\max} = P$).

The adhesion force F_{cc} (N/pellet) through the water cuff will be found as:

$$F_{cc} = F_{\max} - P_r - P_w, \quad (2.3.5)$$

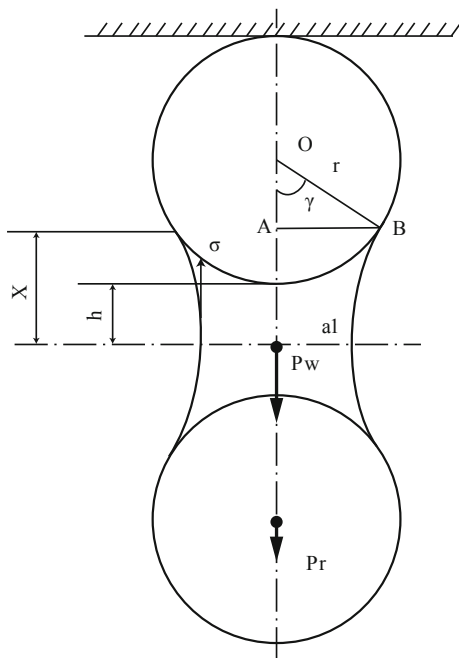
where

P_r —particle weight

P_w —the weight of the fluid of the smallest section of the cuff.

Obviously, when $\sum(P_r + P_w) > F_{\max}$, the adhesion of particles is impossible.

Fig. 2.8 Scheme for calculating the interaction forces between two spherical particles through a liquid medium [23]. X ; h is the distance between particles; a_1 is the radius of the cuff section; σ is the surface tension; φ is the angle of coverage of the liquid; r is the particle radius; AB is the wetting perimeter radius



Taking into account (2.3.4), from (2.3.5), we obtain for the adhesion force F_{cc} :

$$F_{cc} = 1.26 \cdot \pi \cdot \sigma \cdot r \cdot \sin \varphi - P_r - P_w \quad (2.3.6)$$

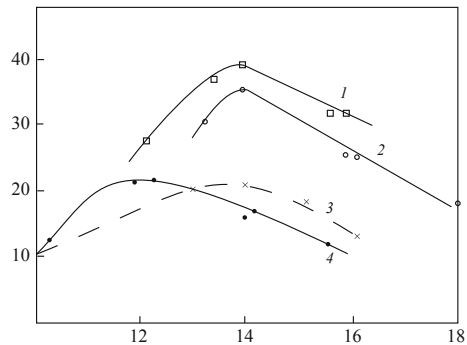
Assuming that the liquid forms a surface of the minimum area during the drawing and takes into account the spherical segments immersed in the liquid, we obtain for the volume of the liquid cuff V_L :

$$V_L = x \cdot a_1^2 \cdot \left(x + a_1 \cdot \left(e^{2x/a_1} - e^{-2x/a_1} \right) / 4 \right) - 2/3 \cdot \pi \cdot r^3 \cdot (1 - \cos \varphi)^2 \cdot (2 + \cos \varphi) \quad (2.3.7)$$

The maximum adhesive force of the particles for the model in question corresponds to a coverage angle of 60° . An increase in moisture content at a given angle will lead to a decrease in adhesion forces due to the weight of the liquid, which qualitatively confirms the dependence of the strength of real raw pellets on moisture (Fig. 2.9).

For the cubic packing of particles in an aggregate (critical number of bonds 26), taking into account the porosity of the aggregate (pellet), introducing the parameter of the specific surface S , expressed through the particle radius according to [23, 24] for the adhesion force, we can write

Fig. 2.9 Dependence of the strength of raw pellets (P) on moisture and particle size distribution [20]. 1—size material—0.06 mm; 2—material size—0.10 mm; 3—material with a large size—0.15 mm; 4—material size—0.25 mm



$$\sum F_{cc} = (1 - \varepsilon) \cdot d^2 [13.85 \cdot S \cdot \sigma \cdot \sin \varphi - 256.8 \cdot \rho_m \cdot (1 + B/100) \cdot d] \cdot 10^{-5} \quad (2.3.8)$$

where

ε is the porosity of the pellet;

d is the diameter of the pellet;

ρ_m —material density;

S is the specific surface of the material (cm^2/cm^3);

B —pellet moisture (%).

A priori, it is believed that the strength of raw pellets is directly proportional to the value of the specific surface of the material. A comparison of the strength values of raw pellets calculated by (2.3.8) with the actual strength values is given in Fig. 2.10, from which it is clear that the more complex dependence of the pellet strength on the specific surface of the iron ore material takes place.

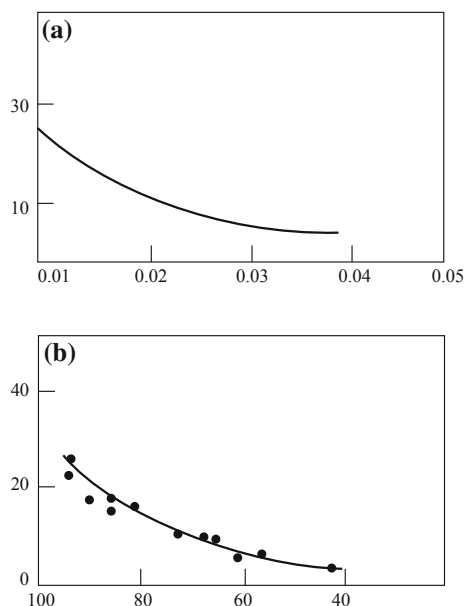
2.3.2 The Nature of the Action of Binding Additives in the Strengthening of Raw Pellets

The role of binding additives in the charge for the production of raw granules is to ensure the plasticity of the unit (to prevent destruction during deformation under the action of technological loads) and its strength.

Upon contact with water, additives (primarily bentonite) form a solution in the area of the moisturizing cuff, which, due to the limited solubility of the additive in water, exists in the form of a suspension. The qualitative characteristics of the suspension can be characterized by its surface tension, which, according to (2.3.8), affects F_{cc} and thus the strength of the aggregate. In turn, the surface tension of the suspension is determined by the concentration of bentonite in it (or in other words,

Fig. 2.10 Effect of material specific surface on the strength of raw pellets [20].

a Calculated curve: material —concentrate of Kachkanarsky GOK, material density 4.38 g/cm^3 , moisture content 7.03%, volume porosity 0.5168; diameter of the pellet is 13 mm;
b experimental data; The abscissa axis “a” is the particle diameter of the concentrate, mm; the abscissa axis “b” is the fraction of particles of a concentrate with a diameter of less than 0.04 mm, %; ordinate axis—compressive strength of raw pellets, N/pellet



the consumption of bentonite in the mixtures⁷). Figure 2.11 shows the dependence of the surface tension of the pore suspension on the content of bentonite in it, which is almost linear.

The concentration of bentonite in the pore solution changes both the pH of the pore solution and its ζ -potential (Fig. 2.12). With an increase in the concentration of bentonite in the suspension, the pH value increases linearly, while the change in the ζ -potential is of an extreme nature. The minimum ζ -potential corresponds to a 10% solution of bentonite in a pore suspension. This means that in order to obtain raw pellets with moisture content in the range from 6 to 8%, the optimum consumption of bentonite to the charge should accordingly be from 0.6 to 0.8%.

Studies on the effect of hydrogen parameter pH on the strength of the pellets taking into account the electrokinetic properties of the liquid phase were carried out in [20]. The pH value of the water supplied to the pelletizing ranged from 3.0 to 12.7. The results of these experiments are given in Table 2.4.

The strength of raw crushing pellets qualitatively reflects the change in electrokinetic potential (Fig. 2.13). The higher ζ -potential of the system (at a certain pH value), the lower is the strength of raw pellets. So when the value of the pH in the range from 6.85 to 6.95, the strength of the pellets is minimal and increases at a pH of less than 7.0 and in the range from 7.0 to 11.0. The addition of small amounts of

⁷The consumption of bentonite in the charge is determined by the technological conditions of specific pelletizing plants, but lies in the range of 0.5–1.5% [25], while the concentration of bentonite suspensions in the pore solution in the pellet is within 10–25%.

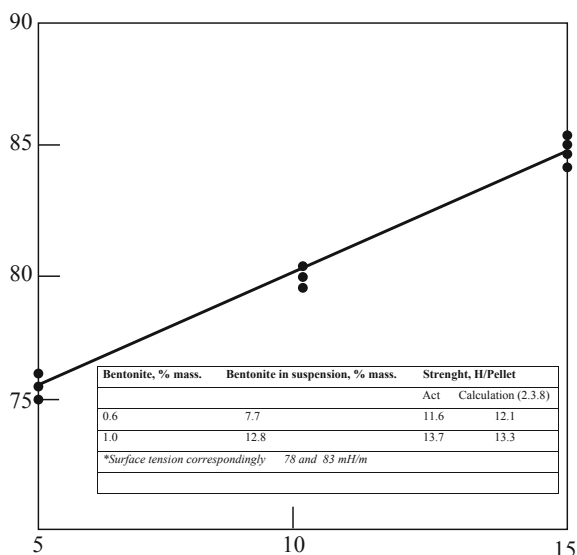


Fig. 2.11 Dependence of the surface tension of the suspension on the content of bentonite and pellet strength [24]. **a** surface tension: solvent—distilled water, bentonite from the Sarigyuhskeye field, holding 60 min. with constant agitation, the surface tension is determined by the method of maximum pressure in the gas bubble; **b** the strength of pellets with a diameter of 14.5 mm in crushing (the material is iron ore concentrate of Kachkanarsky GOK with a specific surface of $1730 \text{ cm}^2/\text{cm}^3$); consumption of bentonite in the mixture of 0.6 and 1%; porosity of 0.38 and 0.363; moisture content of 7.3% and 6.8%, respectively (content of bentonite in suspension is 7.7 and 12.8%). The abscissa axis is the content of bentonite in suspension, %; Y-axis—the surface tension of the suspension, mN/m

the electrolyte FeCl_3 helps to obtain stronger raw pellets over the entire pH range by reducing the ζ -potential.

With increasing pH above a certain value, the strength characteristics of the pellets are reduced.

2.3.3 The Effectiveness of Various Strengthening Additives in Pelletizing

The world practice of pellet production indicates the obligatory use of binders [17, 26, 27], which can be both inorganic and organic. More than 150 such materials are known, including those obtained artificially.

Alkaline-earth bentonites [28], nontronite clays [29], iron ore with aluminous gangue, Callovian hydro-micaceous clay, chalk-like marl, laterite nickel ore, and a number of other materials [30] were studied as inorganic binding materials. The effectiveness of these additives requires their increased consumption, which is

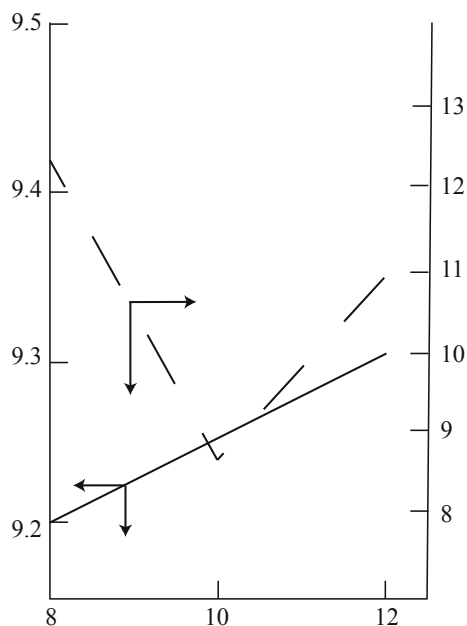


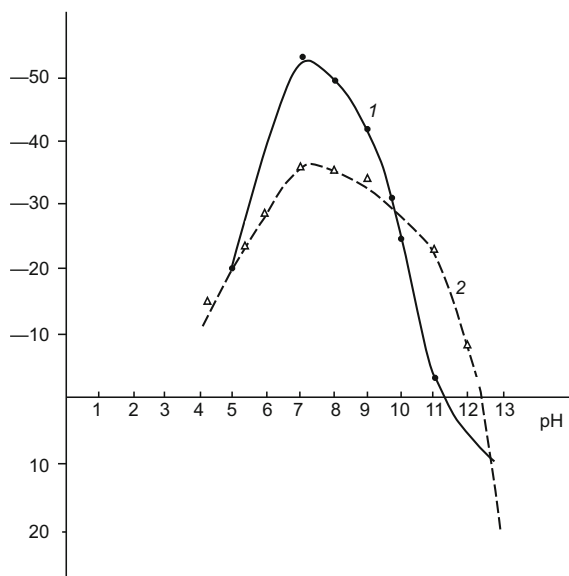
Fig. 2.12 Dependence of the pH of the pore solution and its ζ -potential on the concentration of bentonite in the pore solution [20]. The abscissa axis is the concentration of bentonite in suspension, %; y-axis (left)—indicator pH of suspension; y-axis (right)— ζ -potential, mV

Table 2.4 Effect of the pH of the moistening water on the strength of raw pellets*

No.	Additives consumption		pH of water	Strength of raw pellets (N/pellet)
	Bentonite (%)	FeCl ₃ (ml/l)		
1	0.5	—	3.0	1.7
2	0.5	—	5.05	1.4
3	0.5	—	6.95	1.3
4	0.5	—	9.05	1.4
5	0.5	—	11.0	1.5
6	0.5	—	12.7	1.3
7	1.0	—	2.1	1.7
8	1.0	—	5.02	1.4
9	1.0	—	6.85	1.4
10	1.0	—	10.3	1.6
11	1.0	—	12.7	1.6
12	1.0	1.0	2.1	1.8
13	1.0	1.0	6.8	1.5
14	1.0	1.0	10.55	1.8
15	1.0	2.0	2.1	2.0
16	1.0	2.0	6.8	1.4
17	1.0	2.0	10.55	1.7

*Charge: iron ore concentrate of Kachkanarsky GOK, 7% limestone

Fig. 2.13 Effect of a hydrogen indicator on the value of ζ -potential [20]:
 1—concentration of Kachkanarsky mining and processing plant;
 2—bentonite.
 y-axis—indicator pH;
 y-axis— ζ -potential, mV



undesirable because it reduces the consumer value of the pellet, namely the iron content.

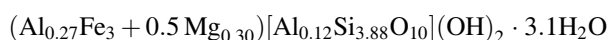
The main binder in the production of pellets remains alkaline bentonite or its derivatives: modified alkaline-earth bentonite or complex binders based on bentonite.

Bentonite

The general characteristics of bentonite and its mineralogical composition, as well as the chemical composition of known bentonites, are given in Sect. 2.2.

The basis of bentonite is the mineral montmorillonite. A specific property of the minerals of the montmorillonite group is the ability to change the basal interplanar spacing within wide limits. Water molecules and other polar liquids can enter interlayer spaces, causing an increase in lattice parameters in the direction of the “c” axis (from 0.96 nm in the absence of water molecules between the layers up to the complete separation of the layers). At the same time, the number of water molecules capable of entering the mineral lattice is determined not only by moisture content, but also by the nature of interlayer cations [31].

In the montmorillonite structure, various substitutions are observed: Silicon in tetrahedral coordination is replaced by aluminum and possibly phosphorus; aluminum in the octahedral element—magnesium, iron, lithium, etc. This defines the various formulas of montmorillonite; as an example, for Cherkasy montmorillonite, you can write:



It is believed that high-quality bentonites with binding properties should contain [32] not less than 70% of montmorillonite aluminum–magnesium variety with an exchange complex of alkaline composition (alkalinity coefficient K_a ⁸ more than 1.0) with a total exchange capacity of at least 70 mg eq/100 g. Such clays are characterized by a fairly high dispersion: the content of the colloidal fraction—0.001 mm exceeds 70%.

Three main indicators: effective viscosity of the bentonite suspension, indicators of swelling, and water absorption (Enslin method) equally reflect the properties of the binder and its role in the formation of quality indicators of raw pellets (Fig. 2.14).

The set of characteristics of bentonites (effective viscosity, swelling index, Enslin index,⁹ colloid) clearly differentiates bentonites into three groups differing in effective viscosity (Table 2.3, Sect. 2.2):

- alkaline-earth, highly modified to the sodium form with an effective viscosity of more than 50 MPa s;
- modified alkaline-earth (activated bentonites) with an effective viscosity of up to 30 mPa s;
- natural bentonites with an effective viscosity of about 5 MPa s.

Modified bentonite

The depletion of high-quality bentonite reserves forces suppliers of this raw material to seek solutions to improve the quality of alkaline-earth bentonites by modifying them.

For the first time, chemical activation of clay soda was applied in the USA [34]. The essence of chemical activation (modification) of Ca-containing bentonites consists in replacing the cations of the diffusion layer of particles of bentonite with sodium cations with both an additive of the reagent in solid form and treatment with a soda solution with a temperature of 80 °C [35].

Modification efficiency is estimated by the modification factor M :

$$M = 0.053 \cdot E/C \cdot (K - K_o), \quad (2.3.9)$$

where

E —exchange capacity (mEq/100 g);

C —soda additive (%);

K, K_o —the rheological index of activated and initial bentonite;

0.053—the conversion factor of sodium in soda (mEq/100 g).

The effect of various properties of bentonites (both natural and modified) on the strength of raw pellets (crush test, kg/pellet) and ductility or impact strength

⁸The coefficient of alkalinity K_a is defined as the ratio of $(Na^+ + K^+)/ (Ca^{2+} + Mg^{2+})$.

⁹Enslin indicator characterizes the water-absorbing ability of clays, %.

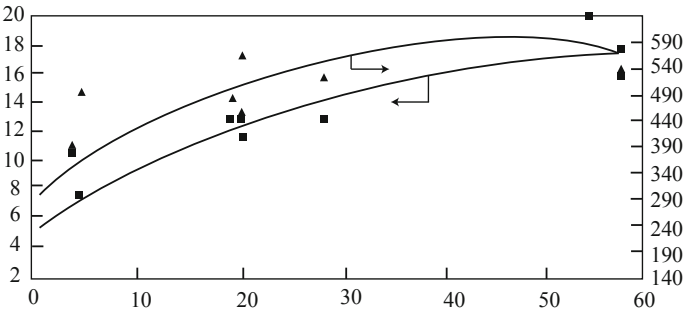


Fig. 2.14 Dependence of swelling index and water absorption index of Enslin on effective viscosity according to [33]. The abscissa axis is the effective viscosity, mPa s; ordinate axis (left) —swelling index, ml/g; Y-axis (right)—Enslin index, %

Table 2.5 Strength and plasticity (impact strength) of raw pellets obtained with bentonites of various qualities

No.	Bentonite (country of origin, field)	Bentonite properties		Quality of raw pellets	
		Swelling index (ml/g)	Effective viscosity (mPa s)	strength (kg/pellet)	Number of drops
1	Greece	17.5	50.0	1.41	9.5
2	Greece	12.4	11.2	0.68	6.3
3	Bulgaria	16.0	52.0	1.42	10.8
4	Bulgaria	13.0	22.0	1.40	8.0
5	Ukraine (Cherkassy)	11.0	19.0	1.27	8.5
6	Ukraine (Cherkassy)	1.5	0.5	1.00	4.6
7	Azerbaijan (Dash-Salakhly)	11.0	28.0	0.75	6.5
8	Azerbaijan (Dash-Salakhly)	12.5	15.3	0.85	4.9
9	India	16.5	69.0	1.19	11.8
10	India	5.25	9.5	1.13	7.3

(the number of drops from a height of 0.4 m before failure) was studied in [30] and presented in Table 2.5 and Fig. 2.15.

As follows from the data of Table 2.5 and Fig. 2.15a, b, reliable correlation dependence of the strength of raw pellets and their plasticity on the swelling index is not detected. On the contrary, the strength and plasticity of raw pellets unambiguously depend on the effective viscosity index (the spread of experimental data indicates the influence of other properties of bentonites and the actual granule on the strength of raw pellets).

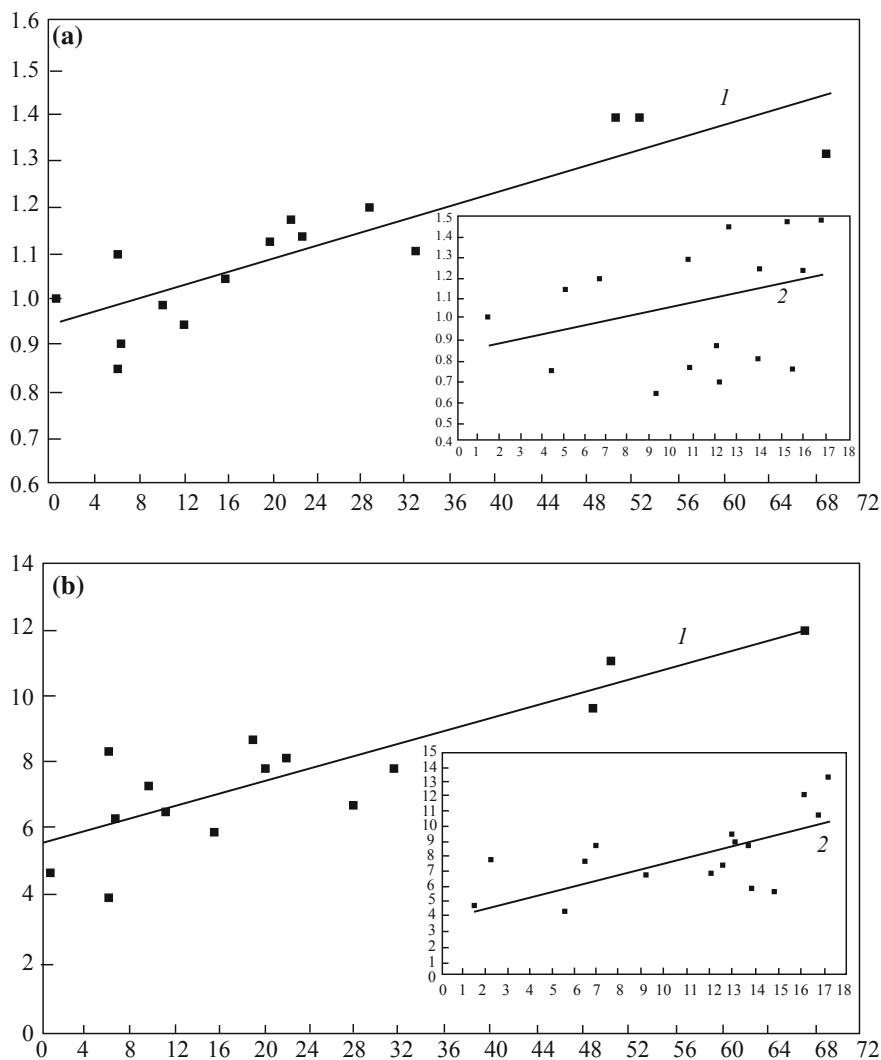


Fig. 2.15 Dependence of strength (a) and plasticity (impact strength) (b) of raw pellets on effective viscosity (1) and bentonites index swelling (2) [30]. (iron ore material—magnetite concentrate of Lebedinsky GOK). Y-axis “a”—strength of raw pellets, kg/pellet, abscissa axis “a” for (1)—effective viscosity, mPa s; abscissa axis “a” for (2)—a swelling index, ml/g; the y-axis “b” is the plasticity of raw pellets (number of drops, times); abscissa “b” for (1)—effective viscosity, mPa s; abscissa “b” for (2)—swelling index, ml/g

Organic binder

The use of bentonite as a binder with all the advantages has a set of disadvantages, which include dilution of pellets, high cost and scarcity of a quality binder, high costs for its transportation, substantial energy costs for preparing bentonite to the technological process.

As an alternative to bentonite, an organic binder based on polyacrylamide (of Floroform type) was investigated in [36–38], which is a loose white powder with a moisture content of 3–5% and a bulk density of 0.85 t/m^3 with a fraction content of 0.212 mm 99.8%.

Due to the significantly lower consumption of organic binder compared with bentonite, its uniform distribution in the charge is ensured when a pore solution is formed and takes a certain amount of time (Fig. 2.16 shows a change in the viscosity of suspensions of polyacrylamide binder and alkaline bentonite). The increase in viscosity over time is caused by swelling, gradual “unfolding” of a polymer molecule, and the formation of the colloidal structure of the binder solution. An increase in the concentration of polyacrylamide in the solution from 0.2 to 3% results in a sixfold increase in viscosity (from 9.2 to 57 mPa s) and a duration until complete dissolution from 7 to 17 min.

Due to the fact that polyacrylamide is a surfactant, it has a positive effect on wettability: The simplest experience of spreading a drop of a solution on the surface (plate) of natural magnetite is illustrated (Table 2.6).

In dispersed media in the production of pellets, nucleus, which is centers of pelletizing, is the fluctuation volumes of high moisture. The stability of nucleus during pelletization of concentrates with an organic binder is achieved due to the spatial coagulation structure formed by the distribution of chains of polymer molecules in the bulk of the material. The process of formation of nucleus in the case of the use of bentonite or organic binder can be represented as follows (Fig. 2.17). At the initial moment of time (Fig. 2.17a, b), there are free charge volumes containing ore particles and binder particles. With the passage of time required for mixing and pelletizing, the binder interacts with the charge moisture with simultaneous swelling of bentonite (Fig. 2.17I, 1a) and the formation of an organic binder solution (Fig. 2.17II, b). At the same time, the distribution of bentonite in the charge is ensured by its substantial volume concentration,¹⁰ and the organic binder—by the formation of a highly mobile solution, which has a high wetting ability with respect to the surface of the ore particles. The formation of contacts between the binder and the ore particles, as well as the consolidation of the structure, is caused by the swelling capacity of bentonite (Fig. 2.17III, a) and the appearance of a colloidal structure during the unwinding of the polyacrylamide molecule (Fig. 2.17III, b).

¹⁰Bulk weight of iron ore concentrate with a moisture content of $\sim 10\%$ is 2.97 t/m^3 , and then, the volume of 1 ton of concentrate is 0.34 m^3 . The volume concentration of bentonite in the charge (at a flow rate of 4 kg, bulk density $\sim 0.98 \text{ t/m}^3$, swelling capacity 20.0) can be calculated as $(4 \times 10^{-3} \cdot 20.0) / (0.98 \cdot 0.34) \cdot 100\% = 24\%$.

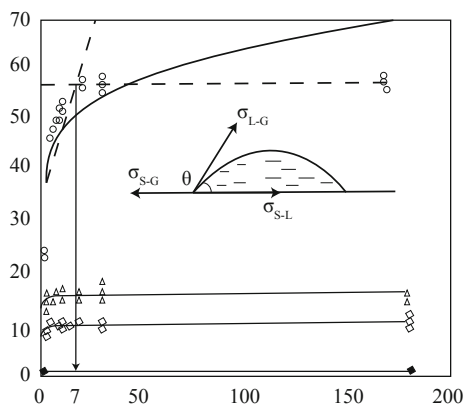


Fig. 2.16 Change in viscosity of binder suspensions. 1—water; 2—0.2% solution of polyacrylamide; 3—1% polyacrylamide solution; 4—alkaline bentonite solution; 5—3% polyacrylamide solution. The abscissa axis—time, min; ordinate axis—viscosity, mPa s

Table 2.6 Characteristics of the wetting ability of binder solutions

No.	Type of solution	Binder consumption (kg/t concentrate)	Wettability ^a	
			Drop area (mm ²)	Measurement error (mm ²)
1	Distilled water	—	38.47	±0.92
2	Bentonite suspension	4.0	35.19	±1.78
3	0.2% polyacrylamide solution	0.2	43.04	±2.64
4	1.0% polyacrylamide solution	1.0	63.85	±4.72
5	3% polyacrylamide solution	3.0	38.73 ^b	±3.68

^aDrop volume in all cases 0.3 ml

^bDue to the counteraction of viscous forces with an increase in the concentration of the polymer solution above 1%, the wettability (the drop area or the length of the water cuff) does not change

The formation of such a structure is indirectly confirmed by data on the viscosity of polyacrylamide solutions (Fig. 2.16) and on the strength of the pellets after drying, provided by the frame structure and point contacts of ore particles with polyacrylamide molecules (Fig. 2.18b).

The compressive strength of raw pellets with an organic binder does not differ from the compressive strength of pellets with bentonite (1.1–1.2 kg/pellet), and for an organic binder, it weakly depends on its consumption in charge (up to 0.3 kg/t of concentrate). The difference in the strengthening mechanism of pellets with bentonite and organic binder (in the first case, strengthening is provided by the formation of long mechanical contacts with a high bulk concentration of the binder; in the second, the frame molecular structure and its point contacts with ore particles)

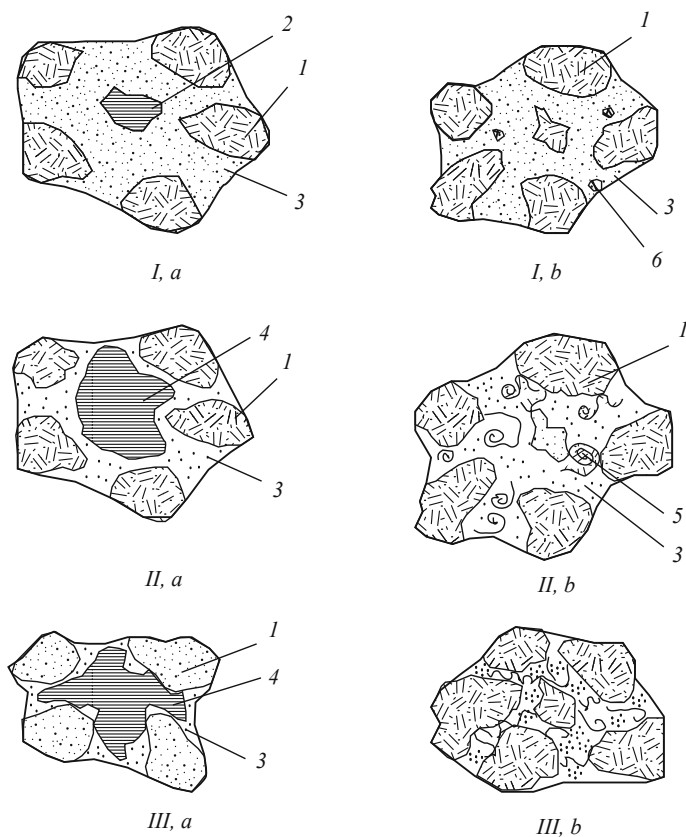


Fig. 2.17 Formation of a coagulation structure using an organic binder. I is the state of the volume of the charge of free moistening; II—state of the charge volume at the initial moment of pelletizing; III—the state of the volume of the charge (granules) after pelletizing. **a** Binding bentonite; **b** organic binder; 1—particles of iron ore concentrate; 2—particle of initial bentonite; 3—moisture charge; 4—particle of swollen bentonite; 5—particles of dissolved polyacrylamide; 6—particles of the original (dry) polyacrylamide

on the value of the strength of the pellets after drying: pellets with an organic binder during drying are practically not strengthened.

The strength of raw pellets for impact (or plasticity) increases with an increase in binder consumption: An increase in bentonite consumption to 4 kg/t concentrate gives an increase in impact strength from 2.3 to 2.5 times, and an organic binder consumption up to 0.2 kg/t of concentrate shows an increase in up to 2.7 times (Fig. 2.18a, b).

Improving the wetting conditions when using an organic binder compared to bentonite leads to a more uniform distribution of the binder in the mixture and is accompanied by the formation of a more uniform particle size distribution (Fig. 2.18c).

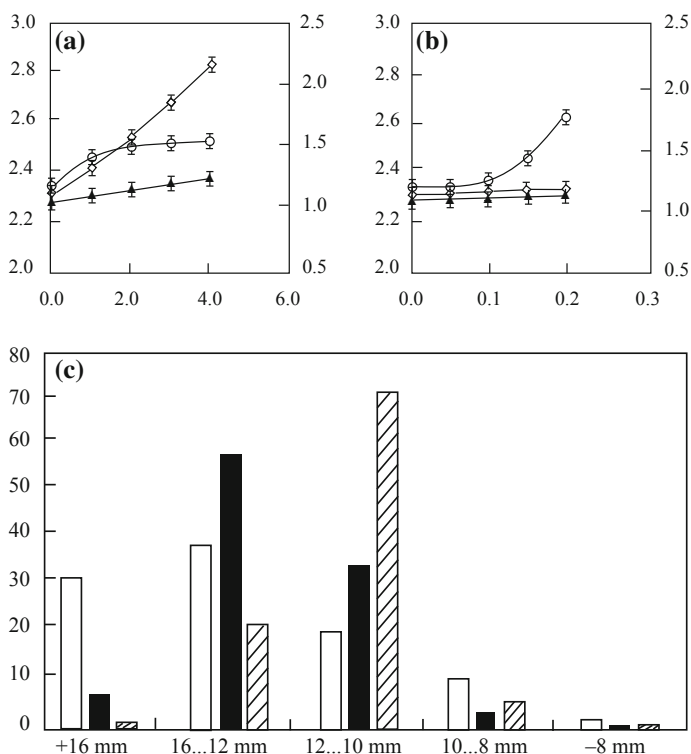


Fig. 2.18 Strength of the pellets obtained with an organic binder. **a** is the strength of pellets with bentonite; **b** strength of pellets with polyacrylamide; **c** granulometric composition of pellets; iron ore material—concentrate Lebedinsky GOK. The abscissa axis “*a*” is the consumption of bentonite, kg/t of pellet; abscissa axis “*b*”—organic binder consumption, kg/t of pellet; abscissa axis “*c*”—size of pellet fractions, mm. Y-axis “*a, b*” (left)—plasticity of pellets (number of drops, times); ordinate axis “*a, b*” (right)—the strength of raw pellets in compression, kg/t pellet; y-axis “*c*”—the output of the corresponding fraction, %: light column—without a binder, dark column—bentonite, hatching column—organic binder

The use of an organic binder determines the structure of the pellet after drying—increased porosity (e.g., pellet produced from iron ore concentrate without additives has a porosity of $\sim 25\%$, with bentonite $\sim 33\%$, with an organic binder $\sim 38\%$).

Production of pellets with an organic binder guarantees significant technical and economic advantages:

- reduction of transportation costs (due to significantly lower consumption in charge) and the consumption of fuel or electricity;
- saving of natural gas and electricity due to the exclusion of the preparation operation (drying) of bentonite to the process;

- an increase in the iron content in the pellets (compared with bentonite), which leads to a decrease in the formation of blast furnace slag and a decrease in coke consumption;
- reduction in fuel consumption due to a decrease in coke shipment volumes.

Bento-polymer binder

The goal of developing a complex bento-polymer binder is to obtain a tool that allows controlling the strength of raw, dried, and calcined pellets on the basis of controlling the rheological properties of the binder.

Bento-polymer compositions with different types of polymers were studied in [33] (Table 2.7).

Let us consider the role of the polymer in the formation of the mechanism of interaction of the bento-polymer composition with iron ore material. The presence of an ionized polymer changes the surface charge of the ore particles. Thus, hydrophilic (negatively charged) terminations of polymer aggregates in suspension with bentonite orient themselves toward the ore surface, imitating the appearance of a positive charge on it (Fig. 2.19). Obviously, the energy of the interfacial interaction of the ore surfaces and the suspension increases by the energy of the electrostatic field:

$$w_a = w_a^0 + \sigma^2 / (8 \cdot \epsilon_0 \cdot \epsilon), \quad (2.3.10)$$

where

w_a —work of adhesion of a suspension of bento-polymeric binder;

σ is the surface charge density, depending on the concentration of the polymer;

ϵ_0 is the electric constant;

ϵ is the dielectric constant of the suspension.

Approximate estimates of the second term in relation (2.3.10) show that its value is 20–50% of the value of the adhesion work of the bentonite suspension w_a^0 .

The study of the effect of bento-polymer compositions (the content of polymers in the binder varied from 0 to 10%, and the consumption of the binder in the mixture for the production of pellets from 0.25 to 0.6%) on the properties of the

Table 2.7 Effective viscosity of bento-polymer compositions, mPa s

Type of polymer	Dosage in composition (%)				
	0	0.5	1.0	1.5	2.0
PB-1 ^a	30	32	36	36	38
PB-2 ^a	30	33	35	39	42
PB-3 ^a	30	32	39	38	40
PB-X ^a	30	35	42	46	48
Floroform	30	35	39	39	44
Peridur	30	32	38	38	40

^aManufacturer-SPC “Bentonite,” Russia

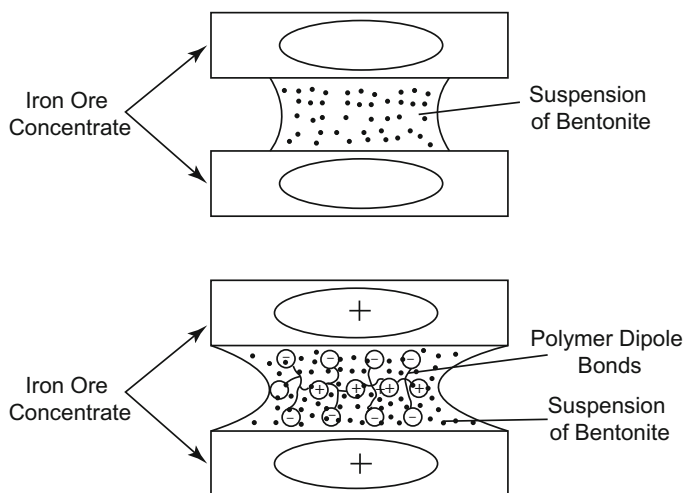


Fig. 2.19 Diagram of the interaction of the polymer in the composition of the bento-polymer composition with iron ore material [33]

pellets was performed on an iron ore concentrate from Mikhailovsky GOK (Russia). The base of the composition was Khakass bentonite.

With an unambiguously positive effect of an increase in the content of bentonite in the mixture on the strength of raw pellets, an increase in the number of polymers introduced into the composition has an ambiguous effect on the physical properties of the pellets: 0.4% increases from $4.75\times$ to $6.75\times$, while the crush strength drops from 1.7 to 1.2 kg/pellet.

It was shown that the polymer of grade PB-3 has optimal properties and its optimum content in the bento-polymer composition lies in the range of 2.0–3.2% with a total content of bento-polymer additive in 0.25–0.4%.

2.4 Cold-Bonded Pellet Production

2.4.1 General Information About Cold Agglomeration

The first experiments on cold agglomeration of ores belong to the end of the nineteenth century: ore briquettes were strengthened at ordinary temperature using 3.5–6% Portland cement as a binder [39].

Work on obtaining iron ore pellets with Portland cement as a binder began relatively recently. Since 1970, an industrial factory with a design capacity of 1.6 million tons of pellets per year has been operated in Sweden by the Grangcold method. The technology of cold agglomeration is quite widespread for the recycling of metallurgical production wastes: In 1978, a plant for pelletizing the blast furnace

dust with a capacity of 550 thousand tons of pellets per year was commissioned in Nagoya (Japan); since 1979, a plant with a capacity of 120 thousand tons of steel-making dust pellets per year has been operating at a plant in Oita (Japan) [40].

At present, there are at least 20 large industrial factories and cold agglomeration plants with a total capacity of about 4 million tons of pellets and briquettes per year.

The principal feature of the cold agglomeration methods is the use of binders, usually of cement type.

Binding agents are compositions based on heterogeneous disperse systems of the solid–liquid type, the components of which enter into physical and chemical interaction with each other, forming a plastic, easily workable mass that turns into a strong stone-like body under certain conditions [41].

The most common in unburned agglomeration received the binders with hydraulic curing.

Cold agglomeration is characterized by a variety of methods used. The classification of binders and cold agglomeration methods is presented in Fig. 2.20.

The interaction of binding compositions such as S–S is the main densification mechanism when briquetting plastic powder bodies (hot briquetting or briquetting with clay binders). The resulting briquettes are marketable products and are sent to the consumer (including the metallurgical processing).

Various methods of carbonization are based on the use of binder's compositions such as SG. The formation of stone-like body occurs as a result of the interaction of the binder (usually lime) with carbon dioxide (flue gases) at a partial pressure less or more than atmospheric, at normal and elevated temperatures, with and without the use of catalysts. The product is shipped to the consumer.

Cold agglomeration methods based on the use of S–L binding compositions include various types of heat treatment: drying (at normal temperatures and with heating), strengthening in a humid environment (at normal temperatures and heat and moisture treatment at atmospheric and elevated pressures), and combined methods (accelerated strengthening).

The most developed mechanisms for the strengthening of such binders as Portland cement (Portland cement with additives, slag Portland cement and magnesia, alumina Portland cement) and lime.

2.4.2 Strengthening Mechanism of Portland Cement Binders

The strengthening of Portland cement¹¹ is a consequence of the physicochemical processes occurring in the substance–water system, whose components can be described by the content of CaO, SiO₂, Al₂O₃, Fe₂O₃, CaSO₄, H₂O, etc.

¹¹Portland cement is a product of fine grinding of clinker obtained by sintering the raw materials of a certain composition, with a wide range of properties depending on the chemical composition

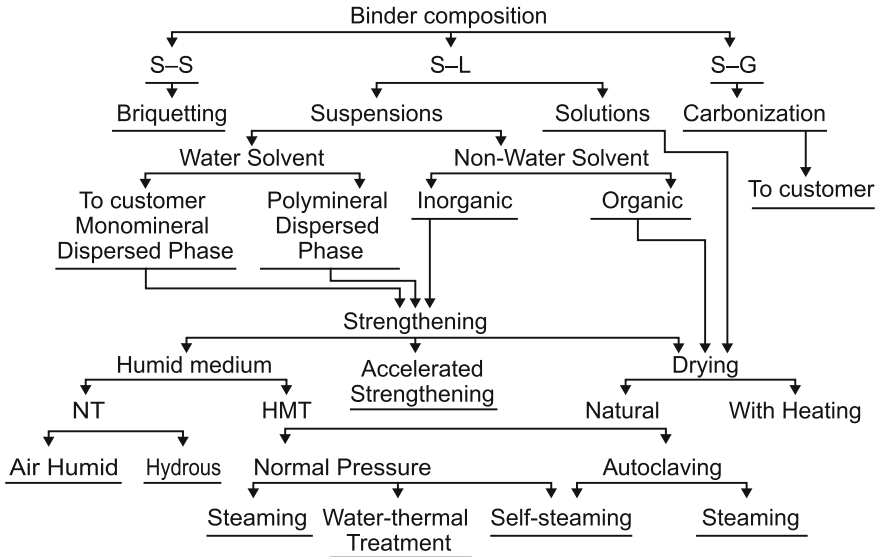


Fig. 2.20 Classification of binders and cold agglomeration methods [47] (SS—solid–solid; SL—solid–liquid; SG—solid–gas; NT—normal temperatures; HMT—heat and moisture treatment)

The chemical transformations that occur with the mineral components of Portland cement when mixed with water can be described by a combination of reactions (2.4.1)–(2.4.3) [42]:



The process of hydration of tricalcium aluminate is carried out by the reaction:



Hydration of calcium aluminoferrites is reduced to hydrolysis with the formation of calcium hydroferrite and tricalcium aluminate:



Under favorable conditions, more complete hydrolysis of calcium aluminoferrites takes place with the formation of calcium and iron hydroxides.

(64–67% CaO; 21–25% SiO₂; 4–8% Al₂O₃; 2–4% Fe₂O₃; 0.5–0.6% MgO; 0.5–1.0% Na₂O + K₂O) [43] with typical mineral composition (C=CaO; S=SiO₂; A=Al₂O₃; F=Fe₂O₃; H=H₂O): 42–60% alite (C₃S), 15–35% belite (C₂S), tricalcium aluminate 5–14% (C₃A), calcium aluminoferrites changing composition from C₈A₃F to C₄AF (10–16%).

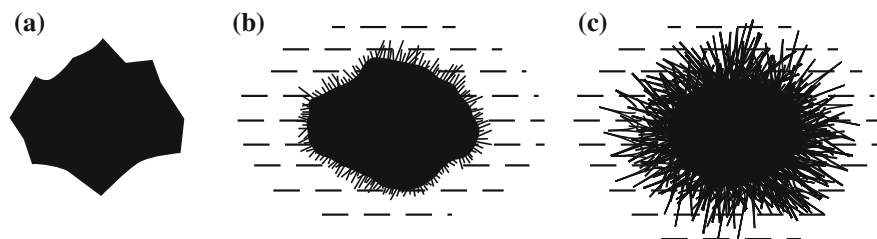
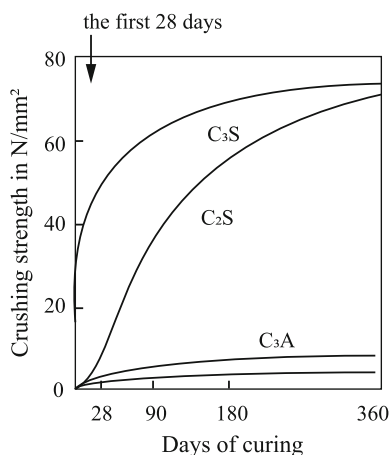


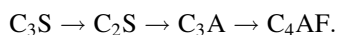
Fig. 2.21 Scheme of growth of new phases when the Portland cement is mixed with water [42] (a—cement particle before mixing with water; b—cement particle after mixing with water (initial stage); c—cement particle after the completion of the hydration reaction)

Fig. 2.22 Change in strength with the destruction of the components of Portland cement at exposure of up to 360 days [42]



The scheme of growth of new phase C_3S_2H when the Portland cement is mixed with water is shown in Fig. 2.21.

The strength of the destruction of samples of individual components of Portland cement in the process of aging is illustrated in Fig. 2.22, from which it follows that the binding properties of the components of Portland cement decrease in sequence:



2.4.3 Cold Strengthening Under Normal Conditions

Strengthening in an air-humid environment at ordinary temperatures in the technology of binders is called normal strengthening. In the methods of normal strengthening, hydraulic bonding of Portland cement type (Portland cement with

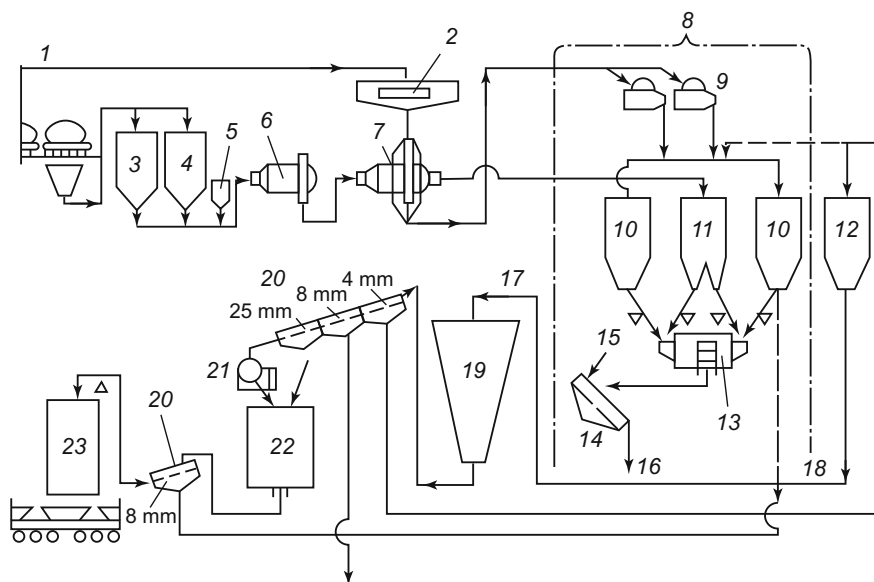


Fig. 2.23 Technological scheme of the production of pellets by the method of Grangcold [44] (1—pipeline supply of concentrate from the processing plant; 2—thickener; 3—clinker; 4—slag; 5—additives; 6—rod mill; 7—ball mill; 8—lines for obtaining pellets; 9—filter; 10—concentrate hopper; 11—cement hopper; 12—underlying material with a particle size of 4 mm; 13—rod mill-mixer; 14—dish granulator; 15—water; 16—raw pellets; 17—raw pellets + bedding concentrate; 18—bedding concentrate; 19—bunker for strengthening; 20—crash; 21—crusher; 22—the second bunker for strengthening; 23—bunker for loading pellets into railway wagons)

additives, slag Portland cement and magnesia, alumina Portland cement) is most common.

The Grangcold method works using slag or Portland cement [44].

The technological scheme of the production of cold-bonded pellets according to the Grangcold method is presented in Fig. 2.23.

The binder, containing about 50% of cement clinker and 50% of granulated blast furnace slag and special additives, is crushed first in a rod mill and then in a two-chamber ball mill with pebble load. Iron ore concentrate pulp with 40% of the solid is fed first into the thickener, from which it is fed with a 75% solid into a ball mill. Filter cake, containing 8–9% moisture, enters the concentrate bunker.

Mixing the concentrate and the binder before pelletizing is carried out in a rod mill-mixer with two-sided loading and central unloading. To obtain uniformly sized raw pellets with proper strength, 8–9% of water is fed into a pan granulator with a diameter of 6 m. Raw pellets arrive at the conveyor, where they preliminarily load concentrate from a separate bunker. Then, the raw pellets are poured with concentrate (the operation prevents the pellets from sticking together when kept in the bunker at the first stage of strengthening). A mixture consisting of 2/3 of the pellets and 1/3 of the concentrate enters the bunker (60 m high), where the pellets pass

through the first strengthening stage. After 30–40 h of movement through the bunker, the pellets arrive at the conveyor at the screen to separate the concentrate and fines less than 4 mm (sent to the bunker to pour the raw pellets); destroyed pellets fraction 4–8 mm (used as raw material in agglomeration); pellets with a particle size of more than 25 mm (are fed for crushing and then returned to the mixture).

Pellets with a size of 8–25 mm are sent to the second bunker, where, when stored for 5 days, they acquire up to 70–80% of final strength. Next, the pellets are delivered to the open warehouse for final strengthening within 2–3 weeks.

Grangcold cold-bonded pellets have strength after drying of 200 kg/pellet (for a particle size of 15 mm), a tumble test—92% (yield of +6.3 mm class), moisture content of 6.5%, Fe content of 59.7%, with basicity about one.

2.4.4 Cold Agglomeration at Moderate Temperatures

Cold agglomeration of iron ore materials at moderate temperatures is carried out with lime or lime with additives as binder combined with autoclaving (i.e., processing at temperatures of 100–400 °C and pressure of 10–15 atm).

An example of such a technology is the cold bond process (Sweden), which is patented in a number of countries [45].

A schematic diagram of the cold bond (COBO) process for iron ore materials is presented in Fig. 2.24.

Raw pellets are obtained on a disk granulator from a mixture pre-homogenized in a rod mill. As a rule, the mixture consists of 2/3 of the coarse grinding concentrate (–0.250 to 0.400 mm) and 1/3 of the finely dispersed concentrate (–0.005 to 0.008 mm) and a binder, which can be used up to 10% of slaked lime or quicklime, up to 10% cement, calcined dolomite or 2–20% finely ground steel-making slag. Raw pellets, if necessary, are dried with hot air, loaded into

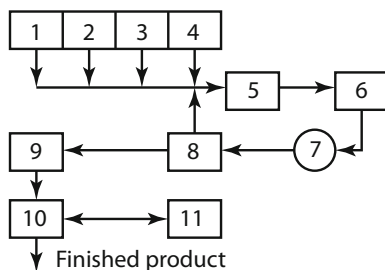


Fig. 2.24 Technological flow diagrams of the cold bond process [45] (1—bin of iron-containing material with a particle size of at least 80% of the class—0.250 mm; 2—bunker of iron-containing material with a particle size of 80% of the class—0.050 mm; 3—binder bin with a particle size of 80% class—0.025 mm; 4—bunker of additives of 80% class size—0.005 mm; 5—rod mill; 6—scales; 7—roll mixer; 8—disk pelletizer; 9—roll screen; 10—dryer; 11—trolley; 12—discontinuous autoclave)

cylindrical trolleys and, after some exposure, are fed to an autoclave, which is kept at a temperature of 160–230 °C for 6–24 h.

The finished pellets with a diameter of 12 mm, containing 7–10% of the binder, have a compressive strength of 100–200 kg/pellet.

The strength of cold-bonded pellets can be enhanced by the addition of highly dispersed silica: pellets from 90% concentrate and 10% slaked lime had strength of 103 kg/pellet; the introduction of 3% of powdered silica into the charge increased the compressive strength of the pellets to 183 kg/pellet.

Hydroxides or alkali metal carbonates (0.25–1.0%) can be used as additives to lime (University of Michigan method [46]).

2.4.5 Cold Agglomeration with Accelerated Strengthening

Cold agglomeration methods (Sects. 2.4.3 and 2.4.4) have some drawbacks:

- strengthening at normal temperatures requires special measures to prevent the pellets from sticking together;
- the strength of the pellets with cold strengthening is completed in 3–4 weeks;
- autoclave method refers to the technology of periodic action.

The technology of cold agglomeration for metallurgical processing, devoid of marked deficiencies, must meet the following conditions: Strengthening should be carried out at normal pressure and duration characteristic of autoclave processes. The accelerated strengthening method satisfies these conditions [47].

A schematic diagram of the accelerated strengthening method is shown in Fig. 2.25.

The dosed ore part and the mineral binder (hydration-strengthening binders¹²) enter the mechanical activation (preliminary selective activation of the mineral binder is possible).

The main stage of accelerated strengthening is heat–moisture treatment, carried out at 70–100 °C and ~100% relative humidity.

There are several types of heat and humidity treatment:

- water heat;
- steaming (water vapor is used as a coolant at a pressure of 1 atm); with this method of processing, one–two-week strength of normal strengthening pellets is achieved in 2–8 h);
- self-steaming (in this case, heating is carried out from an independent source (radiation, electric current, etc.), and the humidity of the environment is created due to evaporation of moisture from the pellets).

¹²Portland cement, lime, slag cements, and a number of special binders are suitable as binders for accelerated curing.

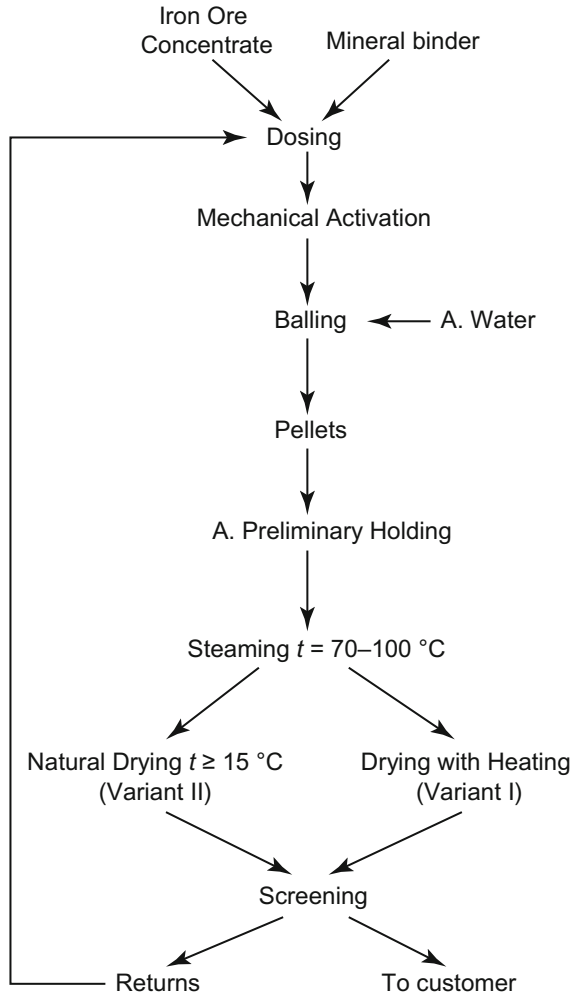


Fig. 2.25 Schematic diagram of the accelerated strengthening method (position A is an option; the rest are mandatory stages) [40]

The preferred technology in the method of accelerated strengthening is steaming.

Raw pellets can enter the steaming chamber immediately or after preliminary exposure, the duration of which depends on the type of cement used and the mineralogical composition of the ore part.

The strength of the pellets when steaming after a certain time reaches constant values, which indicates the completion of the process of hydration strengthening. However, it is possible to further increase the strength of the pellets by drying them (Fig. 2.25) by removing zeolite moisture from the crystalline hydrates formed and accelerating crystallization processes with the formation of additional fusion

contacts. For iron ore pellets, the strength gain of steamed pellets after drying reaches 40–100%.

2.4.6 Advantages of Cold Agglomeration Method

Cold agglomeration methods have undoubted advantages. One of the significant advantages of these methods is a relatively lower capital costs: According to estimates [40], the cost of building a pellet factory is 1/3 of the cost of building a factory of the same capacity for the production of burned pellets.

The production of cold-bonded pellets is characterized by lower energy consumption.

Comparison of energy costs for the agglomeration of roasting–magnetic enrichment of the Lisakovsky GOK (Kazakhstan) by sintering method, pellet production using the method of high-temperature roasting and cold agglomeration, carried out by the method of calculating technological fuel numbers¹³ (TFN) showed that TFN production of cold-bonded pellets was 65 kg of conventional fuel per ton of pellets, while as TFN by the production of roasted pellets is 114.2 of conventional fuel per ton of pellets, i.e., 1.7 times higher (and with sintering TFN is 2.4 times higher than for cold agglomeration).

One of the most important advantages of cold agglomeration methods are environmental indicators of technology. In the absence of high-temperature treatment in the production of cold-bonded pellets, compared with roasting methods, emissions of carbon oxides, nitrogen, sulfur compounds, and volatile organic compounds, including polyaromatic compounds such as dioxins and furans, are not formed.

2.5 Strengthening Pellets with Thermal Methods

In the world practice of pellet production, three methods of strengthening are mainly used:

- high-temperature roasting in special devices;
- autoclaving (heat treatment at low temperatures);
- cold agglomeration method using clinker or cement (see Sect. 2.4).

The greatest commercial distribution was received by the roasting method of strengthening pellets, which produce more than 95% of the total.

The pellets are fired in various units:

- on conveyor roasting machines (about 65%);

¹³Technological fuel numbers (TFNs) determine the energy costs (consumption of electrical energy, fuel, heat, energy resources (air, oxygen, water, steam, process gases, etc.)) along the technological chain of production of specific products (through energy costs) [48].

- in units “grid-kiln-cooler” ($\sim 30\%$);
- in shaft furnaces $\sim 5\%$.

In Russia, all six pelletizing factories are equipped with conveyor roasting machines of various sizes and capacities (see Sect. 2.7).

Heat treatment of pellets on a conveyor machine includes four sequential stages (Fig. 2.26), covering the processes of heat mass transfer: drying of fresh pellets coming from the pelletizing section of the charge; heating the pellets to the temperature of the burning zone or close to it; pellet roasting as the main technological operation, providing strengthening of the pellets; cooling the product to a temperature of safe transportation.

The length (area) of each technological zone as a fraction of the area of the conveying roasting machine in the general case can be characterized by the following relations: the drying zone by blowing and sucking the coolant 20–25%; heating zone up to 10%; roasting zone 25–30%; cooling zone 30–35%.

Each technological zone, with which the characteristic temperature level corresponds, can be brought in accord with a certain type of physicochemical transformations, although in fact physicochemical processes over zones may overlap. The conjugacy of physicochemical processes of different nature allows characterizing the heat treatment of pellets as a very complex object not only for physical and mathematical modeling, but also for control.

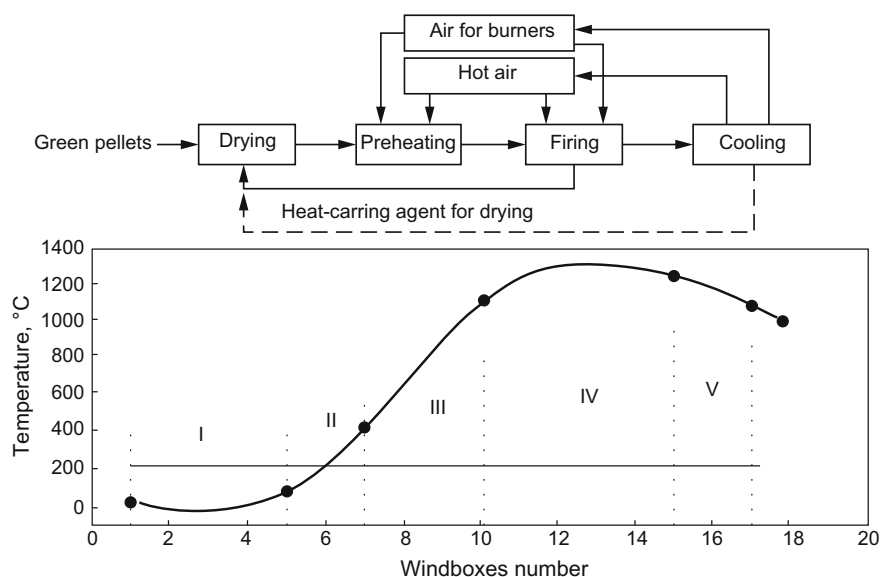
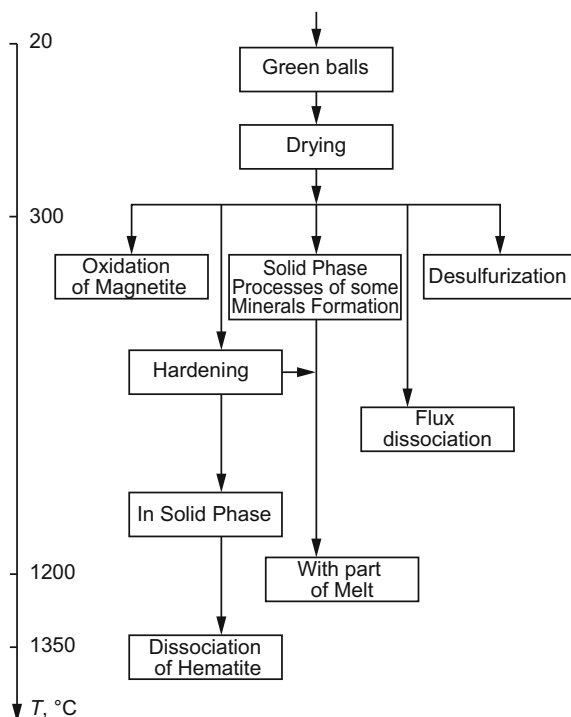


Fig. 2.26 Scheme of the roasting conveyor machine for the production of pellets and temperature distribution in the zones of the unit

Fig. 2.27 General schemes of mass transfer processes during heat treatment of pellets



2.5.1 Phenomenology of Mass Transfer Processes During Heat Treatment of Pellets

The general scheme of mass transfer processes during the heat treatment of pellets can be characterized by Fig. 2.27.

Mass transfer during pellet drying

Drying the pellets is the process of heat transfer of the wet pellet with the heat transfer gas, accompanied by the mass transfer of moisture inside the pellet and the removal of moisture from the pellet into the gas phase. This process takes place due to the difference in pressure of water vapor at the surface of the pellet and in the coolant flow, as well as the temperature difference at the surface and inside the material.

The general relations known for capillary-porous bodies can be applied to the description of the drying process of the pellet [49–51].

The model of heat and mass transfer during drying is described by a set of equations:

- heating the raw pellet from the initial temperature to the temperature of evaporation of moisture (2.5.1);

- changes in the moisture content of the pellet (2.5.2);
- heating of the pellet due to the mechanism of thermal conductivity (2.5.3).

Due to the low thermal conductivity of the pellet, we assume that the evaporation front is localized on its surface, and the evaporation rate is determined by the amount of heat supplied.

$$C \cdot \rho \cdot V \cdot dt/d\tau = \alpha \cdot F \cdot (T - t) \quad (2.5.1)$$

$$\rho \cdot V \cdot q \cdot db/d\tau = F \cdot [\alpha \cdot (T - t) - \lambda \cdot \partial t / \partial r] \quad (2.5.2)$$

$$\partial^2 t / \partial r^2 + 2/r \cdot (\partial t / \partial r) = (\partial t / \partial \tau) \cdot 1/a \quad (2.5.3)$$

Equation (2.5.3) is valid under the following boundary conditions:

$$t = t_o \text{ at } \tau = 0; \partial t / \partial r = 0 \text{ at } r = 0; \lambda \cdot \partial t / \partial r = \alpha \cdot F \cdot (T - t) - q(\tau) \text{ at } r = R, \quad (2.5.4)$$

where

C, λ, a —heat capacity, thermal conductivity, thermal diffusivity of the pellet;

ρ, V, F, R —density, volume, surface, initial pellet radius;

r —current pellet radius;

t_o, t, T —the initial, current temperature of the pellet; heat carrier gas temperature;

τ —time;

b_o, b —initial, current moisture content of the pellet;

$q(\tau) = f(b)$ —the amount of heat spent on the evaporation of moisture from the surface of the pellet.

The solution of the system of Eqs. (2.5.1–2.5.4) allows obtaining the distribution of temperature and moisture content over the section of the pellet; however, it can only be realized by numerical methods.

Neglecting the contribution of thermal conductivity to the heat balance during drying, we transform Eq. (2.5.2) to the form:

$$db/d\tau = (\alpha \cdot F / V \cdot \rho \cdot q) \cdot (T - t) \quad (2.5.5)$$

From 2.5.5, we obtain for the moisture content of the pellet:

$$b = b_o - (\alpha \cdot F / V \cdot \rho) \cdot \int (T - t) \cdot q(\tau) \cdot d\tau \quad (2.5.6)$$

Equation (2.5.6) is a rough approximation describing the process of drying the pellet, but the linear nature of the dependence of the moisture content of the pellet on the drying time is confirmed experimentally [52].

Mass transfer processes in the heating zone

The main mass transfer process in the heating zone is the oxidation of magnetite. According to the general opinion [2, 49, 50, 53], oxidation during the firing of pellets from magnetite concentrates is an important part of the technological process, providing up to 20% of the thermal balance to the input part and having a decisive influence on the strength of the pellet.

Depending on the nature (type) of iron ore concentrate, the oxidation process begins in the temperature range 200–500 °C [54, 55].

Kinetic studies of magnetite oxidation under isothermal conditions show that the reaction rate and the amount of hematite formed depend on temperature, duration of treatment, and the oxidation potential of the gas phase.

The duration of the complete oxidation of magnetite at 1000 °C for different types of magnetite ranges from 8 to 20 min.

In the preheating zone, solid-phase interactions of the components of the gangue without and with the participation of iron oxides, as well as the processes of dissociation of binding and fluxing (in the production of fluxed raw material) components, take place. The degree of development of these interactions is determined by the type of concentrate (nature and chemical composition of the waste rock), the temperature level and duration of treatment, the composition of the pellet charge [2, 53]. Qualitatively, the nature of these mass transfer processes is similar to those described in Chap. 1.

Mass transfer in the roasting zone

In the roasting zone (idealized scheme of heat treatment of pellets), mass transfer is caused only by mass transfer in the sintering process, which is responsible for the formation of the final strength of the pellet (although under certain conditions dissociation of the formed hematite is also possible).

Mass transfer in the cooling zone

There are no mass transfer processes in the cooling zone, although the process of secondary oxidation of magnetite formed during the dissociation of hematite in the burning zone is not excluded [55].

2.5.2 Simulation of Mass Transfer Processes During Heat Treatment of Pellets

The mathematical model of heat treatment of pellets is represented by a system of equations reflecting the essence of the occurring phenomena (Sect. 2.5.1).

On a temporal and spatial basis, the process of pellet roasting should be considered in models with distributed parameters, for which the description of partial differential equations is used.

A general approach to solving heat and mass transfer problems in a layer of granular materials has been developed quite fully [49, 55].

A wide range of phenomena accompanying the process of heat treatment of pellets can be characterized as gas–solid interaction in a heterogeneous system.

Analysis of mass transfer in such systems is the prerogative of kinetic approaches, based mainly on the method of kinetic equations [56].

A kinetic equation is any equation of the form:

$$\partial F / \partial \tau = f(F, \tau, x_1, \dots, x_n), \quad (2.5.7)$$

where

F —composition or quantity of a component, or property;

T —time;

x_i —reaction coordinate.

Due to the difficulties of analytically solving certain types of differential equations or their systems, when evaluating heterogeneous processes of especially topochemical nature, one of their kinetic postulates is used—the principle of the limiting stage. This will make it possible to reduce all the variety of systems with a rather complicated response mechanism to several types of dependencies, which reflect the kinetics of reaction in the system within the framework of additional restrictions.

The need for an in-depth study of the mechanism of the heterogeneous process led to the emergence of kinetic models, which include both kinetic and diffusion parameters and suggest the introduction of factors determining the reaction and transport properties of a solid reagent.

The main difficulty in this approach to mass transfer modeling, i.e., a phenomenon involving its own mass transfer (diffusion) and mass transfer (chemical reaction), consists of precisely in the selection (forecast) of the totality and sequence of stages that corresponds to the actual process.

Another difficulty is caused by the lack of experimental estimates of the structural parameters of a solid, their changes in the response process, as well as the effect on the magnitude of these parameters of temperature and the initial structure of a solid.

The kinetic model [56] corresponds to the real state of the reacting system according to the nature of the reaction surface localization: models with a geometrically uncertain reaction surface, models with a geometrically defined reaction surface (with one, two, three reaction surfaces), mixed models.

Mass transfer model in a single pellet

Structurally, in the kinetic aspect, the pellet is a polydisperse package with a particle size of $\sim 50 \mu\text{m}$ (for some enrichment schemes, $\sim 44 \mu\text{m}$) and a porosity of the order of 0.1–0.5.

By definition, a heterogeneous process is implemented at the interface. In the first approximation, the interface of the phase in the pellet can be estimated by its geometric surface. Due to the fact that the reaction is not localized on the surface of

the pellets, but develops deep into due to the transport of gas reagent throughout the pores, in the second approximation the surface of the reaction is the surface of macropores. As the reaction proceeds, the grains of solid reagent are involved in it, and the surface of the reaction in the next approximation is represented by the surface of micropores.

We characterize the mass transfer flows, which contribute to the overall reaction rate, for a particle where a process with a single reaction surface occurs (Fig. 2.28).

We describe in general terms the individual components of mass transfer in a heterogeneous process with a single reaction surface.

The molar flow of the gas component to the surface of a solid through the boundary layer of the N_β gas (external diffusion) is described by the convective mass transfer equation:

$$N_\beta = 4 \cdot \pi \cdot R^2 \cdot \beta \cdot (C_o - C), \quad (2.5.8)$$

where

β —mass transfer coefficient in gas film;

R —pellet radius;

C_o, C —the concentration of the gas component, respectively, in the stream and on the surface.

The flow of the reagent gas to the reaction surface N_d is carried out by diffusion through the pores of the reaction product:

$$N_D = -4 \cdot \pi \cdot R^2 \cdot D_e \cdot dC/dr, \quad (2.5.9)$$

where

D_e —effective diffusion coefficient of gas in the solid layer of the reaction product.

The rate of internal diffusion of the reagent gas in the pore volume of the solid reaction product is determined from the differential equation:

$$dC/d\tau = D_e \cdot (d^2C/dr^2 + 2/r \cdot (dC/dr)) \quad (2.5.10)$$

The gas consumption for the chemical conversion of N_c is estimated by the ratio 2.5.11:

$$N_c = 4 \cdot \pi \cdot r^2 \cdot L_o \cdot dr/d\tau, \quad (2.5.11)$$

where

L_o —stoichiometric coefficient.

The total flow will be determined through the total resistance of all links of interaction, by analogy with electrical circuits (Fig. 2.28b):

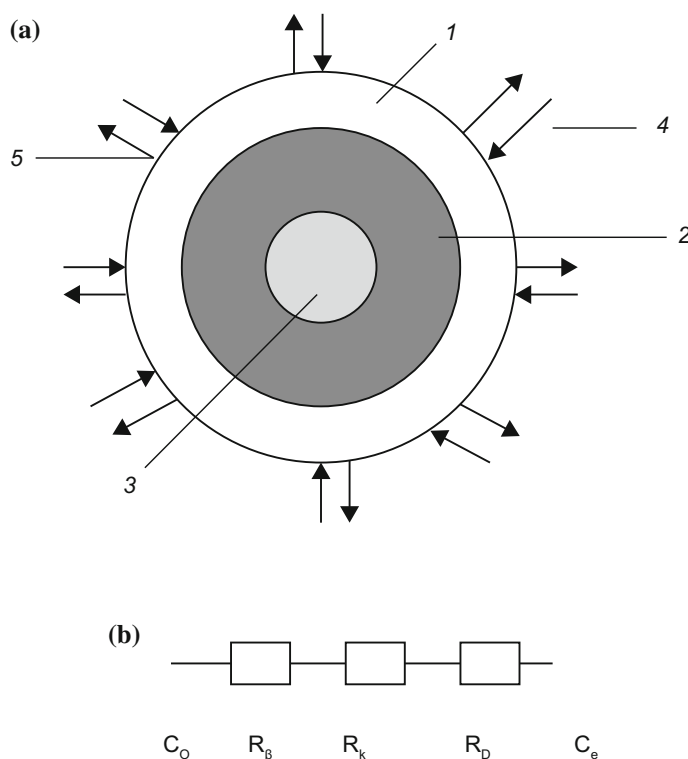


Fig. 2.28 Model of mass transfer in a heterogeneous gas–solid process. **a** is a heterogeneous model of reaction with one reaction surface: 1 is a boundary layer, 2 is a layer of a reaction product, 3 is unreacted solid, 4 is a gas reactant, 5 is a reaction product (gas phase); **b** reaction resistance diagram

$$R_\Sigma = R_\beta + R_d + R_c, \quad (2.5.12)$$

where

R_β , R_d , R_c —resistance to external mass transfer, diffusion of the gas component in the reaction product, resistance, respectively.

The model of mass transfer with three successive resistances is applicable to such interactions during heat treatment of pellets, such as the oxidation of magnetite to hematite, the dissociation of limestone (preheating zone) or hematite (burning zone), the oxidation of sulfides (preheating zone).

Oxidation of magnetite

In relation to the process of magnetite oxidation in the framework of this approach, the mass transfer rate is determined as:

$$N = [4 \cdot \pi \cdot (r(\tau))^2 \cdot P \cdot (Y_e - y)] / \{R_g \cdot T \cdot (1/K + r(\tau)/(R_\beta) + (r(\tau)/D_e) \cdot [1 - r(\tau)/R])\}, \quad (2.5.13)$$

where

N —molar oxygen flow (O_2/s);

R_g —universal gas constant;

P —total gas-phase pressure;

Y_e, y —volume concentration of oxygen (fractions) in equilibrium and in the gas phase;

$r(\tau)$ —position of the reaction surface;

K —oxidation rate constant;

D_e —effective diffusion coefficient O_2 ;

T —temperature (Kelvin).

The rate of mass transfer is more convenient to express through the degree of conversion α . The ratio between the coordinate of the reaction surface in the pellet and the degree of conversion (degree of oxidation, in particular) follows from simple geometric considerations:

$$r(\tau) = R(1 - \alpha)^{1/3} \quad (2.5.14)$$

Taking into account (2.5.14), we will rewrite Eq. (2.5.13) as follows:

$$N = \left[4\pi R^2 (1 - \alpha)^{2/3} \cdot P(Y_e - y) \right] / \left\{ R_g T \left(1/K + (1 - \alpha)^{1/3} / \beta + R(1 - \alpha)^{1/3} \cdot \left[1 - (1 - \alpha)^{1/3} \right] D_e \right) \right\} \quad (2.5.15)$$

N —molar oxygen flow;

α —degree of conversion (oxidation).

During oxidation, the degree of conversion (oxidation) α is defined as the ratio of the amounts of added oxygen to its theoretically possible.

Taking into account the stoichiometry of the oxidation reaction of magnetite to hematite for the degree of conversion during the oxidation, α can be written:

$$\alpha = 29 \cdot (M_i - M_o) / M_o \cdot m, \quad (2.5.16)$$

where

M_i, M_o —current and initial mass of pellet;

M —content (share) of magnetite in the pellet;

29—stoichiometric oxidation reaction coefficient ($2 \cdot \text{Fe}_3\text{O}_4 + 1/2 \cdot \text{O}_2 = 3 \cdot \text{Fe}_2\text{O}_3$), determined from relationship $2 \cdot 232/16$.

The molar oxygen flow during the oxidation of magnetite N is determined as follows:

$$N = d((M_i - M_o)/32))/dt \quad (2.5.17)$$

Replacing $(M_i - M_o)$ in (2.5.17) from (2.5.16), differentiating and substituting in (2.5.15), for the degree of transformation we have:

$$N = \left[4\pi R^2 \cdot 29 \cdot 32 \cdot (1 - \alpha)^{2/3} \cdot P(Y_e - y) \right] / \left\{ R_g T \cdot M_o \cdot m \left(1/K + (1 - \alpha)^{1/3} / \beta + R(1 - \alpha)^{1/3} + R(1 - \alpha)^{1/3} \right) \cdot \left[1 - (1 - \alpha)^{1/3} \right] / D_e \right\} \quad (2.5.18)$$

The use of Eqs. (2.5.13), (2.5.15), and (2.5.18) requires information about the kinetic (K and K temperature dependence) and transport (D_e , β , parameters of the pellet structure) parameters of the reacting system. Let us consider the approaches to determine the specified parameters.

The determination of kinetic parameters is possible by the method of mathematical modeling. The model is based on the numerical integration of Eq. (2.5.18) under certain boundary conditions; the kinetic constant is iterated for each temperature with a subsequent approximation of the temperature dependence.

For the temperature dependence of the oxidation rate constants of various types of iron ore concentrate, Eqs. (2.5.19) and (2.5.20) are applicable:

$$K = 150 \cdot \exp(-5270/(t + 273)), \quad (2.5.19)$$

when the content in the concentrate Fe 72.0%

$$K = 150 \cdot \exp(-5920/(t + 273)), \quad (2.5.20)$$

when the content in the concentrate Fe 67.81%, where t —temperature, °C.

The magnitudes of activation energy of magnetite oxidation obtained from (2.5.19) and (2.5.20) correspond to the range of 44–49 kJ/mol. The known values [2, 50] of the activation energy of magnetite oxidation, depending on the type of concentrate, its particle size distribution, temperature range of oxidation, lie in the range of 21–69 kJ/mol.

In the first approximation, the transport parameters of the reacting system are given by the integral characteristics of the structure, namely porosity ε and tortuosity of the pores V through the effective diffusion coefficient D_e :

$$D_e = D \cdot \varepsilon / \zeta \quad (2.5.21)$$

The actual data on the change in porosity with the roasting temperature for magnetite and hematite with sufficiently wide initial compaction conditions modeled by the granulometric composition of the material and the pressing force are given in Table 2.15. The temperature dependences of the porosity of hematite ε_H , magnetite ε_M , and hematite ε_O , obtained by the oxidation of magnetite, derived by approximating the actual data of Table 2.15, are represented by Eqs. (2.5.22)–(2.5.24):

$$\varepsilon_H = 65.58 - 0.037 \cdot T \quad (2.5.22)$$

$$\varepsilon_M = 66.49 - 0.037 \cdot T \quad (2.5.23)$$

$$\varepsilon_O = 77.88 - 0.041 \cdot T \quad (2.5.24)$$

A more rigorous consideration of the transport properties of the reacting system is to assess the change in porosity not only with temperature, but also over time, due to the development of the shrinkage process (in the case of oxidation at low and moderate temperatures, this process can be neglected).

The pore tortuosity parameter is set arbitrarily, taking into account the physical meaning of the tortuosity.

Diffusion gas flow I through the material can be written as follows:

$$I = S \cdot D_e \cdot dC/dl \quad (2.5.25)$$

The same flow I , referred to the live section of the pores, can be expressed as:

$$I = S_e \cdot D \cdot dC/dl_e, \quad (2.5.26)$$

where

S, l —geometric surface of the material, layer thickness, respectively;
 S_e, l_e —pore surface, pore length.

Equating (2.5.25) and (2.5.26) and taking into account (2.5.21), after simple transformations, we obtain the expression for the tortuosity of pores (2.5.27):

$$\zeta = (l_e/l)^2 \quad (2.5.27)$$

As a priori estimates for ζ , values in the range 2.8–7.0 are recommended. For approximate calculations, you can take its estimate as the inverse of the porosity, expressed in fractions of a unit. At the same time, it should be noted that tortuosity is a more complex function of the porous structure (pore shape, pore size distribution, etc.); with the development of sintering processes, the dependence of pore tortuosity on temperature is unquestionable.

The temperature dependence of the diffusion coefficient of oxygen in a solid material is known and has the form:

$$D = 9.71 \times 10^{-6} \cdot T^{1.75} \quad (2.5.28)$$

The conditions of mass transfer through the gas film are determined through the external mass transfer coefficient β , which in turn is found from the Sherwood Sh criterion:

$$Sh = 2 \cdot \beta \cdot R/D \quad (2.5.29)$$

The empirical dependence of the Sherwood criterion for the range of values of the Reynolds number 0.5–500 allows us to estimate the external mass transfer coefficient β by the parameters of the gas flow:

$$\beta = (2 + Sc^{1/3} \cdot Re^{1/2}) \cdot D/(2 \cdot R), \quad (2.5.30)$$

where

Re —Reynolds criterion $Re = v \cdot (2 \cdot R)/\nu$;

Sc —Schmidt criterion $Sc = \nu/D$,

where

ν —gas flow rate;

ν —gas kinematic viscosity.

Equilibrium oxygen pressure for the reaction $2 \cdot Fe_3O_4 + 1/2 \cdot O_2 = 3 \cdot Fe_2O_3$ is determined during the experiment on the dissociation of hematite in the form:

$$Po_2 = \exp(-55,000/T + 32.43) \quad (2.5.31)$$

The values of diffusion and kinetic parameters for different temperatures, which were used for mathematical modeling of the oxidation of the pellet, are presented in Table 2.8, and the simulation results in Fig. 2.29.

In practice, the oxidation of the pellet is determined by the content of FeO, which is associated with the oxidation state α by the stoichiometric ratios:

$$(FeO) = 9 \cdot [100 \cdot (1 - \alpha) - P \cdot (1 - \alpha)]/(\alpha + 29), \quad (2.5.32)$$

where

(FeO)—FeO content in the pellet (%);

P —gangue content in the pellet (%);

9, 29—stoichiometric coefficients.

The oxidation of pellets (magnetite) practically (until reaching a content of 2% of FeO, which is typical for many pelletizing plants) is completed at the beginning of the roasting zone (Fig. 2.29a, b).

The peculiarities of oxidation of pellets with different iron content are associated with a kinetic parameter, namely the oxidation rate constant, which, as can be seen

Table 2.8 Diffusion and kinetic parameters of the oxidation of pellets from magnetite concentrate (Fe content 72%)

t (°C)	Degree of transformation		Structural characteristics		Parameters			Kinetic resistance		
	FeO (%)	α (share)	ε (share)	ς	β (cm/s)	De (cm ² /s)	K (cm/s)	R_β (s/cm)	R_D (s/cm)	R_K (s/cm)
450	25.03	0.184	0.564	1.77	1.2656	0.1359	0.102	0.739	0.314	9.761
600	17.66	0.419	0.503	1.99	1.9262	0.1786	0.358	0.433	0.542	2.790
750	10.85	0.641	0.441	2.27	2.6810	0.2033	0.869	0.265	0.708	1.151
800	9.01	0.701	0.421	2.38	2.9523	0.2069	1.104	0.227	0.749	0.906
900	5.98	0.801	0.380	2.63	3.5234	0.2071	1.678	0.166	0.821	0.596
1000	3.77	0.874	0.339	2.95	4.1313	0.1982	2.389	0.121	0.853	0.419
1150	2.21	0.926	0.277	3.61	5.1095	0.1696	3.696	0.082	1.006	0.271
1200	2.68	0.910	0.257	3.89	5.4529	0.1567	4.191	0.082	1.105	0.239
1250	4.63	0.849	0.236	4.23	5.8046	0.1425	4.713	0.092	1.222	0.212
1300	10.15	0.667	0.216	4.63	6.1647	0.1273	5.261	0.113	1.165	0.190

from the comparison of Eqs. (2.5.19) and (2.5.20), has higher (1.5–2.5 times) values for pellets from rich concentrates.

The oxidation of pellets at elevated temperatures is associated with certain diffusion limitations (Fig. 2.29c). There is an optimal region in terms of temperature conditions of oxidation, falling within the interval of 1050–1200 °C, which allows obtaining the most oxidized product (Table 2.8). Experimentally, the optimum oxidation temperature was discovered quite a long time ago [50] and was explained by the formation of a melt or a change in the limiting stage of the oxidation process. Obtaining a similar effect through modeling allows us to conclude that the dependence is of a general nature. The explanation of the observed phenomenon follows from the consideration of the dynamics of kinetic resistances both with temperature (Table 2.8) and in time (Fig. 2.30).

The kinetic resistance of a chemical reaction monotonously decreases with increasing temperature in the range of 450–1300 °C from 9.761 to 0.190 s/cm, i.e., almost 50 times (for poor magnetite concentrates, the change in resistance can reach almost two orders of magnitude).

The change in resistance of internal diffusion with temperature (Fig. 2.30) is due both to a decrease in the effective diffusion coefficient and an increase in the diffusion path determined by the development of the oxidation itself, and in the general case by an exponential temperature function. These two factors determine the extreme course of the dependence of diffusion resistance on temperature. The total amount of change in diffusion resistance is no more than five times.

The external diffusion resistance in the analyzed temperature range varies by an order of magnitude from 0.749 to 0.075 s/cm, which indicates its significant contribution to mass transfer during oxidation.

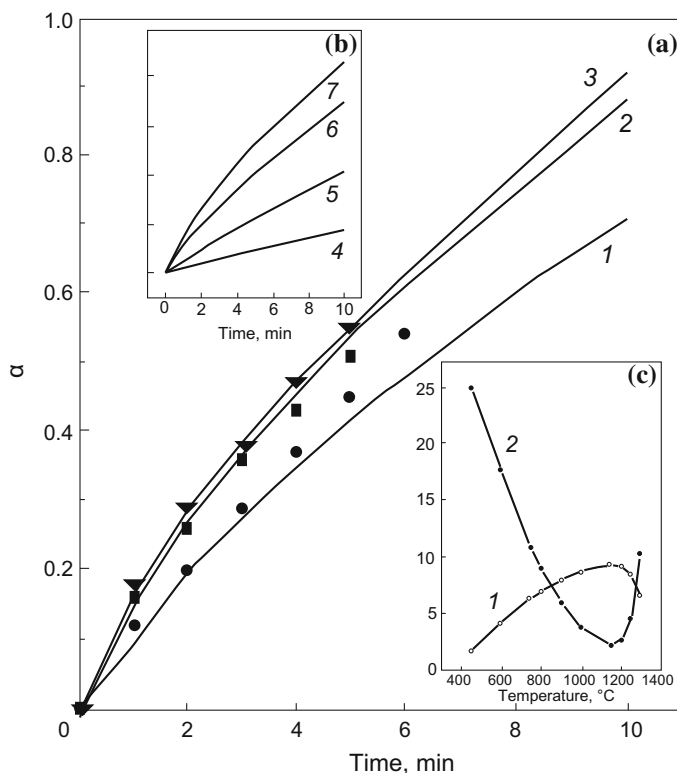


Fig. 2.29 Kinetics of magnetite pellet oxidation (LebGOK magnetite concentrate with Fe content 72.0%; **a** oxidation state α : curves 1, 2, 3—simulation results, respectively, at temperatures of 800, 1000, 1200 °C; points—experimental data; **b** oxidation state α : curves 4, 5, 6, 7; simulation results at temperatures of 450, 600, 800, 1000 °C, respectively; ordinate axis “ a , b ”—oxidation state, fractions; abscissa axis “ a ”—time, min; **c** is the qualitative course of the curve change of oxidation state α (curve 1) and the content of FeO (2) with temperature). Abscissa axis—temperature, °C; ordinate axis—FeO content in the pellet, %

The analysis of the values of kinetic resistances (Table 2.8) makes it possible to abandon the very common misconception about strictly diffusion or kinetic response regimes. At low oxidation temperatures (not higher than 600 °C), the greatest resistance corresponds to a chemical reaction, but already from 800 °C the diffusion and chemical resistance have the same order of magnitude. For this reason, there is no strict diffusion control of the process; even in high-temperature heterogeneous transformations, the contribution of the kinetic factor remains significant.

The role of gas-dynamic factors (gas flow rates and pellet size) in the kinetics of magnetite oxidation is illustrated in Table 2.9.

An increase in the gas flow rate in the range from 0.026 to 0.8 m/s, corresponding to the experimental and industrial variants of pellet roasting, is accompanied by an increase in the oxidation depth (decrease in the FeO content), while the external diffusion resistance decreases by more than three times. At the same time, the

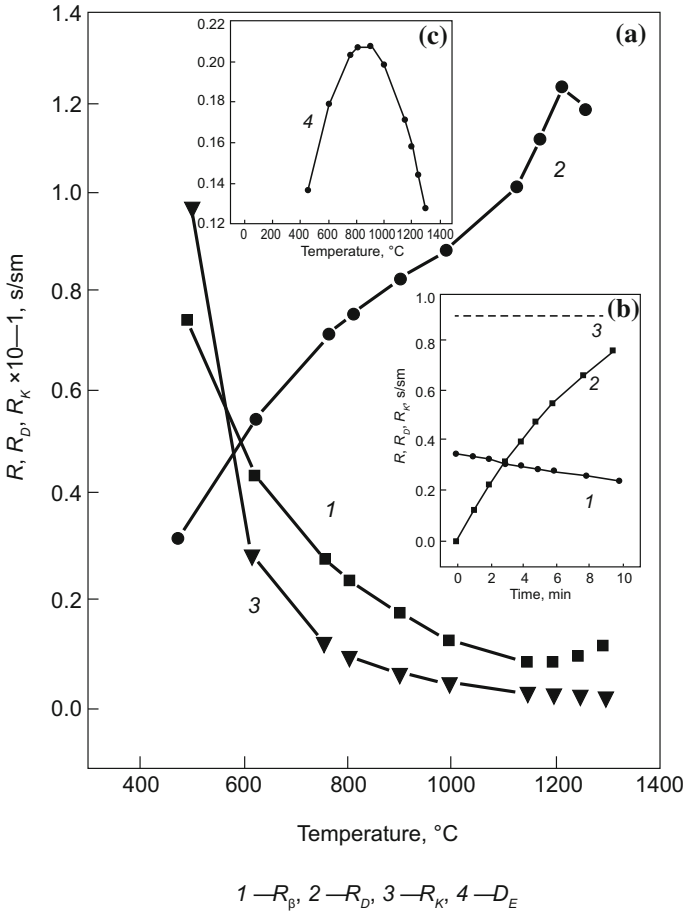


Fig. 2.30 Kinetic and transport parameters of the process of magnetite oxidation (**a** the temperature dependence of the resistances of R_β , R_D , R_K (curves 1, 2, 3); **b** dependence of the resistances of R_β , R_D , R_K on time at $t = 800^\circ\text{C}$ (curves 1, 2, 3); **c** is the change in the effective diffusion coefficient with temperature (curve 4). Y-axis—effective diffusion coefficient, cm^2/s)

improvement of the oxidation conditions leads to an increase in the intradiffusion resistance by an amount not exceeding 10%. With an increase in the pellet radius from 0.4 to 1.0 cm, the oxidation of the pellet (in terms of FeO content) decreases from 10.78 to 20.56%, which illustrates the linear parameters of the pellet with a significant kinetic factor.

Hematite dissociation

The thermodynamic probability of hematite dissociation at oxygen pressure in the gas phase of 0.21 atm according to different sources [57, 58] is correlated with the temperature interval of 1380–1475 °C; however, these boundaries appear to be

Table 2.9 Effect of gas-dynamic flow parameters and pellet size on the pellet oxidation kinetics (iron content 67.81%)

R (cm)	v (cm/s)	Degree of transformation		Structural characteristics		Parameters			Kinetic resistance		
		FeO (%)	α (share)	ε (share)	ς	β (cm/s)	De (cm ² /s)	K (cm/s)	R_β (s/cm)	R_D (s/cm)	R_K (s/cm)
0.4	2.65	10.78	0.621	0.421	2.38	4.6185	0.2069	0.603	0.157	0.387	1.660
0.5	2.65	13.79	0.517	0.421	2.38	3.8551	0.2069	0.603	0.203	0.409	1.660
0.6	2.65	15.95	0.443	0.421	2.38	3.3333	0.2069	0.603	0.247	0.424	1.660
0.7	2.65	17.84	0.378	0.421	2.38	2.9523	0.2069	0.603	0.289	0.424	1.660
0.8	2.65	18.78	0.346	0.421	2.38	2.6608	0.2069	0.603	0.326	0.444	1.660
1.0	2.65	20.56	0.286	0.421	2.38	2.2419	0.2069	0.603	0.399	0.460	1.660
0.7	2.65	17.84	0.378	0.421	2.38	2.9197	0.2069	0.603	0.289	0.421	1.660
0.7	10	17.49	0.390	0.421	2.38	4.1616	0.2069	0.603	0.204	0.437	1.660
0.7	20	17.31	0.396	0.421	2.38	5.1940	0.2069	0.603	0.163	0.444	1.660
0.7	30	17.21	0.400	0.421	2.38	5.9861	0.2069	0.603	0.141	0.448	1.660
0.7	50	17.10	0.403	0.421	2.38	7.2423	0.2069	0.603	0.116	0.452	1.660
0.7	80	17.01	0.406	0.421	2.38	8.7186	0.2069	0.603	0.096	0.455	1.660

rather diffuse. In the systems $\text{Fe}_2\text{O}_3\text{--CaO}$ and $\text{Fe}_2\text{O}_3\text{--MgO}$, dissociation of the oxide solution is possible in the temperature range 110–1360 °C and 1200–1380 °C, respectively [58].

The structure of the mathematical model for the case of hematite dissociation is similar to Eq. (2.5.18) and differs only in the value of the stoichiometric coefficient:

$$d\alpha/d\tau = \left[4\pi R^2 \cdot 30 \cdot 32 \cdot (1 - \alpha)^{2/3} \cdot P(Y_e - y) \right] \left\{ R_g T \cdot M_o \cdot g \left(1/K + (1 - \alpha)^{1/3} / \beta + R(1 - \alpha)^{1/3} \cdot \left[1 - (1 - \alpha)^{1/3} \right] D_e \right) \right\} \quad (2.5.33)$$

where

g —the content (share) of hematite in the pellet;

D_e —effective diffusion coefficient O_2 ;

30, 32—stoichiometric coefficient.

The oxidation (FeO content) of the pellet is determined by the degree of dissociation of hematite α by the relation (2.5.34):

$$(\text{FeO}) = [9 \cdot (100 - P) \cdot \alpha] / (30 - \alpha), \quad (2.5.34)$$

where

(FeO)—FeO content in the pellet (%);

P —gangue content (%).

The kinetic parameters in the dissociation of hematite (obtained by the oxidation of magnetite concentrate with an Fe content of 72%) are determined by the dissociation rate constant:

$$K = 3880 \cdot \exp(-12,800/(t + 273)), \quad (2.5.35)$$

where

t —temperature ($^{\circ}\text{C}$).

To assess the transport parameters of the reacting system in the case of hematite dissociation, relations (2.5.21)–(2.5.24) are applicable.

In the area of real roasting temperatures that can be provided in traditional units for heat treatment of pellets ~ 1250 to 1350 $^{\circ}\text{C}$, the process of dissociation is not only possible, but proceeds in various limits at different partial pressures of oxygen (Table 2.10). For pellets of magnetite concentrate with an Fe content of 67.81% with a partial pressure of oxygen of 0.0001 atm, degree of dissociation in 10-min treatment in the temperature range 1250 – 1350 $^{\circ}\text{C}$ increases from 0.225 to 0.612 with a corresponding increase in the content of FeO to 17.63%.

An increase in the partial pressure of oxygen to 0.1 atm, corresponding to the oxygen content in the coolant in the heating furnaces of the firing machines, is accompanied by a regular decrease in the degree of dissociation of hematite: In the same temperature limits, the content of FeO varies from 2.42 to 14.2%.

Table 2.10 Diffusion and kinetic parameters of hematite dissociation of pellets from magnetite concentrate

t ($^{\circ}\text{C}$)	Degree of transformation		Structural characteristics		Parameters			Kinetic resistance		
	FeO (%)	α (share)	ε (share)	ζ	β (cm/s)	De (cm ² /s)	K (cm/s)	R_{β} (s/cm)	R_D (s/cm)	R_K (s/cm)
The content of Fe in concentrate is 72%, and the partial pressure of oxygen is 0.0001 atm										
1250	4.45	0.148	0.20	4.94	5.8046	0.1045	0.32	0.163	0.331	3.084
1300	9.40	0.312	0.18	5.44	6.1647	0.0924	0.46	0.143	0.783	2.172
1320	12.06	0.399	0.18	5.67	6.3111	0.0874	0.53	0.134	1.055	1.900
1350	16.70	0.555	0.17	6.05	6.5330	0.0799	0.64	0.117	1.568	1.563
The content of Fe in concentrate is 67.81%, and the partial pressure of oxygen is 0.0001 atm										
1250	6.39	0.225	0.20	4.94	5.8046	0.1045	0.32	0.158	0.501	3.144
1300	10.94	0.383	0.18	5.44	6.1647	0.0924	0.42	0.138	0.959	2.372
1320	13.36	0.466	0.18	5.67	6.3111	0.0874	0.47	0.129	1.227	2.130
1350	17.63	0.612	0.17	6.05	6.5330	0.0799	0.55	0.112	1.731	1.821
The content of Fe in concentrate is 67.81%, and the partial pressure of oxygen is 0.1 atm										
1250	2.42	0.086	0.20	4.94	5.8046	0.1045	0.32	0.167	0.191	3.144
1300	6.99	0.246	0.18	5.44	6.1647	0.0924	0.42	0.148	0.619	2.372
1320	9.60	0.336	0.18	5.67	6.3111	0.0874	0.47	0.138	0.892	2.130
1350	14.20	0.495	0.17	6.05	6.5330	0.0799	0.55	0.122	1.422	1.821

The process of hematite dissociation in the temperature range studied (as follows from the data in Table 2.10) is a kinetically controlled process: In the entire temperature range, the resistance value of the chemical interaction exceeds the diffusion resistance value and more than an order of magnitude of the external diffusion resistance.

Limestone dissociation

The kinetic model with a single reaction surface for dissociating limestone differs from the models describing the oxidation of magnetite or the dissociation of hematite, only by the stoichiometric coefficient:

$$d\alpha/d\tau = \left[4\pi R^2 \cdot 44 \cdot (1 - \alpha)^{2/3} \cdot P(Y_e - y) \right] / \left\{ R_g T \cdot M_o \cdot p \left(1/K + (1 - \alpha)^{1/3} / \beta + R(1 - \alpha)^{1/3} \cdot \left[1 - (1 - \alpha)^{1/3} \right] D_e \right) \right\}, \quad (2.5.36)$$

where

α —the degree of dissociation of limestone, share;

p —limestone content in the pellet;

D_e —effective diffusion coefficient CO_2 ;

44—stoichiometric coefficient.

The temperature dependence of the rate of dissociation of limestone is described by the expression (2.5.37):

$$K = 152 \cdot \exp(-4785/(t + 273)), \quad (2.5.37)$$

where

t —temperature ($^{\circ}\text{C}$).

The change in the equilibrium partial pressure of CO_2 , obtained from thermodynamic data, is described by the relation (2.5.38):

$$\text{Po}_2 = \exp(-9220/(t + 273) + 7.80) \quad (2.5.38)$$

The dependence of the diffusion coefficient of CO_2 on temperature according to [59] is:

$$D = 6.21 \times 10^{-6} \cdot T^{1.78} \quad (2.5.39)$$

The transport parameters of the reacting system in the case of dissociation of limestone can be estimated from relations (2.5.21)–(2.5.24).

Thus, the essentially kinetic mode of limiting during the oxidation of magnetite and the exclusively kinetic limiting in the processes of dissociation of hematite creates prerequisites for the intensification of the burning process due to the activation of chemical reaction.

2.5.3 Pellet Roasting as a Complicated Case of Sintering

Sintering is a physicochemical process in dispersed systems when they are heated, consisting in the formation and increase of interparticle contacts, accompanied by a decrease in the porosity of the unit and an increase in its density (and strength) [60].

Pellet as a dispersed system is distinguished by a high level of free surface energy and its corresponding non-equilibrium. The tendency of the system to thermodynamic equilibrium is realized during roasting through the sintering phenomenon, which is provided by one or another mass transfer mechanism.

Basically, sintering in the pellet as a physical process is complicated by the following circumstances:

- the complexity of the system;
- the flow of heterogeneous transformations solid–solid and gas–solid;
- the possible formation of a liquid phase (melt).

The sintering theory applied to roasting pellets developed in the direction of physical modeling of processes in the pellet according to the principle “from simple to complex”: the behavior of one-component systems, then systems with concomitant heterogeneous processes, and finally systems involving the liquid phase (melt) was studied.

2.5.3.1 The Main Laws of Sintering Kinetics

The cumulative result of mass transfer processes during sintering is shrinkage (decrease in porosity) and, in connection with this, a change in the properties of the aggregate, primarily the strength properties. The patterns of solid-phase hardening are described in detail in [61–63].

The kinetic curves of shrinkage of individual mineral phases (hematite and magnetite) are given in Fig. 2.31.

The specificity of changes in shrinkage over time indicates a significant difference in iron ore oxides: The shrinkage rate of hematite during solid-phase sintering (up to 1200 °C) reaches 25%; for magnetite, the shrinkage value under these conditions does not exceed 5%. At the same time, the dependence of the kinetics of oxide shrinkage on the partial pressure of oxygen is manifested: In the entire temperature range (1000–1300 °C), the amount of shrinkage of hematite at a partial pressure of 0.0001 atm (argon) has higher values than with a partial pressure of oxygen of 0.21 atm (air).

Under the assumption that sintering is a solid-phase reaction and taking into account the power law nature of the dependence of shrinkage in time, a formal kinetic equation of the form is applicable to describe the kinetics:

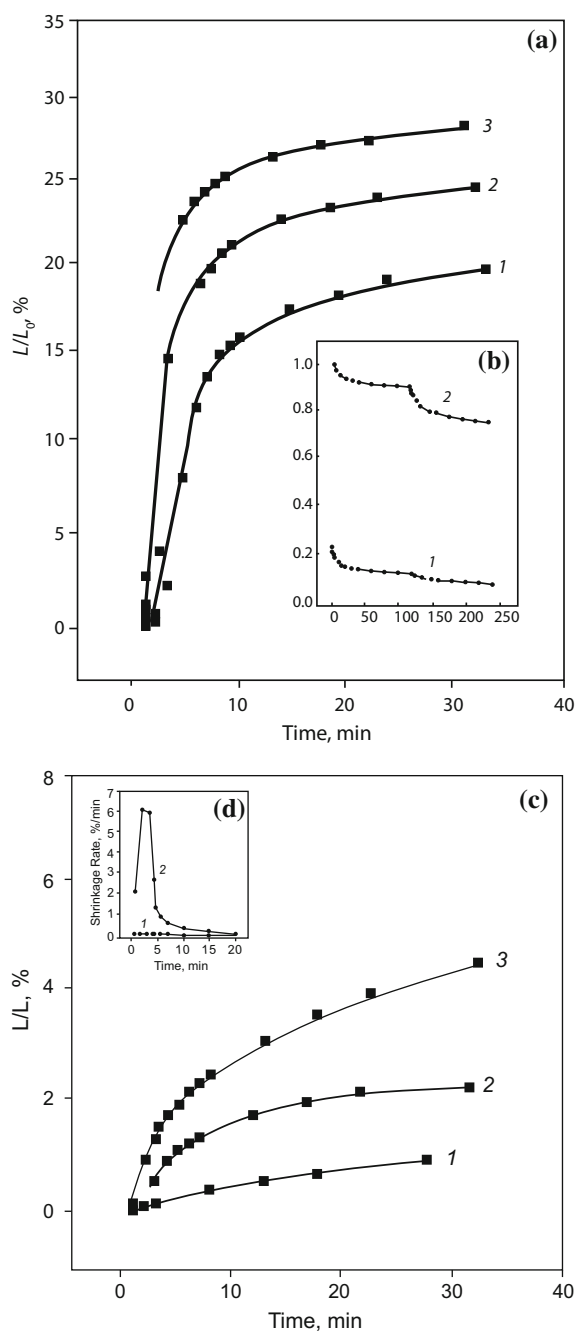


Fig. 2.31 Kinetics of sintering hematite and magnetite. **a** Kinetic curves of shrinkage of hematite at temperatures: 1–1000 °C; 2–1100 °C; 3–1200 °C; **b** relative change in the pore volume V_i/V_n with step sintering of 0–120 min (1000 °C), 120–240 min. (1100 °C); 1—magnetite, 2—hematite; abscissa axis—time, min, ordinate axis— V_i/V_n , shares; **c** kinetic curves of magnetite shrinkage at temperatures: 1–1000 °C; 2–1100 °C; 3–1200 °C; ($P_{O_2} = 0.02$ MPa); **d** shrinkage rate at $t = 1000$ °C; 1—magnetite, 2—hematite; abscissa axis—time, min, ordinate—shrinkage rate, %/min

$$\Delta l/l = k_o \cdot \exp(-E/R_g T) \cdot \tau^n, \quad (2.5.40)$$

where

$\Delta l/l$ —shrinkage, %;

k_o , E —pre-exponential factor, apparent activation energy;

R_g , T —universal gas constant, temperature (K);

n —exponent;

τ —time.

The kinetic characteristics of sintering of oxides according to (2.5.40), calculated on the basis of the experimental data of Fig. 2.31, are given in Table 2.11.

In the general provisions of the theory of sintering, developed in the works of Frenkel Ya.I., Pines B.Ya., Kuczynski GC, Kingery WD, Clark PW, Coble RL, Balshina M.Yu., Geguzina L.E., Fedorchenko I.M., Ivensen V.A. and others, the parameter “ n ” serves as an important characteristic of mass transfer during sintering: The value of “ n ” is equal to 0.5 for the mechanism of plastic flow; the volume diffusion mechanism is 0.2 to 0.5; the surface diffusion mechanism is 0.14. In this context, estimates of the parameter “ n ” for hematite and magnetite (Table 2.11) suggest that the sintering of these oxides is carried out by different mass transfer mechanisms (depending on the firing temperature, the parameter “ n ” for magnetite is within 0.2–0.6, and for hematite—in the range of 0.05–0.18), but do not guarantee unambiguous information about the mechanism of mass transfer.

In the theory of the transition state, the factor $\exp(-E/R_g T)$ determines the proportion of “active” for the interaction of particles. At the same temperature level, a decrease in E is accompanied by an increase in “active” particles. Thus, even such a formalized assessment notes the differences in the level of activity of hematite and magnetite (Table 2.11).

The nature of the different behavior of iron oxides to a certain extent allows us to reveal the approach in the concepts of the theory of return and creep, developed in [64] for metallic powders.

2.5.3.2 Sintering Mechanism of Iron Oxides

The relative change in pore volume during sintering is described by Eq. (2.5.41):

Table 2.11 Kinetic parameters of sintering iron oxides

Oxide	E (kJ/mole)	k_o	n_{av}
Hematite $Po_2 = 0.0001$ atm	33 ± 2.0	0.4×10^3	0.11
Hematite $Po_2 = 0.1$ atm	48 ± 2.0	10^3	0.11
Magnetite	144 ± 4.0	1.2×10^5	0.47

$$V_i = V \cdot (q \cdot m \cdot \tau + 1)^{-1/m}, \quad (2.5.41)$$

where

V_i , V —relative pore volume after and before isothermal sintering, respectively;
 q —coefficient having a reduction rate of 1 cm^3 of pore volume at the beginning of isothermal sintering ($\tau = 0$);
 m —dimensionless constant;
 τ —time.

Based on the concept of the relationship between imperfections of the crystalline structure (see Sect. 2.5.3) and mass transfer (shrinkage) during sintering (applicable, taking into account the effect of slowing the sintering rate of iron oxides with time, Fig. 2.31g), Eq. (2.5.41) according to [64], we structure it as follows:

$$V_i/V = [aN_0 \exp(-E_a/R_g T) \tau + 1]^{-1/((a/b) \exp(\Delta E/R_g T))}, \quad (2.5.42)$$

where

aN_0 —kinetic characteristic of the relative concentration of imperfections at the time of the onset of isothermal sintering, $1/h$;
 E_a —activation energy of the healing process (annihilation) of imperfections, kJ/mol ;
 E_b —activation energy of mass transfer due to imperfections of the crystal lattice, kJ/mol ;
 $\Delta E = E_a - E_b$, kJ/mole ;
 a , b —constants (pre-exponential factors of the rate constants of the corresponding processes).

Comparing (2.5.41) and (2.5.42), we obtain the expression for “ m ”:

$$m = (a/b) \exp(\Delta E/R_g \cdot T) \quad (2.5.43)$$

Changing the temperature of heat treatment of oxides (pellets) activates two processes:

- sintering of iron oxide (mass transfer) at a given concentration of crystal lattice imperfections;
- annealing (annihilation) of crystal lattice imperfections, which reduces their concentration.

In order to assess the influence of each of these flows, step sintering is carried out, which makes it possible to separate processes with a constant and varying concentration of lattice deficiencies.

Experimental data on the stepwise sintering of hematite and magnetite are shown in Fig. 2.31b. The constants of the kinetic Eq. (2.5.42) are calculated by

Table 2.12 Kinetic parameters during sintering of iron oxides in step heating mode

Parameter	Oxide	
	Hematite	Magnetite
The activation energy of the process of elimination (healing) of the imperfections of the crystal lattice E_a (kJ/mol)	190	425
Activation energy of mass transfer due to the presence of imperfections, E_b (kJ/mol)	225	550
The ratio of pre-exponential factors (a/b)	0.356	4.75×10^{-4}
Kinetic characteristic of the relative concentration of crystal lattice imperfections in the initial oxide aN_0 (h^{-1})	∞	1.05×10^{20}
The kinetic concentration of the imperfections of the crystal structure of aN after heat treatment at temperatures (h^{-1})		
1000 °C	1.91×10^{16}	6.6×10^{19}
1100 °C	9.67×10^{14}	8.1×10^{18}

successively determining the parameters aN_0 , ΔE , E_a , E_b , a/b , m . The calculation results are shown in Table 2.12.

The kinetic constant a/b depends on both the dispersity of the oxide particles and the type of imperfections. With the same particle size, such a significant difference in the values of a/b for hematite and magnetite (Table 2.12) is due exclusively to the defectiveness of oxides.

The constant “ m ” according to (2.5.41) characterizes the intensity of the decrease in the rate of shrinkage during sintering; then, according to (2.5.43), the constant a/b determines the decrease in the rate of shrinkage at a constant temperature (i.e., just for the case when the process of healing the imperfections of the crystal lattice is dominant). The a/b value in metal powders compacted by diffusion according to [68], lies within $(8.06\text{--}1.15) \times 10^{-4}$. The proximity of these values with the a/b parameter of magnetite is in favor of the diffusion mechanism of sintering of magnetite (which is also confirmed by high values of activation energy and the value of the parameter “ n ” (equal ix (2.5.40) equal to 0.2–0.5).

The significantly higher a/b value for hematite compared with magnetite, the low value of the activation energy of the elimination process of imperfections, confirms the conclusion about the high mobility of defects in hematite.

The aN parameter is a conditional characteristic of the imperfections of the crystal structure and rather reflects not the concentration of defects, but their mobility, since it has the size of the kinetic constant (and thus, to some extent, the type of defect).

The change in the concentration (mobility) of imperfections in hematite is several orders of magnitude: from infinitely large (on the basis of $1/aN_0 \rightarrow 0$) to a value of 9.67×10^{14} at a temperature of 1100 °C. The concentration of imperfections (mobility) in magnetite for the same sintering conditions changed slightly more than an order of magnitude.

Hematite sintering is characterized by an activation energy of 2–2.5 times less than the activation energy of diffusion of iron and oxygen ions in hematite. This fact

can be the result of acceleration of diffusion in non-equilibrium (defective) objects. It is known [65] that the activation energy of diffusion along edge dislocations (the “short-circuit” mechanism) is half the activation energy of bulk diffusion. The anomalously high value of the pre-exponential factor in the diffusion equation for the Fe^{+3} ion in hematite, as summarized by the authors [66], cannot be explained from the standpoint of the vacancy mechanism of diffusion. These facts, as well as the value of the parameter “ n ” in the kinetic equation 0.1–0.15, suggest that the dislocation mechanism plays an essential role in mass transfer during sintering of hematite. In dispersed materials, where the particle sizes are comparable to the critical size of a dislocation loop, the stresses may be sufficient to ensure the dislocation glide. In defective crystals, thermally activated dislocation gliding is possible [67]. Both of these processes require less than the diffusion mechanism of activation energy.

To be fair, it should be noted that not all dislocation mechanisms are low activation: For example, the movement of dislocations by the “crawling” mechanism is carried out by absorbing vacancies, and the activation energy of such a process is equal to the diffusion activation energy.

2.5.3.3 Characteristics of Iron Oxide Structure Defects

The ideal crystalline structure of a solid is a regular and periodic arrangement of an unlimited number of atoms (ions) in three-dimensional space. There are 14 original spatial lattices (Bravais cells) defined by a set of linear and angular parameters, as well as the order of placement of atoms, which are combined into seven systems (syngonies) [68].

Syngony	Linear parameters	Angle parameters
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma$
Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma$
Trigonal	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ$
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ \gamma = 120^\circ$
Rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$

Any deviation of atoms or groups of atoms from their ideal position is called disordering, and areas in which a violation of the order is noted are called defects of the crystal structure.

Defects in the structure of an ideal crystal are distinguished according to a geometric feature [69, 70]:

- zero-dimensional, for which the regions of violation of the periodicity of the structure in all dimensions do not exceed the lattice parameter (thermal vibrations of atoms, point defects);

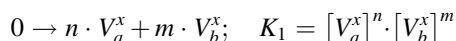
- one-dimensional, where violations in one direction are commensurate with the crystal size, and in the other two do not exceed the lattice parameters (dislocations);
- two-dimensional (planar) extend in two dimensions at distances comparable to the size of the crystal, and in the third—commensurate with the lattice parameter (packing defects, shear crystallographic structures, phase boundaries, the surface of a real crystal);
- three-dimensional (volume) violations cover areas commensurate with the size of the crystal (predisposition and release of a new phase, pores).

Unlike point defects of a dislocation, packing defects and crystallographic shear structures sometimes share the common name extended defects.

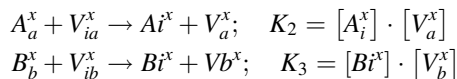
The thermodynamically stable state of a crystal corresponds to the equilibrium concentration of point defects, which makes it possible to apply the apparatus of classical thermodynamics to their description, as applied to nonmetals in [69].

In the case of oxide AB , the state of a crystal is described by quasichemical reactions, depending on the type of disordering:

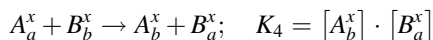
- Schottky defect (simultaneous existence of uncharged vacancies V_a^x in sublattice A and V_b^x in sublattice B):



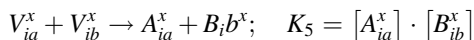
- Frenkel defect (vacancies and interstitial atoms in one or two sublattices):



- anti-structural defects (atoms A occupy sites in sublattice B , and atoms B in sublattice A):



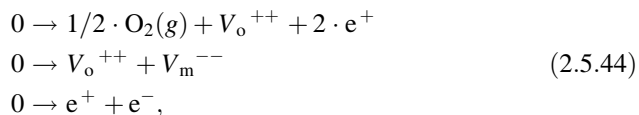
- the disorder caused by the introduction of atoms A and/ or B into the corresponding intersite sublattice sites:



where K_1 , K_2 , K_3 , K_4 , K_5 —equilibrium constants of the corresponding quasichemical reactions.

In the formation of charged point defects most characteristic of metal oxides, it is necessary to take into account the electroneutrality condition. For example, for oxide MO , Schottky disordering, taking into account the crystal surface as a drain

and a source of vacancies and the formation of charged defects, can be described by a combination of three quasichemical reactions:



where

V_{o}^{++} —positively charged vacancy in the oxygen sublattice;

V_{m}^{--} —negatively charged vacancy in the metal sublattice;

e^+ , e^- —hole, electron.

The condition of electroneutrality of the crystal for this case is:

$$2 \cdot [e^+] + [V_{\text{o}}^{++}] = 2 \cdot [e^-] + [V_{\text{m}}^{--}] \quad (2.5.45)$$

The corresponding equilibrium constants for the quasichemical reactions (2.5.44) and (2.5.45) are represented by (2.5.46):

$$\begin{aligned} K_6 &= [V_{\text{o}}^{++}] \cdot [e^+] \cdot \text{Po}_2^{1/2} \\ K_7 &= [V_{\text{o}}^{++}] \cdot [V_{\text{m}}^{--}] \\ K_8 &= [e^+] \cdot [e^-] \\ K_9 &= [V_{\text{m}}^{--}] \cdot [e^-]^2 / ([V_{\text{o}}^{++}] \cdot [e^+]^2) = f(K_6, K_7, K_8) \end{aligned} \quad (2.5.46)$$

From the ratio of the quasichemical reaction constants, we can estimate the concentration of defects: For example, for $[V_{\text{m}}^{--}]$, by (2.5.44)–(2.5.46) we have:

$$[V_{\text{m}}^{--}] = K_7 \cdot (K_6 - K_8^2 \cdot (\text{Po}_2)^{1/2}) / (K_6 \cdot K_7 \cdot K_8 - 2 \cdot K_8 \cdot (\text{Po}_2)^{-1/2}) \quad (2.5.47)$$

In stoichiometric oxide $[V_{\text{o}}^{++}] = [V_{\text{m}}^{--}]$, then $[V_{\text{m}}^{--}] = K_7^{1/2}$ and does not depend on the partial pressure of oxygen. In the case of non-stoichiometric oxide $[V_{\text{o}}^{++}] \neq [V_{\text{m}}^{--}]$ and the concentration of point defects depends on Po_2 . In a generalized form, this dependence can be represented by the equation:

$$N = K \cdot (\text{Po}_2)^{\pm 1/m} \cdot \exp(-\Delta G/R_g \cdot T), \quad (2.5.48)$$

where

N —defect concentration;

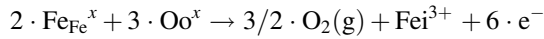
K , m —constants;

Po_2 —oxygen partial pressure over oxide;

$-\Delta G$ —defect generation energy

The confirmation of the model of the defective crystal structure is usually estimated by the constant “ m ” [71], obtained by processing the experimental data of the dependence of some structural-sensitive properties (diffusion, electrical conductivity, thermo-emf) on the temperature and partial pressure of oxygen [71–73].

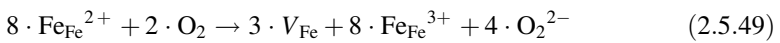
As applied to *iron oxide* Fe_2O_3 , according to the dependence of diffusion and electrical conductivity [74, 75] on the partial pressure of oxygen in the gas phase, it was found that the main point defects in iron oxide (crystalline structure of the corundum type) are interstitial iron atoms formed quasichemical reaction:



$$K_{10} = [\text{e}^-]6 \cdot [\text{Fe}^{3+}] \cdot \text{Po}_2^{3/2}$$

At the same time, the opinion [76] dominates that at present, it is impossible to identify dominant disordering in the structure of the corundum type based on the available experimental data, and the types of defects in such a structure should be described by probabilistic models (Table 2.13).

Iron oxide Fe_3O_4 with the structure of reversed spinel according to the equilibrium diagram is characterized by a metal deficiency relative to the stoichiometric composition, which leads to the appearance of cationic vacancies [74]. Moreover, in the structure of Fe_3O_4 , point disordering occurs in both cationic sublattices. According to [71], the quasichemical equation of cationic disordering for the case of a statistical distribution of vacancies over *A* (tetrahedral) and *B* (octahedral) sublattices is written by the equation:



Taking into account the ratios (2.5.50) of the types of defects and the degree of non-stoichiometric iron oxide Fe_3O_4 , we obtain for the equilibrium constant (2.5.51).

$$\gamma = 3 \cdot [V_{\text{Fe}}]; [\text{Fe}_{\text{Fe}}^{2+}] = (1 - \gamma)/3; [\text{Fe}_{\text{Fe}}^{3+}] = 2 \cdot (1 + \gamma)/3 \quad (2.5.50)$$

Table 2.13 Models of self-disordering in oxides with a structure of corundum type

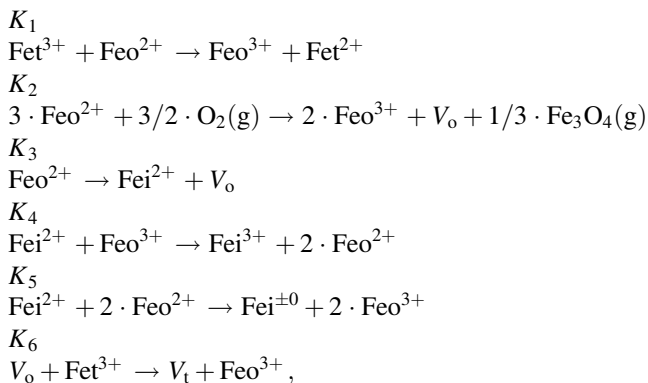
Rating parameter	Disordering patterns			
	I	II	III	IV
Most prevalent type of disordering	Frenkel defects	Defects of introductions	Schottky defects	Anti-Frenkel defects
Constant of disordering	$K_F = [\text{Al}^{3+}] \cdot [\text{V}_{\text{Al}}^{3-}]$	$K_i = [\text{Al}^{3+}]^2 \cdot [\text{O}^{2-}]^3$	$K_s = [\text{V}_{\text{Al}}^{3-}]^2 \cdot [\text{V}_{\text{O}}^{2+}]^3$	$K_{F-O} = [\text{V}_{\text{O}}^{2+}] \cdot [\text{O}^{2-}]$
Prevailing defect type	$\text{Al}^{3+}, \text{V}_{\text{Al}}^{3-}$	$\text{Al}^{3+}, \text{O}^{2-}$	$\text{V}_{\text{Al}}^{3-}, \text{V}_{\text{O}}^{2+}$	$\text{V}_{\text{O}}^{2+}, \text{O}^{2-}$
The least probable type of defect	$\text{V}_{\text{O}}^{2+}, \text{O}^{2-}$	$\text{V}_{\text{Al}}^{3-}, \text{V}_{\text{O}}^{2+}$	$\text{Al}^{3+}, \text{O}^{2-}$	$\text{Al}^{3+}, \text{V}_{\text{Al}}^{3-}$

$$K_{11} = \left[\gamma \cdot (1 + \gamma)^{8/3} / (1 - 3\gamma)^{8/3} \right] \cdot (\text{Po}_2)^{-2/3}$$

or at small values of γ :

$$K_{12} = \gamma \cdot (\text{Po}_2)^{-2/3} \quad (2.5.51)$$

The study of natural and synthetic magnetites (iron oxide Fe_3O_4) by nuclear gamma resonance spectroscopy showed that for Fe_3O_4 of different genesis, the ratio of the intensities of the characteristic lines *A* and *B* of the sublattices is close to 0.5, which theoretically corresponds to the equally probable distribution of cation vacancies [77]. However, in-depth studies of Fe_3O_4 by X-ray diffraction [78] have established that, depending on the oxygen potential of the gas phase, Fe_3O_4 can form both cation vacancies and interstitial atoms. The authors came to a similar conclusion [79]. Based on the studies on the diffusion of cations in magnetite, they proposed six types of point disordering in the spinel structure, which can be described by the following quasichemical equations:



where

V_o , V_t —vacancies in the octahedral and tetrahedral sublattices, respectively;
 Fei^{2+} , Fei^{3+} —interstitial atoms.

For some limiting cases of disordering, when vacancies are localized in the octahedral sublattice ($K_6 = 0$), or only in the tetrahedral sublattice ($K_6 = \infty$), or, conversely, distributed evenly in the octahedral and tetrahedral sublattices ($K_6 = 1/2$ or 1), six models of the defective state are obtained:

- A_1 ($K_1 = 0$, $K_6 = 0$)—spinel reversed, only V_o ;
- A_2 ($K_1 = 0$, $K_6 = 1/2$)—spinel reversed, $V_t \sim V_o$;
- A_3 ($K_1 = 0$, $K_6 = \infty$)—spinel reversed, only V_t ;

- $B_1 (K_1 = 1, K_6 = 0) - [\text{Fe}^{2+}] = [\text{Fe}^{3+}], \text{ only } V_o;$
 $B_2 (K_1 = 1, K_6 = 1) - [\text{Fe}^{2+}] = [\text{Fe}^{3+}], V_t \sim V_o;$
 $B_3 (K_1 = 1, K_6 = \infty) - [\text{Fe}^{2+}] = [\text{Fe}^{3+}], \text{ only } V_t.$

It is assumed [81, 82] that the most adequate model of disordering in Fe_3O_4 is B_2 , for small concentrations of vacancies and interstitial atoms; the dependence of their concentration on oxygen activity (a_{O_2}) has the form:

$$[V_t] \sim [V_o] \sim a_{\text{O}_2}^{2/3}; [\text{Fe}^{2+}] \sim [\text{Fe}^{3+}] \sim a_{\text{O}_2}^{-2/3}$$

The model of point disordering of the spinel structure is confirmed by structural studies [80], as well as a series of studies of electrical conductivity, thermo-emf, diffusion [81, 82].

At the same time, an unambiguous interpretation of any physicochemical properties based on point disordering is impossible in cases where extended defects are present in the crystal structure. It was noted [83] in particular that, in the spinel structure, the growth of stacking packing defects can occur in accordance with an increase in the concentration of interstitial Fe^{2+} cations.

Thus, affecting the disordering, extended defects (dislocations, mosaic blocks, packing defects) are not described by the thermodynamic method, since they are not the equilibrium type of defects.

A *dislocation* is a linear imperfection that forms the boundary of the shear zone inside the crystal. The main quantitative characteristic of the dislocation, reflecting the degree of crystal distortion, is the Burgers vector $\mathbf{b}$. The magnitude and direction $\mathbf{b}$ are along the Burgers contour [70]. The appearance of a dislocation in a crystal increases its internal energy by the elastic distortion energy $\varepsilon \sim G(b) 2 \cdot l$, where G is the shear modulus, l is the dislocation length, and b is the Burgers vector. However, when a dislocation occurs, the configurational and vibrational components of the entropy increase, which ultimately leads to a decrease in the free energy F of the crystal.

Under the influence of external and internal stresses, the dislocation can slide along the shear plane along a certain crystallographic direction. For ionic crystals, edge dislocations are characteristic; in this case, the direction of motion of the dislocation coincides with the Burgers vector. The motion of a dislocation must ensure, during a run, the identical translation of the crystal lattice in the $\mathbf{b}$ direction (complete dislocation). In the crystal, there are directions (b_1, b_2) that are energetically more favorable for the cooperative displacement of atoms, although they do not correspond to the identical translation of the crystal. In these directions, partial dislocations are formed, which are, as it were, a complete splitting, and the following equality holds for the Burgers vectors: $b = b_1 + b_2$. Due to the appearance of partial dislocations, the crystal region above the slip plane becomes shifted with respect to the region under the plane by the magnitude of the Burgers vector of the partial dislocation. In this case, in the region of the crystal enclosed between two partial dislocations, a violation of the sequence of the arrangement of the planes of the atoms in the direction perpendicular to the slip plane appears. Such a violation is called a *packaging defect*.

The packaging defect occurs not only under the action of stresses in the crystal, but also during its growth, when the crystal plane was “missed” or “inserted” during atom packing or the growth direction changed by an angle multiple to the angles between the main directions vectors in the crystal (twin packaging defect).

In the *spinel structure* (Fe_3O_4), the slip plane is the $\langle 111 \rangle$ dense packing plane. Perpendicular to this plane (i.e., in the direction $\langle 111 \rangle$), the spinel is described by three-layer packaging of packages according to the law ... ABC ..., each package in turn consists of 8 layers of anions, cations of 2 grades and structural vacancies [84]. Each subsequent stacking package in the spinel structure is obtained by displacing the previous layer parallel to the plane $\langle 111 \rangle$ in the direction $\langle 112 \rangle$.

A specific feature of the Fe_3O_4 structure is that of shear dislocations, there are half (with dissociation order 2) with Burgers vector $1/4 \cdot a_o\sqrt{2}$ in the $\langle 110 \rangle$ direction and fourfold (with dissociation order 4) with vector b in direction parallel to $\langle 112 \rangle$ and equal to $1/12 \cdot a_o\sqrt{6}$.

The twin packaging defect in spinel occurs when a four-dimensional dislocation passes through each four layers and can be represented as a rotation of the twinned atoms by 180° around the $\langle 111 \rangle$ axis with a subsequent displacement of $1/2 \langle 110 \rangle$ [85].

A hexagonal $\alpha\text{-Al}_2\text{O}_3$ corundum cell (to which hematite $\alpha\text{-Fe}_2\text{O}_3$ belongs) in the $\langle 0001 \rangle$ direction can be represented by a packet formed by alternating 12 layers of $c_3Ac_1Bc_2Ac_3Bc_1Ac_2B$, where A and B are layers of oxygen ions, c_1 , c_2 , c_3 are cationic layers with different arrangement of vacancies, combined with each other by turning to 120° and 240° .

In the structure of the corundum type, there are complete dislocations with the Burgers vector in the direction $\langle 1120 \rangle$ and $\langle 1010 \rangle$, equal to a_o and $a_o\sqrt{3}$, respectively [86].

According to the minimum energy criterion, the dislocation with $b = a_o \langle 1120 \rangle$ is most probable; however, in real conditions, the total dislocation splits to form binary ones (as well as in the case of spinel having dissociation order 2) in the direction $\langle 1010 \rangle$ s , $b_2 = a_o/\sqrt{3}$ and quaternary dislocations (the order of dissociation 4) in the direction $\langle 1120 \rangle$ with $b_4 = 1/3a_o$. The quaternary dislocation model with $b_4 = 1/3a_o \langle 1120 \rangle$ suggests [86] that during the shift along the Burgers vector b_4 , the cation sublattice is shifted with the oxygen sublattice unchanged. At the same time, the package structure changes from ordinary to $c_3Ac_1Bc_2'Cc_3'Bc_1Ac_2B$, where two layers of c_2' and c_3' cations and a cation layer of C form a packing defect. Due to the peculiarities of the corundum-type ionic structure, full displacement according to b_4 is impossible and there is a “synchro shift” of cations by $\Delta = 1/3a_o \langle 1100 \rangle$, which, in addition to the structural structure, forms an “electrostatic” defect expressed in the diagonally symmetric arrangement of cations and structural vacancies of the packing defect. The structure of the most likely package of planes along $\langle 0001 \rangle$ can be represented as $c_3Ac_1Bc_2Ac_1Bc_2Ac_3B$.

The twin packaging defect in the corundum-type structure represents [87] a specular reflection relative to the $\langle 0001 \rangle$ plane plus a shift to the fourfold dislocation with $b_4 = 1/3a_o \langle 1120 \rangle$. The shift occurs in any of the equivalent directions $\langle 1100 \rangle$, $\langle 1010 \rangle$, $\langle 0110 \rangle$ and is carried out by successive displacement of oxygen layers with

a synchronous shift of intermediate cations. For example, at an offset in the $\langle 1010 \rangle$ direction, the 12-layer packet will transition to $a_2Ca_3Ba_1Ca_2Ba_3Ca_1B$.

With the appearance of packaging and dislocation defects in the crystal, elastic deformations of the lattice appear, the areas of compression and tension, separated by the plane in which the defect is located. In the bulk of the crystal, these micro-stresses of the lattice $\sqrt{\langle \varepsilon_2 \rangle}$ are balanced, but the rms micro-strain can be different from zero depending on the nature of the distribution of dislocations in the crystal [70].

The structure of a real crystal can also be characterized by separate regions free from defects. The size of these areas (mosaic blocks) as well as the level of micro-strain determines the degree of defectiveness of real crystal.

Diagnostics of real crystal defects (pointwise, extended) is carried out by X-ray diffraction methods, which have been developed in detail to study the fine crystal structure, including oxide crystals [84, 88].

2.5.3.4 Dependence of the Defectiveness of the Hematite Structure on the Genesis of Oxide

The change in the defectiveness of Fe_2O_3 oxide (lattice parameters, mosaic block sizes (CSR—Coherent scattering regions), fine crystal structure parameters) at different temperatures of heat treatment (roasting) was studied on iron oxide pure for analysis and a natural hematite from the oxidation zone of an iron ore magnetite deposit (Sarbai field, Kazakhstan Republic).

The results of X-ray diffraction studies are shown in Table 2.14 [89–91].

The different genesis of iron oxides is reflected in the peculiarities of the imperfections of the crystal structure in the initial state and after heat treatment.

Natural hematite

In the initial state, hematite (pure for analysis) is characterized by a small size of dispersed blocks (44 nm) and a low level of micro-strain (0.76×10^{-3}), as well as the presence of twin packaging defects. Natural hematite is characterized by larger mosaic blocks (94 nm), a large micro-strain of the crystal lattice (1.3×10^{-3}).

The studied iron oxides Fe_2O_3 are characterized by practically identical parameters of the crystal lattice “*a*” and “*c*”. Assessment of the level of point defects by the results of X-ray structural studies is possible with a comparative analysis of their behavior in the process of heat treatment (roasting). It should be borne in mind that the elastic strain field of a point defect has spherical symmetry [70]. In the case of anisotropy of elastic crystal constants along certain crystallographic directions, spherical symmetry is distorted, but nevertheless, the deformation remains voluminous, which in this particular case should lead to changes in both the “*a*” parameter and the “*c*” Fe_2O_3 crystal lattice. The lattice parameters of the studied hematites with roasting temperature practically do not change

Table 2.14 Parameters of the crystal structure and imperfection of hematites

Type of hematite	T _{roasting} (°C)	Crystal lattice parameters		Average size CSR ^c (nm)	Parameters of fine crystal structure			
		a ^a (nm)	c ^b (nm)		Micro-deformation ($\sqrt{\langle \varepsilon^2 \rangle} \times 10^3$)	Probability of packaging defects		
						$\alpha_1 \times 10^3$	$\alpha_2 \times 10^3$	$\beta \times 10^3$
Hematite pure for analysis	Original	0.5030	1.3779	44 ± 2	0.76 ± 0.05	0	0	3.1 ± 0.3
	400	0.5030	1.3779	44 ± 2	0.86 ± 0.09	0	0	4.7 ± 0.4
	550	0.5031	1.3774	46 ± 3	0.61 ± 0.05	0	0	8.1 ± 0.5
	700	0.5031	1.3770	74 ± 4	0.47 ± 0.08	0	0	16.0 ± 2.0
	1000	0.5032	1.3770	220 ± 20	0.35 ± 0.10	0.31 ± 0.2	0.64 ± 0.2	0.1 ± 0.08
Natural hematite	Original	0.5030	1.3776	94 ± 1	1.30 ± 0.20	7.6 ± 0.9	0.20 ± 0.1	0.3 ± 0.07
	400	0.5031	1.3776	82 ± 4	1.52 ± 0.12	5.8 ± 0.7	10.0 ± 1.0	0
	550	0.5031	1.3777	70 ± 2	1.70 ± 0.10	6.3 ± 0.9	11.0 ± 1.2	0
	700	0.5031	1.3777	97 ± 3	1.19 ± 0.02	2.3 ± 0.7	11.0 ± 1.0	0
	1000	0.5032	1.3774	126 ± 12	0.70 ± 0.20	0.0 ± 0.1	6.1 ± 0.5	0
Hematite OM	Magnetite oxidation at Po ₂ = 0.1 MPa							
	600	0.5029	1.3747	44 ± 2	1.9 ± 0.1	4.9 ± 0.3	0	4.7 ± 0.3
	750	0.5030	1.3749	62 ± 2	1.3 ± 0.1	0.3 ± 0.1	1.2 ± 0.2	0.2 ± 0.1
	820	0.5031	1.3749	177 ± 5	1.1 ± 0.15	0.6 ± 0.3	1.7 ± 0.3	0.5 ± 0.2
	900	0.5031	1.3749	127 ± 5	0.8 ± 0.08	0.2 ± 0.1	3.1 ± 0.3	1.9 ± 0.25
	1000	0.5030	1.3747	93 ± 2	0.6 ± 0.1	5.6 ± 0.3	6.2 ± 0.3	0
(continued)								

(continued)

Table 2.14 (continued)

Type of hematite	T _{roasting} (°C)	Crystal lattice parameters		Average size CSR ^c (nm)	Parameters of fine crystal structure			
		a ^a (nm)	c ^b (nm)		Micro-deformation ($\sqrt{\langle \varepsilon^2 \rangle} \times 10^3$)	Probability of packaging defects		
						$\alpha_1 \times 10^3$	$\alpha_2 \times 10^3$	$\beta \times 10^3$
Hematite OM	Magnetite oxidation at Po ₂ = 0.02 MPa							
	600	0.5028	1.3747	82 ± 2	2.34 ± 0.08	d	d	d
	750	0.5028	1.3747	87 ± 4	2.19 ± 0.1	0.8 ± 0.2	0.6 ± 0.2	1.5 ± 0.2
	820	0.5030	1.3749	57 ± 3	1.09 ± 0.04	0	0	3.8 ± 0.2
	900	0.5030	1.3749	111 ± 3	1.09 ± 0.09	0.38 ± 0.25	0.1 ± 0.08	0.51 ± 0.25
	1000	0.5029	1.3746	102 ± 4	0.6 ± 0.1	0.42 ± 0.2	0.1 ± 0.08	1.0 ± 0.3

^aDetermination error ±0.0001

^bDetermination error ±0.0003

^cCSR—coherent scatter areas (mosaic blocks)

^ddetermination of the type and probability of packing defects in this mode is impossible due to the overlap of the lines of the X-ray spectrum of Fe₂O₃ and residual Fe₃O₄

α_1 —probability of formation of packaging defects from binary dislocations

α_2 —probability of formation of packing defects from quadruple dislocations

β —the probability of formation of packaging defects from twin dislocations

Hematite OM—hematite obtained by the oxidation of magnetite (with a Fe content of 72%)

(Table 2.14). This means that the concentration of point defects does not exceed the thermodynamically equilibrium level.

The fine structure of hematite (pure for analysis) in the initial state is characterized by twin packaging defects, the formation probability of which is 3.1×10^{-3} . In contrast to hematite (cd), the fine structure of natural hematite is represented by deformation packaging defects from binary dislocations (α_1) 7.6×10^{-3} , quadruple dislocations (α_2) 0.2×10^{-3} , and twin dislocations (β) 0.3×10^{-3} .

In the process of heat treatment (roasting) in hematite (pure for analysis), the growth of the size of mosaic blocks and the reduction of micro-strain starts from a temperature of 550 °C. In natural hematite, changes in the defective structure are already observed at 400 °C and are characterized by a decrease in the average size of blocks and an increase in micro-strain. In this case, there is a decrease in the probability of deformation defects of the packing α_1 , caused by the presence of binary dislocations in the crystal, and an increase in the deformation defects of the packing α_2 from fourfold dislocation. The main mechanism of motion of a binary dislocation in a corundum-type structure according to [92] is crawling, the speed of which is determined by diffusion processes, while the quadruple dislocation moves by sliding.

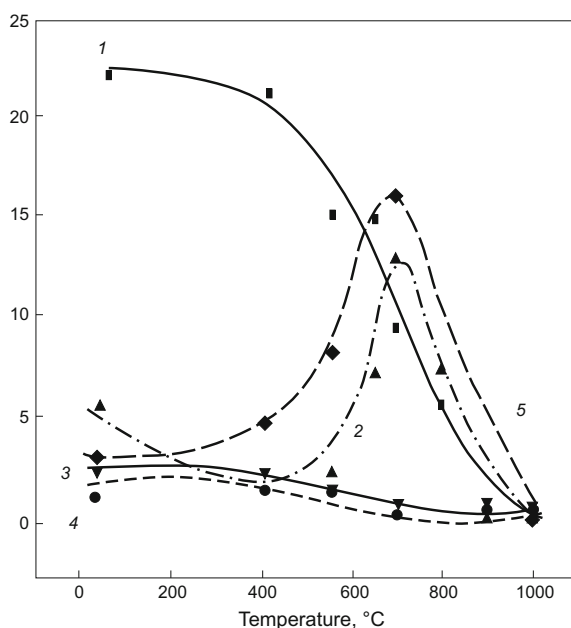
The difference in the mechanisms of motion of dislocations leads to the fact that the decrease in the probability of packing defects from binary dislocations α_1 to the firing temperature of 550 °C is not significant and occurs mainly by splitting into quaternary dislocations. The latter causes an increase in the total imperfection of the crystal. A further increase in temperature is accompanied by a sharp decrease in the concentration of defects, which is reflected in the increase in the size of coherent scattering regions, a decrease in micro-deformation, and the likelihood of deformation defects of the package α_1 and α_2 .

Shear-type packing defects from binary dislocations only infringe on the cationic sublattice of oxide, with quaternary dislocations; defects are formed in both cationic and anionic planes. Since the self-diffusion coefficient of iron cations is usually 2–4 orders of magnitude higher than the oxygen self-diffusion coefficient [74], deformation of packing from binary dislocations is less thermally stable and annealed at lower temperatures, which is observed during the heat treatment of natural hematite.

Unlike natural hematite in Fe_2O_3 of “pure for analysis” grade as the roasting temperature increases, the growth of twin packaging defects is observed, the probability of which passes through a maximum at 700 °C and then decreases. The dependence of the change in twin packaging defects on the roasting temperature is due to the ratio of the rates of sintering and annealing of defects.

The generation of twin packaging defects is possible with alternating layer-by-layer passing of binary and quaternary dislocations or as a result of the growth (sintering) of oxide particles [86]. As in hematite of “pure for analysis” grade no deformational packaging defects were detected; therefore, the source of twinning packaging defects is the surface of the fusible particles. Then, the rate of formation of twin packaging defects to a temperature of 700 °C is determined by the sintering rate and greater than the rate of annihilation of packaging defects, while at higher roasting temperatures the rate of formation of twin packaging defects is comparable to the rate of their annealing. Confirmation of the onset of sintering of hematite at

Fig. 2.32 Specific surface area and the probability of formation of packaging defects depending on the heat treatment temperature (1, 2, 5 —hematite, pure for analysis; 3, 4—natural hematite; 1, 3— S —Specific surface, m^2/g , determined by adsorption of the dye “Congo red” from an aqueous solution; 2, 4— $b_s \times 10^{-5}$ —adsorption intensity; 5— $\beta \times 10^3$ —probability of formation of packing defects from twin dislocations; ordinates axis— S , $b_s \times 10^{-5}$, $\beta \times 10^3$)



such low (~ 550 °C) temperatures is the change in the specific surface of the oxide under study, calculated from the adsorption data (Fig. 2.32).

The nature and level of changes in the specific surface as well as the dislocation structure with increasing temperature show that the most developed sintering processes are obtained at temperatures above 700 °C (Fig. 2.32), where mass transfer processes are significantly intensified.

The specific surface of natural hematite also decreases with increasing temperature, but in terms of the level and rate of change, it is an order of magnitude lower than in the case of hematite pure for analysis. This gives grounds for concluding that a higher annealing rate for packing defects β (whose presence is not detected in this case) as compared to the sintering rate.

The dependences of the adsorption intensity b_s and the probability of formation of twin packing defects β on the roasting temperature in hematite (Fig. 2.32) reveal their equal nature. Bearing in mind that the b_s parameter characterizes the energy state of the surface, it can be concluded that the dislocation defects of iron oxide are localized on the crystal surface. This fact confirms once again that extended defects play an active role in the processes occurring on the surface of crystalline materials [89].

Hematite obtained by the oxidation of magnetite

Depending on external conditions (temperature, pressure, partial pressure of oxygen), the formation of a new phase during oxidation proceeds with various disruptions in its crystal structure.

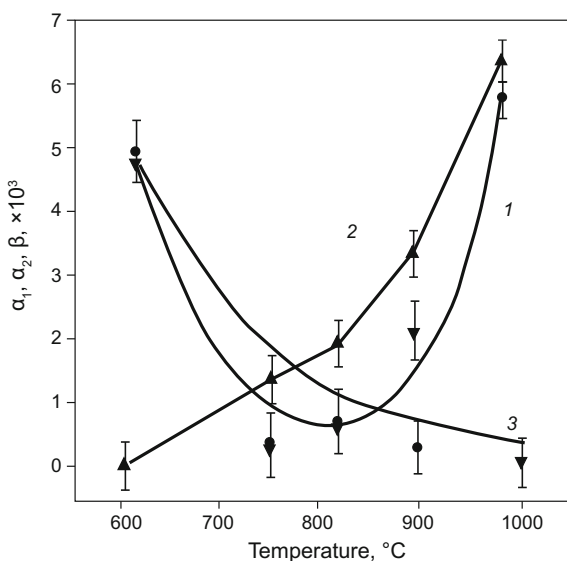
To determine the patterns of formation of the defective structure of iron oxide Fe_2O_3 during the interaction of magnetite Fe_3O_4 (72% Fe, Lebedinsky GOK) with oxygen, the oxidation was carried out under isothermal conditions in the temperature range of 600–1100 °C and a partial pressure of oxygen of 0.02 and 0.1 MPa (Table 2.14).

The calculation of the Fe_2O_3 lattice parameters for the entire range of oxidation conditions showed (Table 2.14) that the parameters “ a ” and “ c ” with increasing oxidation temperature and changing the oxygen partial pressure within the statistical error remain constant. Thus, in the magnetite formed by the oxidation of Fe_2O_3 after its completion, there are no excess concentrations of point defects.

Oxidation of magnetite at 600 °C and a partial pressure of oxygen of 0.1 MPa lead to the formation of a hematite structure with a fine block size (CSR) of about 44 nm and a micro-strain level of 1.9×10^{-3} . In this case, the fine structure of hematite is represented by deformation packaging defects from binary α_1 dislocations and twinning defects β . Oxidation at 600 °C and oxygen partial pressure of 0.02 MPa provide in the structure of hematite mosaic blocks (OCD) with a size of 82 nm and a level of micro-strain 2.3×10^{-3} .

An increase in the oxidation temperature to 750 °C (at Po_2 0.1 MPa) leads to an increase in mosaic blocks (CSR) and a decrease in micro-strain (which naturally decreases to processing temperatures of 1000 °C and regardless of oxygen conditions). At the same time, there is a decrease in the probability of α_1 packing defects from binary dislocations and β from twinning dislocations, but the appearance of deformation packing α_2 from quadruple dislocations is noted (Fig. 2.33).

Fig. 2.33 Effect of oxidation conditions on the deficiency of iron oxide structure (1— α_1 is the probability of formation of packaging defects from binary dislocations; 2— α_2 is the probability of formation of packaging defects from quaternary dislocations; 3— β —the probability of formation of packaging defects from twin dislocations $\text{Po}_2 = 0.1$ MPa)



The defective structure of hematite formed at $P_{O_2} = 0.02$ MPa is characterized by the presence of three types of packing defects, the probability of which α_1 , α_2 , β is estimated to be of the order of 1.0×10^{-3} .

Oxidation of magnetite in the temperature range above 750 °C reveals the specific features of the formation of the structure of hematite under different oxygen partial pressure conditions. At 820 °C, in the case of $P_{O_2} = 0.02$ MPa, the size of mosaic blocks decreases to 58 nm and the likelihood of twinning packaging increases to 3.8×10^{-3} , in contrast to the conditions at $P_{O_2} = 0.1$ MPa, when the mosaic blocks are enlarged to 177 nm and the simultaneous decrease in the probability of deformation of packaging from binary dislocations (α_1) and twin packaging defects (β) and a significant increase in the probability of deformation of packaging from quadruple (α_2) dislocations.

A further increase in the oxidation temperature of magnetite to 1000 °C and a oxygen pressure of 0.1 MPa is accompanied by the formation of a block structure of hematite with relatively small blocks (93 nm) and a high level of defectiveness, determined by a significant increase in the probability of deformation of packaging from binary and quaternary dislocations (Fig. 2.33).

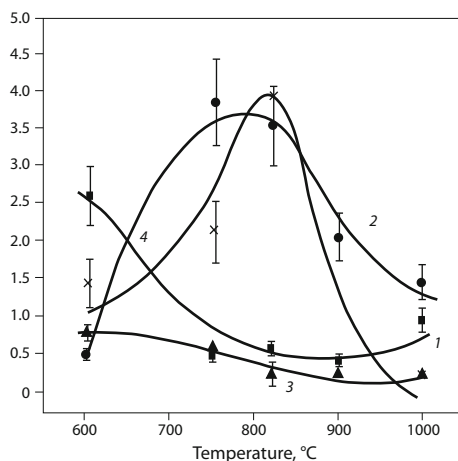
The tendency to increase the overall level of the structure's defects (grinding of mosaic blocks to 102 nm and an increase in the likelihood of packaging deformation defects α_1) during the transfer of the oxidation process to high temperatures is also observed when the partial pressure of oxygen decreases to 0.02 MPa.

Thus, hematite, which is formed as a result of the interaction of Fe_3O_4 with oxygen, is characterized by predominantly extended defects, the level of which depends entirely on the oxidation conditions. At the same time, there are two temperature ranges, when the level of non-perfection of the crystal lattice increases. In the region of low oxidation temperatures (below 750 °C), the defective structure of hematite has a significant length of low-angle boundaries (small size of CSR), a high probability of the formation of deformation packing defects from binary dislocations and twin packaging defects. When oxidized in the region of relatively high temperatures (900–1000 °C), the defective structure of hematite is described by a large size of mosaic blocks, a low level of micro-strain in the blocks (about 0.5×10^{-3}), but at the same time a significant concentration of deformation packaging as from binary to quadruple dislocations.

2.5.3.5 Defects in the Crystal Structure of Iron Oxides and Sintering Processes

The behavior of defects in the crystal structure of dispersed Fe_2O_3 oxides during heat treatment [89, 90] is determined by the combination of the processes of annealing of defects and sintering. During the oxidation of magnetite, a combination of three processes takes place: the formation of defects in the structure of Fe_2O_3 , determined by the conditions of oxidation; annealing of defects, depending on the temperature and level of the elastic energy of the crystal, and sintering, due to the diffusion characteristics of the crystal and the value of the specific surface.

Fig. 2.34 Specific surface S of hematite and b_s adsorption intensity depending on oxidation conditions (1, 2— S , b_s at Po_2 0.1 MPa; 3, 4— Po_2 0.02 MPa)



The formation and annealing of defects in the crystal structure of the formed hematite, on the one hand, and the sintering of freshly formed oxide, on the other hand, are characterized by a change in the surface properties, namely the specific surface corresponding to the sintering level reached during the heat treatment, and the adsorption intensity b_s , which reflects a different measure of the degree of imperfection of the crystal.

Iron oxide Fe_2O_3 , which is formed at an oxidation temperature of 600 °C and Po_2 of 0.1 MPa, has a higher specific surface area than hematite, obtained by oxidation at the same temperature and partial pressure of oxygen of 0.02 MPa (Fig. 2.34).

An increase in the oxidation temperature to 750 °C, regardless of the oxygen partial pressure, is accompanied by the formation of hematite with a lower specific surface area ($0.5 \text{ m}^2/\text{g}$ at Po_2 0.1 MPa and $0.25 \text{ m}^2/\text{g}$ at Po_2 0.02 MPa).

The intensity of adsorption b_s (Congo red dye from an aqueous solution) on hematite obtained by oxidation at 600 °C (Po_2 0.1 MPa) is $0.5 \times 10^4 \text{ l/mol}$, which is almost three times less than the value obtained on hematite at same temperature, but with Po_2 0.02 MPa. However, at an oxidation temperature of 750° the intensity of adsorption on hematite oxidized at Po_2 0.1 MPa increases significantly and amounts to $3.9 \times 10^4 \text{ l/mol}$, exceeding the b_s value during oxidation at Po_2 conditions of 0.02 MPa almost two times (Fig. 2.34). With an increase in the oxidation temperature to 1000 °C and regardless of the partial pressure of oxygen, a decrease in b_s is observed, but the level of b_s during oxidation under the conditions of Po_2 0.1 MPa is about five times higher.

Similarly, the relationship between the intensity of adsorption and the likelihood of twin packaging defects identified by the example of the temperature dependence of these parameters for hematite of “pure for analysis” grade (Fig. 2.32), we also assume that in this case the change in the adsorption intensity is related to the probability of formation of twin packing defects (β).

Comparison of the temperature dependence of $\beta(t)$ (Table 2.14) and $b_s(t)$ (Fig. 2.34) for hematite obtained by oxidation at P_{O_2} 0.02 MPa also reveals in this case (as for hematite, “pure for analysis”) the similar character of changes in $\beta(t)$ and $b_s(t)$. However, for hematite, which was formed at P_{O_2} 0.1 MPa, this correspondence is not observed. Analyzing the data in Table 2.14, it should be noted that the non-similar behavior of the $\beta(t)$ and $b_s(t)$ dependences is characteristic of iron oxides with a high probability of the formation of deformation packaging defects [91]. This is due to the fact that the motion of dislocations in addition to thermal activation is caused by the level of elastic stresses in the crystal.

Dislocation in a crystal increases its elastic energy by $\varepsilon \sim Gb^2l$; therefore, binary dislocations with the Burgers vector $a_o\sqrt{3}$ increase ε (provided that the dislocation length is equal) compared to the quaternary or twin dislocation, the modulus of Burgers vector of which is $a_o/3$, in three times. Information on defect formation in Fe_2O_3 , obtained by dissociation of salts and hydroxides [88], as well as the data in Table 2.14, shows that twinning dislocations are the least thermally stable extended defects in the hematite structure. The action of these two factors causes a high rate of annealing of twinning package defects.

Reducing the probability of formation of packaging defects, including twin packaging defects, can be accomplished by annihilating dislocations with anti-parallel Burgers vectors, partial dislocations on the crystal surface forming a step, capturing dislocations formed earlier by a small-angle boundary (CSR) or forming a small-angle boundaries by a network of moving dislocations [70].

The intense annealing of binary dislocations at oxidation temperatures of 750–820 °C and P_{O_2} 0.1 MPa is evidence of the equality of the rates of formation and annealing of deformation packing defects from α_1 binary dislocations.

With an increase in the oxidation temperature, the probability of the formation of fourfold dislocations, which are the most thermally stable extended defects in the Fe_2O_3 structure, significantly increases. This leads to the formation of mosaic blocks with a smaller size compared to Fe_2O_3 , obtained by oxidation at 820 °C and P_{O_2} 0.1 MPa. In other words, with an increase in the concentration of deformational packing defects within the mosaic blocks, the latter become less mobile at a given temperature.

A lower level of deformational packing defects in the structure of Fe_2O_3 after oxidation at P_{O_2} 0.02 MPa (Table 2.14) in the temperature range 750–820 °C does not significantly affect the pattern of movement of twin packaging defects, but shifts the ratio of the concentration of formed and annealed twinning defects β toward higher temperatures compared with similar processes in hematite of “pure for analysis” grade. Some increase in deformation of packaging from binary dislocations in the range of 900–1000 °C is hindered by complete annealing of twinning package defects.

The generation and movement of defects are responsible for the mass transfer during sintering, in particular, of iron oxides. Management of the defective state of the oxide allows to intensify the mass transfer processes during the heat treatment of the pellets of iron ore concentrates (see Sect. 2.6).

2.5.4 The Pellet Macrostructure and Strength

Heat treatment of pellets is designed to form its proper metallurgical quality, especially strength.

The strength of the pellet as a physical body is determined by its ability to withstand certain loads until the destruction. For the pellet, which is a brittle body (the deformation diagram does not have a flow area), the effective stress determines the level of strength.

The crush force, which simulates the destruction of the pellets in the process redistribution (during overload, transportation, loading into the blast furnace and movement of the blast furnace mine), corresponds to the compression deformation used to assess the strength of brittle materials. This type of testing is always associated with the uncertainty of the system of stresses causing destruction.

At least two types of destruction are possible, caused by the action of tensile stresses: from friction forces accompanied by the propagation of cracks along the surface of the specimen; or due to shear, when the cracks are localized in the direction of maximum tangential stresses. An experimental study of the nature of fracture on industrial pellets [93] showed that in 80% of cases, the destruction of pellets corresponds to the second scheme.

For conditions of one-sided compression (in the technological redistribution, the pellet is subjected to comprehensive compression), Hooke's law takes the form:

$$\sigma = E \cdot \delta / (\mu - 1), \quad (2.5.52)$$

where

σ —effective tension equal to F/S , F —compression force, S —load application cross section;

E —Young's modulus;

δ —relative deformation, $\Delta d/d$;

μ —Poisson's ratio.

For estimating the value of Young's modulus, the approach [94], which uses the interrelation of the Young's modulus of elasticity and the material melting point, is useful: For hematite, having a melting (dissociation) temperature of 1350 °C, the Young modulus is $\sim 0.7 \times 10^4$ kg/mm²; magnetite with a melting point of 1590 °C has a Young's modulus of $\sim 1.0 \times 10^4$ kg/mm².

For insignificant (not more than a percent) deformations inherent to the pellet at failure, the theoretical strength of the oxide phases according to (2.5.52) will be ~ 30 kg/mm².

The experimentally found strength of hematite and magnetite minerals is equal to 26.7 and 36.9 kg/mm², respectively [95], while the strength of the aggregate with initial porosity typical of the pellet does not exceed 20 kg/mm² in hematite and 8 kg/mm² in magnetite. Such a significant difference in the strength of the pellet from the theoretical strength of the phases is explained by the influence of porosity.

In the presence of porosity, the pellet should be considered as a two-phase system in which each phase undergoes an independent deformation. At the same time, the porosity (ε) has a modulus of elasticity almost equal to zero. Assuming a value of 0.3 for the Poisson's ratio, for a two-phase system with isolated pores we have a dependence for the Young's modulus:

$$E = E_{\text{ph}} \cdot (1 - 1.9 \cdot \varepsilon + 0.9 \cdot \varepsilon^2), \quad (2.5.53)$$

where

E_{ph} —Young's modulus of elasticity for a separate phase (hematite, magnetite, others).

Substituting (2.5.53) into (2.5.52), we have for the strength of the porous system:

$$\sigma = E_{\text{ph}} \cdot (1 - 1.9 \cdot \varepsilon + 0.9 \cdot \varepsilon^2) \cdot \delta / (\mu - 1) \quad (2.5.54)$$

In a medium with uninsulated pores, the effect of porosity is more significant than is dictated by Eq. (2.5.54). Thus, in the general theoretical aspect, the relationship between strength and porosity is not linear, and is determined not only by the absolute value of porosity, but also by the characteristics of the porous texture of the aggregate (pellet). For this reason, equations proposed for various materials and sintering conditions, reflecting the dependence of strength on porosity, are represented not only by power law (predicted theoretically), but also by hyperbolic, exponential functions.

The data on the change in the porosity of the aggregates during sintering of iron oxides of different fractional composition (in the form of briquettes obtained at different pressing pressures) in a wide temperature range is shown in Table 2.15.

Table 2.15 Dependence of the porosity of iron oxides on temperature^a

Material	Size (mm)	P^b (kg/cm ²)	Roasting temperature (°C)					
			900	1000	1100	1200	1300	1350
Magnetite	−0.1	1000	34.0	29.8	—	20.9	24.7	—
	−0.05	2000	37.0	27.6	—	15.9	14.3	—
	−0.05	1000	34.8	30.8	—	18.1	18.0	—
	−0.05	500	31.4	30.2	—	23.7	16.5	—
Oxidized magnetite	−0.1	1000	56.3	33.3	—	28.6	22.0	—
	−0.05	2000	34.0	31.0	—	23.8	20.1	—
	−0.05	1000	32.6	26.0	—	24.4	21.4	—
	−0.05	500	41.5	40.1	—	35.2	27.0	—
Hematite	−0.1	1000	—	25.0	20.3	17.9	14.2	—
	−0.05	1000	—	22.3	17.7	17.1	15.4	14.6
	−0.05	500	36.5	25.8	30.0	18.9	22.7	—
	−0.05	200	—	27.2	31.9	25.2	20.8	—

^aRoasting duration 60 min

^b P —oxide briquette pressing load

The strength values of iron oxides depending on the porosity of the aggregate are shown in Fig. 2.35 and summarized by empirical dependence:

$$\sigma = 34,700 \cdot \exp(-7.7 \cdot \varepsilon) \tag{2.5.55}$$

Since the change in porosity is the result of sintering, manifested through the shrinkage of the aggregate, it is obvious that the latter is involved in the strengthening of the aggregate, which can be described by an empirical equation:

$$\sigma = \exp(a + b(\Delta l/l)), \tag{2.5.56}$$

where

σ —unit strength, kg/cm²;
 $\Delta l/l$ —shrinkage, %
 a, b —coefficients (Table 2.16).

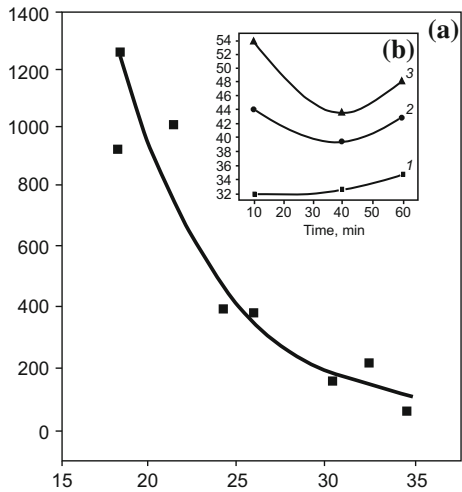


Fig. 2.35 Dependence of unit strength on its porosity. **a** Strength, kg/cm²; abscissa axis—porosity, %; y-axis—crush strength, kg/cm². **b** Pore healing kinetics; numbers on curves—starch content: 1—without starch, 2–5%, 3–10%; magnetite, temperature 1250 °C, atmosphere—argon; roasting time 60 min; abscissa axis—time, min; ordinate axis—average pore size, microns

Table 2.16 Coefficients of the empirical Eq. (2.5.56)

Material	a	b	The correlation coefficient
Magnetite	4.15 ± 0.4	0.4 ± 0.1	0.93
Oxidized magnetite	5.34 ± 0.18	0.225 ± 0.06	0.94
Hematite	6.35 ± 0.14	0.048 ± 0.006	0.99

The reduction of the free surface energy of an ensemble of pores in an aggregate (pellet) can be realized by two processes:

- healing of individual pores, accompanied by shrinkage (sintering);
- coalescence of pores, which occurs due to the merging of individual pores with their constant volume.

Let us estimate to what extent these processes are likely. Suppose that the pellet has n then with a radius of r . Free sintering surface energy (F_s) is expressed as:

$$F_s = 4 \cdot \pi \cdot r^2 \cdot \gamma \cdot n, \quad (2.5.57)$$

where

γ —surface tension.

Let us assume that in the case of coalescence, all the n pores are united into single pore with radius R . The change in surface energy in this case will be:

$$F_c = 4 \cdot \pi \cdot \gamma \cdot (n \cdot r^2 - R^2) \quad (2.5.58)$$

From the condition of preserving the pore volume, it is easy to obtain a ratio for R and r :

$$R = n^{1/3} \cdot r \quad (2.5.59)$$

Substituting (2.5.59) into (2.5.58), we obtain for F_c :

$$F_c = 4 \cdot \pi \cdot r^2 \cdot \gamma \cdot n \left(1 - n^{-1/3} \right) \quad (2.5.60)$$

The ratio F_s/F_c from (2.5.57) and (2.5.60) will be:

$$k = F_s/F_c = 1 - n^{-1/3} \quad (2.5.61)$$

It is obvious from (2.5.61) that, for large n (i.e., $k \sim 1$), the process of coalescence of pores and sintering is thermodynamically equiprobable.

A study of the kinetics of pore healing was carried out [96] on a model system consisting of magnetite and 1, 2, 5, 10% starch, during heat treatment in argon and at a temperature of 1250 °C (Fig. 2.35b). The kinetic curve for pore size is described by an extremum function, in which the downward branch responds to the pore healing process (with a corresponding decrease in its size), and the upward branch (after a long processing time) is due to the development of the coalescence of pores. Note that in real conditions of heat treatment of pellets, the process of coalescence of pores does not receive development due to the short processing time in the burning zone.

The healing of pores is realized through the mechanisms of mass transfer and, along with the kinetics of shrinkage, provides information on the transport mechanism.

According to [60], the criterion for the action of a mechanism is the parameter χ (2.5.62), which, depending on the properties of the medium containing the pore or ensemble of pores, takes on certain values. The dimensionless parameter χ is the ratio of the pore size and the average distance between sources and vacancy drains, which in turn are determined by the type and density of defects in the crystalline oxide.

$$\chi = R/d, \quad (2.5.62)$$

where

R is the average pore size;

d is the average distance between sources and vacancy drains (e.g., grain size, mosaic block, distance between dislocations)

When $\chi < 1$, the mechanism of diffusion pore dissolution, which consists in the vacancy dissolution of the pore, will be decisive; when $\chi > 1$, healing of the pore is carried out by means of diffusion-viscous flow.

2.6 Metallurgical Properties of Iron Ore Pellets

2.6.1 Pellet Quality Test Methods

Iron ore pellets, as well as sinter, are the charge component of blast furnace smelting (in some countries, the charge for blast smelting is 100% of pellets, in Russia in the range of 15–62% [97]). The global trend of increasing the share of pellets in the blast furnaces of those blast furnaces makes the requirements for the quality of pellets a necessary condition for ensuring highly efficient operation of blast furnaces.

As with sinter (Sect. 1.7), in relation to pellets as a raw material component of blast smelting it is advisable to distinguish three groups of properties: indicators of manufacturability, transportability, environmental friendliness. Transport quality indicators in the case of pellets are essential because of their long-distance transport, not just technological overloads.

A set of indicators of the quality of pellets, reflecting the above-selected groups of properties, and methods for their determination are presented in Table 2.17.

Test methods and quality indicators of pellets should simulate the behavior of this type of raw material during further metallurgical processing. Thus, the strength characteristics of the pellets (compressive failure force, impact or abrasive failure parameters) reflect the dynamic conditions that are formed during transport and overload during the delivery of pellets to the blast furnace, as well as during movement in the blast furnace shaft, complicated by reduction processes.

Table 2.17 Indicators of the quality of iron ore pellets and methods for their determination

Property (level of quality)	Equipment, measuring principle	Defined parameters
<i>General properties</i>		
Granulometry	Different sets of sieves with apertures: 0.5; 0.6; 1; 3; 5; 8; 10; 15; 16; 18; 20; 25; 40; 50 mm	di, % in the sieve, $d_{\min}$, $d_{\max}$
Chemical composition	Analytical equipment	Fe, FeO, Fe ₂ O ₃ , CaO, MgO, SiO ₂ , Al ₂ O ₃ , P, S, and others (if required), %
Mineralogical composition	Method of ore microscopy in reflected light (microscopes for ore microscopy, including with analyzers)	Quantitative assessment of the phase content: hematite, magnetite, mineral binder, pores, micro-cracks
Physical properties	Pycnometer; measuring capacitances at 1, 3, 5 dm ³	Bulk mass, density (true, apparent), open porosity
	Russian Standard GOST 15165-69 [8]	Apparent density
<i>Metallurgical properties</i>		
Mechanical strength (cold strength)	Crush test diameter of pellet 12–15 mm, not less than 20 pellets GOST 24765-81 [98] Machine MP-0.5–1	Strength, kg/pellet
	Tumble test ISO 3271-75, LKAB, Sweden [98] (drum d 1000 × 500 mm, 2 shelves, rotation speed 25 ± 1 rpm, only 200 rpm, loading 6.3–40 mm sinter in the amount of 15 kg)	Impact strength +6.3 mm, %; abrasion –0.5 mm, %
	ASTM tumble test, USA (drum d 914 × 457 mm, 2 shelves, rotation speed 24 ± 1 rpm, only 200 rpm, sinter 10–50.5 mm is loaded in the amount of 22.5 kg)	Impact strength +10 mm, %; yield of fractions 6–3 mm, % 3–0.6 mm, %; abrasion –0.6 mm, %
	Tumble test Lurgi, Germany (3) (drum d 914 × 457 mm, 2 shelves, rotation speed of 25 rpm, only 200 rpm, sinter of 8 mm is loaded in the amount of 11.34 kg)	Impact strength +5 mm, %; abrasion –0.6 mm, %
	Tumble test IISM-8712, Japan [98] (drum d 914 × 457 mm, 2 shelves, rotation speed 24 ± 1 rpm, only 200 rpm, sinter of 5 mm is loaded in the amount 230.23 kg)	Impact strength +5 mm, %; abrasion –1.0 mm, %
	Tumble test GOST 15137-94 (drum d 1000 × 500 mm, 2 shelves 50 mm wide; sample weight 15 kg fraction 5–40 mm, bar-ban rotation frequency 25 rpm, duration 8 min)	Impact strength +5 mm, %; abrasion –0.5 mm, %

(continued)

Table 2.17 (continued)

Property (level of quality)	Equipment, measuring principle	Defined parameters
Reducibility, rate of reduction	Gravimetric estimate at a constant temperature for reducing pellets:	
	ISO 4695 Reduction time 40 min, Weight loss during reduction	Reducibility, %/min
	The mass of 1 kg with particle sizes of 5–8, 11.2–16, 31.5–40 mm; Reducing atmosphere 40% CO, 60% N ₂ , 60 min [99]	Reducibility RI, %; rate of reduction V_{40} , O ₂ /min, additionally—fraction –0.5 mm, %
	GOST 21707-76 A mass of 300 g of a fraction of 10–15 mm is reduced in a stream of hydrogen at 800 °C for 60 min with continuous control of the mass [100]	Reducibility RI, %; rate of reduction V_{40} , O ₂ /min
Reduction disintegration (hot strength) Thermoplastic properties	Reduction at certain temperatures, gas composition, loads, duration	The level of destruction at the output of the fines fraction, % The degree of reduction, %
	RDI, Japan (500 g of pellets, 15–20 mm fraction is reduced at 550 °C for 70 min with gas of composition: 30% CO, 70% CO ₂ , with a drum rotation frequency of 30 rpm; then after cooling in N ₂ current the sample is subjected to dynamic effects in the drum 130 × 200 mm with a rotation speed of 60 rpm for 5 min)	The reduction disintegration index is determined RDI ₊₃ , %
	Lurgi (Germany, USA) (500 g of pellets with a fraction of 10–22 mm is reduced when the temperature changes (20–700 °C; 700–1000 °C) in a current of 30% CO, 10% CO ₂ at the 1st stage; 35–38% CO, 5% CO ₂ , 2% H ₂ at the 2nd stage, in a drum 160 × 150 mm with a revolutions of 9 rpm, cooled in an inert gas	The reduction disintegration indexes are determined RDI ₊₆ ; RDI ₊₃
	GOST 27446-87 (500 g of pellets, fraction 15–20 mm is reduced at 500 °C for 30 min with a gas of composition: 20% CO, 20% CO ₂ , 60% N ₂ , then after cooling in a current N ₂ , the charge is subjected to dynamic effects in the drum 130 × 200 mm for 30 min) [101]	The reduction disintegration index is determined RDI _{+6,3} , %

(continued)

Table 2.17 (continued)

Property (level of quality)	Equipment, measuring principle	Defined parameters
	Heating of samples of pellets with a weight of 30 g of a fraction of 5–8 mm at a rate of 10 °C/min without air access (in a reducing atmosphere) to 1580 °C under a load of 0.5 kg/cm ²	The temperatures of the beginning and end of the softening, the softening interval are determined
	A sample with a particle size of 2–3 mm is placed in a 40 mm layer in a cylindrical cup made of heat-resistant steel with a diameter of 20 mm, on which is placed in an electric furnace heater. The cylinder is covered with a piston with a rod, which exerts pressure on the sample of 0.2 MPa. The sample is heated at a rate of 10 °C/min to a temperature of 1400 °C, recording the volume changes of the sample (according to the position of the rod) [100]	The temperatures of the beginning and end of the softening, the softening interval is determined

2.6.2 Quality Requirements for Pellets

Chemical composition

Fe Content. The pellets are produced from iron ore concentrate produced by various enrichment methods (due to the significant world reserves of ferruginous quartzite involved in mining, the method of wet magnetic separation is most common). In view of this circumstance, iron ore concentrates are characterized by a rather high iron content of 58–68% (Table 1.1). For special purposes (in particular, for the production of metallized pellets or briquettes), an additional concentrate with an iron content of 70% or a high-quality concentrate with an iron content of 72% is obtained by further enrichment.

Depending on the type of source ore processed, the iron content in it, the beneficiation process plan, and the destination of the pellets, each particular producer establishes certain technical conditions for the concentrate, including the content of iron in it.

At the same time, there is a point of view [11] that the optimal depth of concentrate enrichment (or iron content) should be determined on the basis of technical and economic considerations, comparing the additional enrichment costs with economic preferences obtained in blast furnace smelting. Reducing the amount of gangue in super-rich concentrates is accompanied by a decrease in the hot strength

of pellets produced from such concentrates, and levels the effects in blast furnace smelting from the use of raw materials with high iron content. According to an approximate estimate [11], to ensure proper hot strength of the pellets, 10–12% of the melt is sufficient (or the content in the pellets is 3.0–3.5% SiO_2).

Basicity. The world produces non-fluxed and fluxed pellets. The basicity of the pellets is in the range of 0.15–1.4. The increase in basicity over the specified range is not possible due to the adhesion of the pellets due to the formation of significant amounts of the liquid phase.

As a rule, the manufacturer determines the basicity level acceptable for the quality indicators of pellets, and the basicity of the blast furnace charge is adjusted by the basicity of the sinter.

FeO Content. For pellets, the content of FeO is an indicator of the completeness of magnetite oxidation and to a certain extent serves as a universal indicator of quality. The zonal structure in the form of a magnetite core and an outer shell oxidized to hematite causes a low strength of the pellets due to the formation of concentric cracks along the boundary of the core and the outer shell when the pellets are cooled. Ordinarily, the content of FeO is regulated at a level of up to 2%, but if the technology of heat treatment of pellets is insufficiently adjusted, the content of FeO can reach 12% [102].

Stability of chemical composition. It is determined by the conditions of averaging concentrate at the concentrating plant or pelletizing plant. As in the case of the sinter, it is set by the deviation parameter from the calculated content (in terms of Fe content, basicity). The deviation value for Fe is $\pm 0.2\%$, for basicity— $\pm 0.02\%$ [11].

Content of harmful impurities. In iron ores, sulfur in most cases is in the form of iron sulfides (pyrite FeS_2 , pyrrhotite FeS_{1+x}). When heated in an oxidizing atmosphere, iron sulfides are oxidized to form SO_2 (at temperatures above 1000 °C) and SO_3 (at temperatures below 600 °C) [2].

In the production of non-fluxed pellets, there are no problems with the removal of sulfur, despite the possibility of the formation of secondary ferrous sulfate. But in the production of fluxed pellets, the formation of secondary calcium sulfate, which is a fairly strong compound, can complicate the removal of sulfur. The main factor determining the efficiency of desulfurization of pellets during roasting is the heat treatment temperature (Fig. 2.36). Increasing the firing temperature to 1300 °C leads to a decrease in the sulfur content in the pellets to 0.01–0.03%.

Strength

With regard to pellets, the priority metallurgical property is technological and transport strength.

Fired pellets must be resistant to softening during transportation from the moment of leaving the conveyor machine to loading into the blast furnace, whatever the length of this path and whatever number of overloads this path is followed, and also when moving in a blast furnace.

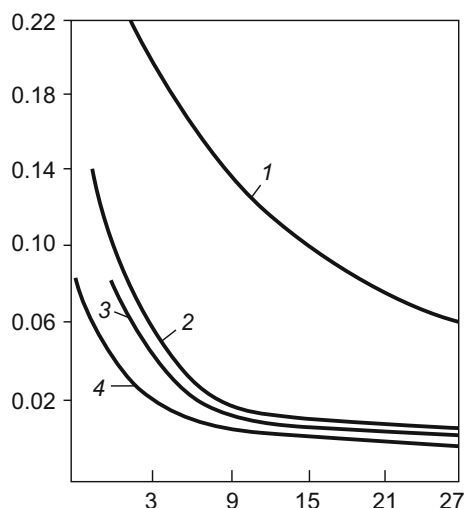


Fig. 2.36 Efficiency of sulfur removal from pellets [2]. 1, 3—basicity of the pellets 1,46; 2,4—non-fluxed pellets; 1,2—1200 °C; 3,4—temperature 1300 °C; abscissa axis—roasting time, min; Y-axis—sulfur content in pellets after roasting, %

The pellets must withstand a load of at least 2–2.5 kN without destruction, and the tumble test result (yield of fraction with sizes smaller than 5 mm) must be no more than 4–5% [8]. On average, compressive strength is estimated to be at a level no lower than 150 kg/pellet (ISO 4700), while the content of pellets with strength below 60 kg/pellet should not exceed 4% [103]. Tumble test result (yield of fraction with sizes larger than 6.3 mm) should not be below 95%, and the yield of the fraction with size smaller than 0.5 mm should be below 5%.

Depending on the composition of the pellets, the cold crush strength can be characterized by the values presented in Table 2.18 [103].

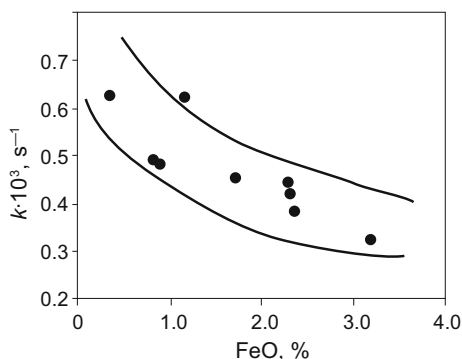
Table 2.18 Typical pellet compositions and cold strength values

Type of pellets	Basicity CaO/SiO ₂	Fe (%)	SiO ₂ (%)	MgO (%)	Compressive strength (kg/pellet ^a)
Acid pellets	<0.15	64–67	2–5	<0.2	250–300
Olivine pellets	<0.15	64–67	2.5–5	1.3–1.8	150–200
Low basic pellets ^b	<0.5	60–66	3.0–5.5	до 1.3	До 250
Basic pellets	до 0.8–1.0	60–64	3.5–5.5	1.3	200–250
Fluxed pellets	до 1.1–1.3	60–63	3.5–5.5	1.5	200–250

^aFor transfer to N/pellet: $10 \cdot N/\text{pellet} \sim 0.98 \text{ kg/pellet}$

^bAccording to [104]

Fig. 2.37 Dependence of the rate constant of reduction on the content of FeO in the pellets (reduction temperature 600 °C, reducing gas—H₂) [8]



The hot strength of the pellets (in the yield of the fraction greater than 6.3 mm after reduction) must be higher than 80% and the yield of the fraction less than 0.5 mm lower than 15% [103].

Reducibility

The main mineral component of calcined pellets is represented by hematite, which belongs to easily reducible phases; therefore, compared with sinter, pellets have higher rates of reduction. Reduction rate (%/min) must be at least 0.8%/min [103].

In [105], when studying the kinetics of pellet reduction, it was shown that there is a relationship between the effective reduction rate constant and the content of FeO. The lower the FeO content, the higher the effective reduction rate constant, which makes it possible to predict the recoverability of the pellets from the FeO content (Fig. 2.37).

Softening (temperature of the beginning of (t_b) and end of softening (t_f)).

The parameters t_b and t_f are determined by the mineralogical composition of the pellets (in turn, depending on the chemical composition of iron ore concentrate and additives).

In summary, it should be noted that high-quality pellets should have the following characteristics [106]:

- uniform size or optimal particle size, size 8–16 mm more than 90% (ISO 4701), fraction content –6.3 mm not more than 5%;
- homogeneous and favorable chemical composition;
- low content of harmful impurities (including alkaline components);
- homogeneous and favorable phase composition (the minimum possible content of magnetite);
- favorable cold strength (strength indicator %);
- a favorable indicator of hot strength ($RDI_{-3.15}$ not more than %);
- favorable reducibility;
- high softening and melting temperature (depending on the overall composition of the mixture);
- narrow softening interval;
- low tendency to stick together.

Table 2.19 Requirements for the metallurgical properties of pellets for blast furnace smelting [107]^a

No.	Metallurgical properties	Value of parameter
<i>Physico-mechanical properties</i>		
1	Fractional composition of pellets (mm)	8–18 (8–16)
	– yield of pellets (% mass)	>90.0
	– fines content (<5 mm) (% mass)	<5.0
2	Compressive strength σ (kN/pellet)	2.0–3.0 (>1.5)
3	Tumble test	
	– impact strength N (>5 mm) (% mass)	95.0
	– abrasion index I (<0.5 mm), (% mass)	<3.0 (<5.0)
<i>Properties during reduction</i>		
4	Hot strength	
	– yield of fraction >5 mm (% mass)	>80.0
	– yield of fraction <0.5 mm (% mass)	<5.0 (<15.0)
5	Swelling (%)	<12.0
6	Reducibility (%/min)	>0.5 (>0.8)
<i>Stability of composition</i>		
7	Allowable fluctuations in composition	
	– iron content, % mass	–0.2
	– basicity	–0.02

^aValues in brackets according to [103]

A quantitative measure of the requirements for the metallurgical properties of pellets in the aspect of the efficiency of blast smelting is presented in Table 2.19.

2.6.3 Basic Solutions for Improving the Quality of Pellets

The pellet can be considered as a complex of equal-sized grains of the crystalline phase with a size “ d ”, the gaps between which are filled with a bonding phase (bond), which is either amorphous (glass) or a disordered structure of the crystalline phase, with an average statistical distance between the grains “ a ” [2].

Let us denote the strength of the crystalline phase σ_{cr} , the strength of the binding phase σ_b , the bond strength between the crystalline and binding phase (with “ a ” 0), or the cohesive bond between the grains of the crystal phase (with “ a ” = 0) σ_a . In this model, depending on the ratio of phase strengths, three types of destruction are possible:

- by the grains of the crystalline phase (conditions of the lowest strength: $\sigma_{cr} < \sigma_a < \sigma_b$ or $\sigma_{cr} < \sigma_b < \sigma_a$ for “ a ” 0; $\sigma_{cr} < \sigma_a$ for “ a ” = 0);
- on the binding phase (the conditions of the lowest strength: $\sigma_b < \sigma_a < \sigma_{cr}$ or $\sigma_b < \sigma_{cr} < \sigma_a$ for “ a ” $\neq$ 0; for “ a ” = 0, there is no binding phase;

- on the border between the crystalline and bonding phases (conditions of the smallest strength: $\sigma_a < \sigma_b < \sigma_{cr}$ or $\sigma_a < \sigma_{cr} < \sigma_b$ for “a” 0; $\sigma_a < \sigma_{cr}$ (for “a” = 0).

Thus, an increase in the strength of the pellet will be facilitated by measures aimed at strengthening the crystal matrix (Sect. 2.6.3.4), the binder phase (Sect. 2.6.3.3), and the improvement of the interfacial interactions.

2.6.3.1 Optimization of the Ratio of Fine and Coarse Fractions of the Concentrate

The regulation of the granulometric composition of the concentrates entering the pelletizing, aims to influence the porous structure of the pellet. It should be taken into account that the initial density of the pellet has an ambiguous impact on the strengthening process. On the one hand, an increase in density leads to an increase in the number of contacts between particles and is thus favorable for strengthening. On the other hand, a decrease in porosity hinders the process of magnetite oxidation, which is a negative factor for strength. It is for these circumstances that when mixing concentrates of various sizes, it is necessary to choose their optimal mix ratio, proper pelletizing mode, and rational pellet firing.

There are solutions for strengthening pellets by optimizing the structure of the granules by mixing concentrates of different dispersity. The granulometric composition of the concentrates is shown in Table 2.20.

The results of strengthening experiments on pellets with a different ratio of concentrates K_1 and K_2 , respectively (10:90; 30:70; 50:50; 70:30; 90:10), are shown in Fig. 2.38.

The best indicators of cold strength are given by the ratio of “fine” and “coarse” concentrates as 70:30 with the minimum strength of pellets in the case of a 50:50 ratio of concentrates.

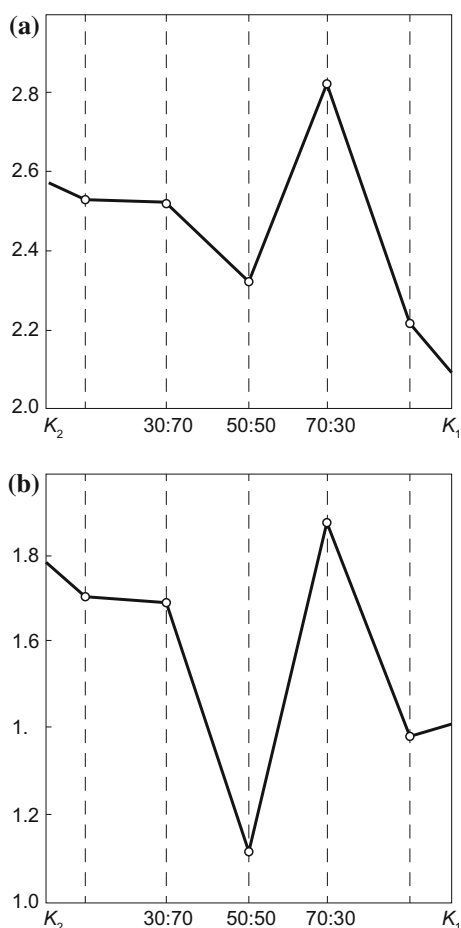
The characteristics of the microstructure of the pellets obtained by mixing “fine” and “coarse” concentrates for extreme values of strength (Fig. 2.37) are given in Table 2.21.

The cold strength of the pellets increases with a decrease in the total porosity and a decrease in the average equivalent pore size (Table 2.21).

Table 2.20 Granulometric composition of concentrates (LebGOK, Russia)

Fraction	The contents of the fraction (%)	
	Fine concentrate K_1	Coarse concentrate K_2
–0.044 mm	90.3	80.8
0.044– 0.074 mm	8.6	15.7
+0.074 mm	1.1	3.5

Fig. 2.38 Cold strength of pellets made from a mixture of concentrates (roasting temperature 1280 °C, **a** bentonite content of 0.5%; **b** the content of bentonite 0.25%). The abscissa axis is the ratio of the concentrates in the mixture, %; ordinate axis —strength of calcined pellets, kN/pellet



2.6.3.2 Minimization of the Zonal Structure of the Pellet

In industrial conditions, pellets obtained from concentrates produced from ferruginous quartzites are often characterized by a zonal structure, represented by a magnetite (Fe_3O_4) core and an outer hematite (Fe_2O_3) shell, separated by deep concentric and radial cracks, sometimes overlying the surface of the pellet. Ferruginous quartzites contain alkaline silicates.

The magnitude of the magnetite core depends on the diameter of the pellet. The largest sizes of cores 6–8 mm were observed in pellets with a diameter of 10–12 mm. With a decrease in the diameter of the pellet to 8–10 mm, the size of magnetite cores decreased to 3–4 mm [102]. The core zone of the pellets is represented by the mineral composition of magnetite and iron silicate glass phase of complex composition. The outer oxidized shell consists of large crystals of hematite, the space between which is

Table 2.21 Characterization of the microstructure of pellets obtained from a mixture of concentrates

No.	Characteristics of iron ore pellets	Distribution of pore size		The distribution of distances between the pores	
		Average size (μm)	Share (%)	Average size (μm)	Share (%)
1	Pellets from mixtures of concentrates of K_1 and K_2 at a ratio of 50:50	14.4	79.2	14.4	72.3
		40.8	18.3	37.2	24.1
		60.0	1.0	68.8	3.1
		100.8	1.5	120.0	0.5
	Average equivalent size (μm)	21.02		22.09	
	Total porosity (%)	48.76			
2	Pellets from mixtures of concentrates of K_1 and K_2 at a ratio of 70:30	13.0	86.9	15.2	60.6
		39.0	12.0	43.2	32.8
		72.0	1.1	70.0	4.4
				90.0	2.2
	Average equivalent size (μm)	16.77		28.44	
	Total porosity (%)	37.09			

filled with a small porous mass of needle-like hematite crystals formed during oxidation, with a limited development of the glass phase.

The transformation of high-silicate alkali silicates of the concentrate into the glass phase (binder) of pellets occurs during oxidative roasting at the stage of liquid-phase strengthening. The glass phases are complex silicon-containing amorphous formations, in the composition of which almost all components of the charge are found: calcium, aluminum, and magnesium flux; silicon and alkali silicates of the iron ore part; iron fraction of the concentrate.

In case of under-oxidation of the pellet in the zones of moderate temperatures, the melt blocks the magnetite core and causes the formation of zonal pellets with low strength properties.

In order to obtain oxidized pellets from concentrates of ferruginous quartzites with high strength properties (minimizing the zonal structure), a different temperature-time firing mode is proposed (Fig. 2.39).

The new mode provides for an increase in the residence time in the heating zone from 5 to 6.5 min with a reduction in the duration of high-temperature roasting to 5 min.

2.6.3.3 Introduction of Modifying Additives

The strength of the pellets, especially the hot strength, is essentially determined by the presence and properties of the binder phase.

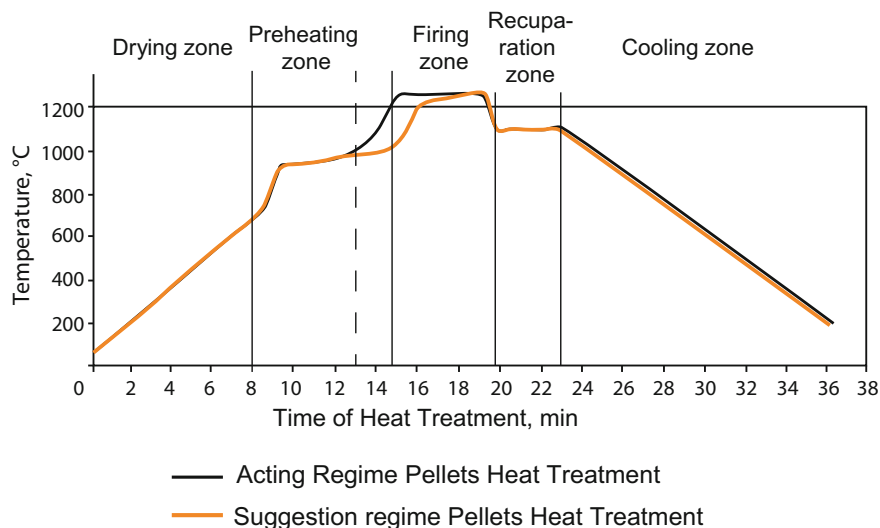


Fig. 2.39 Mode of oxidative roasting (implementation on an industrial roasting machine with the sintering area of 306 m², [108])

The volume fraction of the liquid phase (silicate binder) in the fluxed pellets during their heat treatment is approximately 10–12%, with the prevalence of easily reducible calcium ferrites. Non-fluxed and fluxed pellets with modifying additives, made of magnetite concentrate¹⁴ with 70% Fe, have a volume fraction of the liquid phase of about 5%. With the introduction of bauxite, an aluminum-containing bond of the Brownmillerite type is formed, stronger and more difficult to reduce than ferritic [105].

Analysis of the most important indicators (hot strength and reducibility), as well as the properties and composition of the binder, showed that the optimal ratio of modifying additives is 1% bauxite +1% limestone, as well as 1% bauxite¹⁵ +1% siderite (Table 2.22).

The influence of the properties of the binder phase is due to the addition of the MgO-containing component to the charge in the production of fluxed pellets.

According to [104], when fluxing iron ore pellets in the range of 0.5–1.2, the introduction of dolomite with an MgO content in the range of 0.5–1.8% makes it possible to increase the strength of fired pellets by 28.9 kg/pellet for every 1% growth MgO.

¹⁴Concentrate of MikhGOK, Russia.

¹⁵Bauxite is a rock that is based on aluminum hydroxide Al (OH) 3; siderite—FeCO₃.

Table 2.22 Effective reduction rate constant^a for pellets with modifying additives [105]

Name	Composition (%)						
Bentonite	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Limestone	3	1	0	3	0	1	0
Bauxite	0	1	1	1	0	1	0
Siderite	0	0	1	0	2	0	0
$k \times 10^3, \text{s}^{-1}$ (at 600 °C)	0.44	0.45	0.62	0.41	0.48	0.38	0.63

^aThe effective rate constant k is determined from the equation $\varphi = 1 - e - k\tau$, where φ is the degree of recovery, of a fraction; τ is time

2.6.3.4 Oxide Structure Defect Management

The heterogeneity of the stress state, which causes a decrease in the strength of the pellet, is aggravated by such factors as the difference in the physical properties of the phase components (thermal expansion coefficient, elastic limit, etc.), the presence and types of structure defects.

To assess the effect of imperfections of the structure on the strength of the pellets, crush tests were performed on two sets of samples: highly porous pellets pelletized at a concentrate moisture content of 11% and dense briquettes pressed at a pressure of 14.71 MPa (which corresponds to the loads pellets in industrial aggregates).

The nature of the change in strength (Table 2.23) shows that the oxidation conditions (oxygen partial pressure, temperature, duration) are decisive strengthening factors.

The strength of the aggregates obtained by oxidation with P_{O_2} equal to 0.1 MPa, under conditions adequate in heat treatment time, is about two times higher than with oxidation with P_{O_2} equal to 0.02 MPa, regardless of the absolute value of the firing time (Table 2.23). Therefore, to obtain a high level of strength, it is necessary

Table 2.23 Change in the strength of the unit, depending on the oxidation conditions of magnetite [109]

Oxidation time (min)	Roasting time ^a (min)	Oxidation temperature (°C)	The partial pressure of oxygen P_{O_2} (MPa)	Compressive strength (N/cm ² $\times 10^{-4}$)
10	10	600	0.1	1.02
10	10	600	0.02	0.44
10	10	1000	0.1	1.60
10	10	1000	0.02	0.80
2	18	1000	0.1	1.99
3	17	1000	0.02	1.03
2	10	1000	0.1	1.46
3	10	1000	0.02	0.76

^aRoasting temperature 1250 °C

to oxidize in such a way that the emerging structure of the pellets is characterized by fine grains and grain aggregates and a high concentration of deformation defects of the package (see Sect. 2.5.3.5). These requirements are met by the oxidation regime with an increased concentration of oxygen in the gas phase.

From the analysis of the defective structure of hematite (see Table 2.14, Sect. 2.5.3.4) resulting from oxidation, it follows that with differing concentrations of deformation packaging defects, micro-strain within the blocks, as well as their sizes are close in their values. Consequently, the deformation defects of the packaging are concentrated not at the volume, but at the grain boundaries. When the particle size is comparable with the grain size in the case of dispersed materials, the deformation packaging defects are localized at the interface. On the other hand, the interface is the source of dislocations (in particular, deformation packaging defects) during crystal growth [110]. When oxidized, such a source can be the hematite–magnetite phase boundary due to its high elastic energy. This is vividly illustrated by the dependence of the probability of the formation of deformation packaging defects on oxidation conditions, that is, the conditions for the nucleation and growth of a new phase. In other words, the initiation of hematite–magnetite and magnetite–hematite phase transitions at high temperatures, on the one hand, causes the generation of deformation packing defects, and, on the other hand, ensures their annealing. These processes together contribute to the intensification of mass transfer, i.e., sintering.

The generation of Fe_3O_4 oxide at a high calcination temperature can be caused by reducing the partial pressure of oxygen, thereby stimulating the dissociation of hematite at a lower temperature than the equilibrium for the partial pressure of Po_2 (0.02 MPa). The subsequent oxidation of the newly formed magnetite leads to the formation of highly defective Fe_2O_3 oxide.

Thus, by organizing repeated (cyclic) changes in the oxygen partial pressure (in other words, concentration non-stationarity) in the process of high-temperature calcination, it is possible to significantly increase the strength properties of the pellets.

The scheme of such a firing mode is presented in Fig. 2.40. The processing cycle includes the pre-oxidation of magnetite to the high-temperature zone by the gas phase with a maximum oxygen content of Po_2 (0.1 MPa or 0.02 MPa) followed by dissociation of hematite at a partial pressure of 10^2 Pa. The duration of calcination at a given partial pressure of oxygen is determined by the half-cycle (cycle) length. Such a cycle can be repeated many times.

The result of the intensification of mass transfer in the organization of the calcination variant that is non-stationary in oxygen partial pressure is manifested in an increase in the strength of the samples (Fig. 2.41), which, under optimal conditions, can be up to 40%.

2.6.3.5 Regulation of Liquid-Phase Sintering

Sintering in the presence of a liquid phase (melt) is one of the effective ways to increase the hot strength of the pellet.

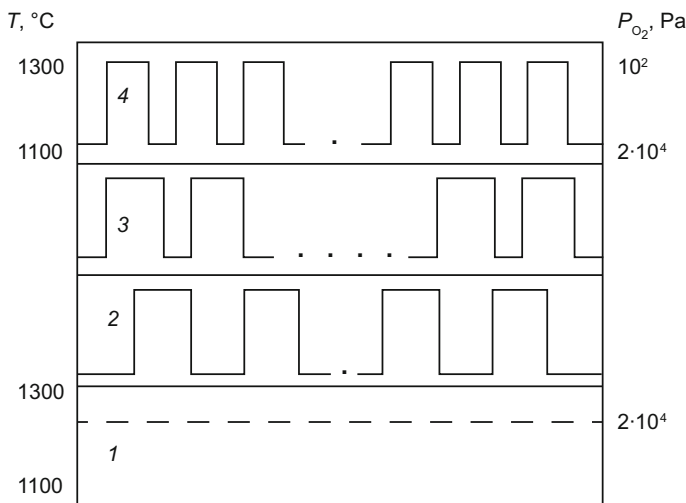


Fig. 2.40 Options for non-stationary heat treatment modes (1—basic mode; 2, 3, 4—non-stationary modes, characterized by the half-period length (2, 3), and the number of cycles (4). The abscissa axis is the duration of heat treatment, min; the axis of ordinat is the treatment temperature, °C

Fundamental as measures for regulating the process of liquid-phase sintering are two directions:

- ensuring the proper amount of the liquid phase (optimal concentration of the concentrate, fluxing (see Sect. 2.1.1), etc.);
- ensuring the quality of the liquid phase by introducing additives that determine the change in the surface tension of the melt, wettability, viscosity.

A prerequisite for increasing the strength of the pellets during liquid-phase sintering is high liquid mobility of the melt (low viscosity) and good wettability of the solid phase. With good wettability, the liquid mobile melt spreads over the surface of the solid phase, increasing the total area of interparticle contacts.

The criterion of the liquid-phase hardening can be taken as the parameter of the rate of impregnation rate K_s :

$$K_s = (d \cdot \sigma \cdot \cos \theta) / 2 \cdot \eta, \quad (2.6.1)$$

where

d is the average pore size;

σ is the surface tension of the melt;

θ is the wetting angle with the melt of the solid phase;

η is melt viscosity.

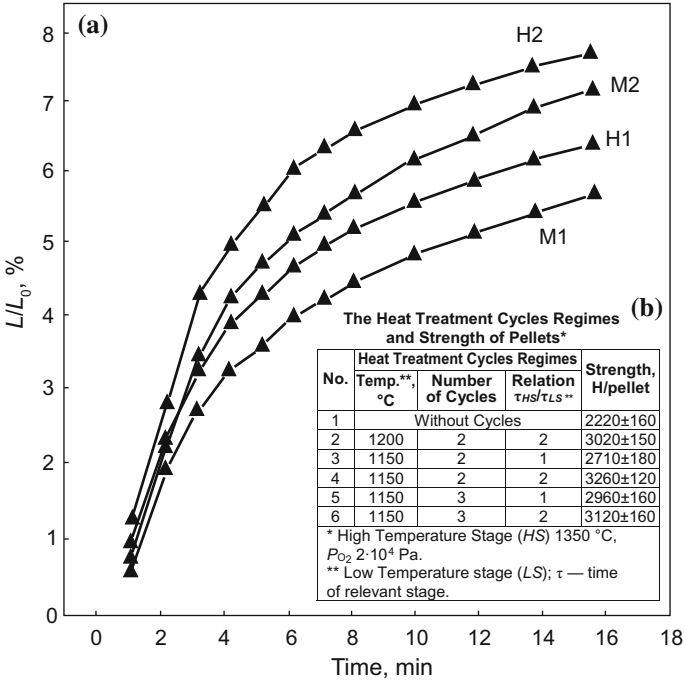


Fig. 2.41 Intensification of mass transfer in the transient calcination mode (a—shrinkage kinetics of the samples ($\Delta l/l$) during sintering, temperature 1300 °C; M1, M2—primary magnetite, secondary magnetite (after dissociation); H1, H2—primary hematite, secondary hematite; b—dependence of the strength of the samples on the number of processing cycles; 1—concentration non-stationarity $P_{O_2} = 10^2$ – 2×10^4 Pa, temperature 1250 °C; 2— $P_{O_2} = 10^2$ – 2×10^4 Pa, temperature 1300 °C; 3— $P_{O_2} = 10^2$ – 10^5 Pa, temperature 1250 °C; 4— $P_{O_2} = 10^2$ – 10^5 Pa, temperature 1300 °C)

Impregnation takes place only if $\cos \theta > 0$. The impregnation rate is the higher, the higher the wettability, the surface tension and the lower the melt viscosity.

The characteristics of some melts (viscosity and surface tension) are shown in Table 2.24.

As the melt basicity increases, the viscosity of the melt decreases and the surface tension increases. The viscosity of the melt, which is close in composition to $2FeO \cdot SiO_2$, at a temperature above 1300 °C lies in the range of 0.1–0.15 Pa s.

Strong bonds at the interphase boundaries upon contact of the oxides with the silicate melt are created when the surface of the oxides is wetted and characterized by the work of adhesion W_A :

$$W_A = \sigma_{S-G} + \sigma_{L-G} - \sigma_{S-L}, \tag{2.6.2}$$

Table 2.24 Viscosity and surface tension of melts produced during the agglomeration of iron ores [8]

Chemical composition (% mass)					Viscosity ^a -η (Pa s)					Surface tension ^b σ (N/m)				
FeO	Fe ₂ O ₃	SiO ₂	CaO	B ^a	1200	1250	1300	1350	1400	1200	1250	1300	1350	1400
52.50	6.70	31.00	9.80	0.31	0.75	0.20	0.15	0.14	0.12	0.37	0.38	0.39	0.40	0.42
42.00	3.00	33.00	22.00	0.67	0.25	0.14	0.08	0.07	0.06	–	0.42	0.43	0.44	0.45
32.10	6.60	34.00	27.30	0.81	0.26	0.17	0.13	0.1	0.08	0.50	0.51	0.51	0.51	0.52
38.90	1.90	29.20	30.00	1.03	0.21	0.15	0.12	0.1	0.08	0.46	0.46	0.47	0.47	0.48

^aB—basicity CaO/SiO₂

^bViscosity and surface tension at a temperature, °C

where

σ_{S-G} —solid–gas surface tension;

σ_{L-G} —liquid–gas surface tension;

σ_{S-L} —interfacial tension solid–liquid.

2.7 Resource Saving in the Production of Pellets

2.7.1 Resource Consumption in the Production of Pellets

Material resources

The resource base for the production of calcined iron ore pellets is described in Sect. 2.2. The basis of the charge composition for the production of pellets is iron ore concentrate. Approximate compositions of iron ore concentrate from its leading manufacturers in Russia are given in Chap. 1 (Sect. 1.2).

To ensure the strength of raw pellets (and further calcined pellets), binder additives are used (primarily bentonite, as well as complex additives). In the production of fluxed pellets, it is necessary to introduce flux (limestone).

Depending on the iron ore base, the purpose of the pellets, the requirements for their technological and transport strength, strengthening components are introduced into the mixture (for example, olivine, and bauxite).

The consumptions of components in the charge composition for the production of pellets, reflecting the best European practices, are shown in Sect. 2.8 (Table 2.28). Taking into account the experience of pelletizing plants in Russia [15], it should be noted that the consumption of the main material resources for the production of pellets can be characterized by such quantities, kg/t pellets:

- iron ore concentrate—1034 to 1100;
- bentonite—2.5 to 10;
- limestone (for fluxed pellets)—0 to 70;
- bauxite—0 to 12.

Energy Resources

The production of calcined pellets, like other metallurgical technologies, is coupled with high-temperature strengthening processes, the formation of heated waste gases, and the inevitable heat loss, which leads to a significant consumption of fuel and electrical energy.

The consumption of heat energy in the process of production of calcined pellets takes place during heating of the roasting units, drying operations when grinding lumpy materials (flux, binding components of the charge for the production of pellets).

Table 2.25 Energy consumption levels in the production of calcined pellets in relation to roasting units [15]

No.	Parameter	Type of roasting machine			
		OK-306	OK-520	OK-592	L-480
1	The working area of the machine (m ²)	306	520	592	480
2	The height of the layer of raw pellets (mm)	320	325	430	310
Non-fluxed pellets					
3	Specific capacity (t/(h m ²))	0.976	1.2875	1.066	Not produced
4	Specific gas consumption (m ³ /t)	11.84	9.52	10.0	
5	Specific power consumption (kW h/t)	39.95	34.98	36.0	
6	Specific consumption of water (m ³ /t)	2.8	8.32	8.4	
Fluxed pellets					
7	Specific capacity (t/(h m ²))	0.85	1.15	Not produced	1.0
8	Specific gas consumption (m ³ /t)	13.85	13.78		9.4
9	Specific power consumption (kW h/t)	47.8	38.84		39.9
10	Specific consumption of water (m ³ /t)	2.8	8.16		0.326

The main costs of electricity in the production of pellets are caused by the crushing, mixing, transporting, pelletizing, and other equipment in the preparation of the charge, conveyor roasting machine drives, screens for pellet screening, gas cleaning equipment and smoke exhausters, and blower equipment.

The energy consumption levels are determined primarily by the nature of the concentrate (its ability to sinter and to strengthen), the basicity of the charge, as well as the characteristics of the roasting unit. The energy consumption indicators for the best European practices are given in paragraph 2.8 (Table 2.28), taking into account the experience of pellet production factories given below:

- electricity consumption—32.5 to 48.5 kW h/t;
- natural gas consumption—11.6 to 20.2 kg of conventional fuel/t;
- technical water consumption—0.31 to 8.5 m³/t.

The consumption of fuel, electric energy, water in the production of calcined pellets based on specific indicators for some types of roasting machines in Russia are given in Table 2.25.

2.7.2 Energy Efficiency of Conveyor Machines as Units for Pellets Roasting

In contrast to sintering machines, roasting machines are designed in such a way that, to some extent, depending on the organization of gas flows (its thermal circuit), provide for the utilization of secondary energy resources. For example, the hot

Table 2.26 Distribution of the working area of the roasting machine by technological zones

No.	Parameter	Type of roasting machine			
		OK-306	OK-520	OK-592	L-480
1	The working area of the machine (m ²)	306	520	592	480
2	Drying zone area (%)	22.8	20.0	24.3	15.2
3	Heating zone area (%)	17.1	15.4	10.8	22.4
4	Roasting zone area (%)	14.3	12.3	16.2	20.0
5	Recuperation zone area (%)	8.6	6.15	8.2	7.5
6	Cooling zone area (%)	37.1	46.15	40.5	35.0

air from cooling zone 1 is used as the dilution air in the burners of the heated zones of the hearth of the roasting machine. In turn, part of the heat flux of the burning zone is fed to the drying zone; the heat flow of the cooling zone 2 can also be supplied to the drying zone.

The operation of the thermal circuit provides the necessary heat treatment mode for obtaining calcined pellets with a given quality. The thermal scheme of the roasting conveyor machine also determines the main indicators of the efficiency of production of calcined pellets: specific productivity, specific consumption of energy carriers (Table 2.25), as well as the composition and amount of gases evacuated to the atmosphere.

Important components of the heat scheme of the roasting machine are the distribution of the working area of the machine among technological zones (Table 2.26) and the system for providing these zones with the necessary and sufficient amount of heat carrier and cooling agent with the temperature set for specific production conditions and requirements to the quality of the finished product.

An example of the thermal scheme of the roasting conveyor machine is shown in Fig. 2.42.

The heat scheme of the roasting machine determines the direction of movement of the gas flows: the supply to a separate zone of the machine the necessary amount of heat carrier or cooling agent, and to the burner—secondary air; evacuation of low- and high-temperature gas flows from vacuum chambers, the necessary aspiration of work sites.

The thermal circuit includes:

- fans for air supply, smoke exhausters for gas transportation;
- overflow system for supplying heated air in the cooling zone;
- burner devices;
- gas cleaning equipment;
- gas ducts;
- throttle valves to control the flow of air and coolant supplied to a specific technological zone of the machine or section of the gas system.

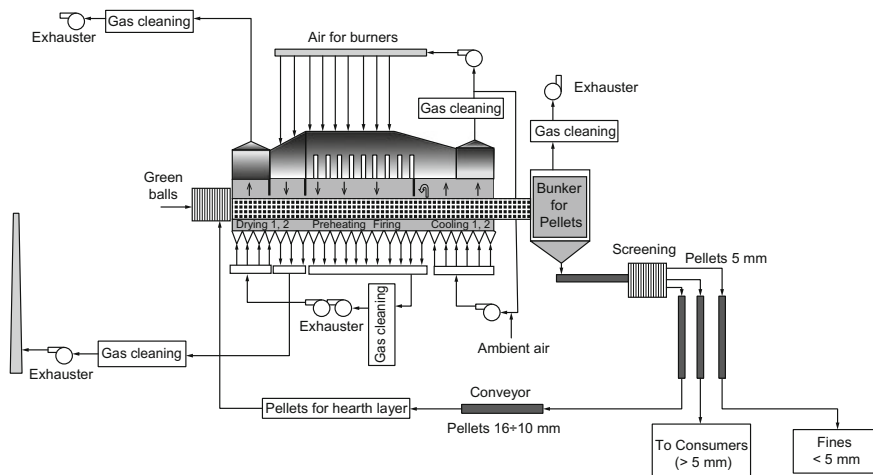


Fig. 2.42 Diagram of gas flows of the roasting conveyor machine OK-306 [15]

Roasting conveyor machines for the production of iron ore pellets have significant secondary airflows from the cooling zones to the hearth and heating (pre-heating) zones. In addition, heated air is used as air supplied to the burner.

The hearth burners operate in conjunction with a prechamber, into which air at 800–1200 °C is injected from the overflow manifold.

The efficiency of the burner affects the composition of the flue gases discharged into the atmosphere. The following types of burners are used on roasting conveyor machines:

- injection burners;
- vortex burners;
- vortex gas oil burners;
- combined burners;
- gas burners in the bed.

In order to reduce the content of nitrogen oxides, injection burners and burners with two-stage air supply are priorities for use.

The cooling zone of pellets (to a temperature of less than 160 °C) by blowing atmospheric air forms the coolant:

- overflow air (in cooling zone 1);
- combustion air and dilution air (cooling zone 2).

The effectiveness of the cooling zone is determined by the amount and temperature of air flowing through the layer, the conditions of heat exchange between air and pellets.

Table 2.27 Best available technologies for resource saving in the production of pellets

No.	Measure	Parameter	Note
1	Use of unshaped refractory materials for lining roasting machines	Reduced fuel consumption by 5–10%	Applicable with technological feasibility
2	The use of variable cross-sectional collector design, or several collectors	Reduced fuel consumption by 5–10%	Applicable in the reconstruction of existing roasting machines (in the absence of geometric constraints), in the design of new pelletizing plants
3	The use of electrostatic precipitators or other dust-gas cleaning plants with low gas-dynamic resistance for cleaning the gas flows from the roasting machine	Reduced power consumption	

2.7.3 *Best Available Technologies (BAT) in the Production of Pellets Aimed at Improving Energy Efficiency*

2.7.3.1 General BAT Solutions

The current trend in energy efficiency in the production of calcined pellets is to reduce the consumption of energy resources through the introduction of the best available technologies. The best available energy-saving technologies in the production of pellets can be summarized in two directions:

- Providing an environmentally flawless and energy-efficient pellet production process by improving manufacturing operations and reducing energy consumption, including:
 - Using as much heat as possible of the different zones of the roasting conveyor machine
 - Transfer, if required, of excess heat to consumers on the side (third persons) [111].
- Efficient use of equipment of pelletizing plants, reduction of heat loss, energy costs using at least one of the methods given in Table 2.27 [15].

2.7.3.2 Improving Thermal Schemes of Roasting Conveyor Machines

The following areas have been identified as the main areas of energy and resource saving in the technical re-equipment of roasting conveyor machines [112]:

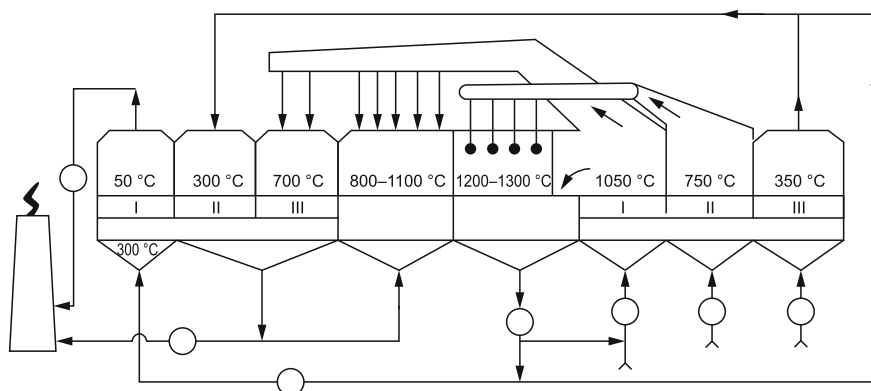


Fig. 2.43 Thermal diagram of a new generation roasting conveyor machine [112]

- increasing the degree of recirculation of gas-airflows in order to improve the efficiency of their use in the technological zones of the machine;
- an increase in the gas tightness of hearths and gas-air chambers of the firing machine, collectors, gas ducts, and gas-blowing and gas cleaning equipment in order to reduce the specific energy consumption;
- optimization of the ratio of the sizes and designs of the technological zones of the roasting machine while eliminating the reverse of refrigerants in the cooling zone in order to reduce specific fuel consumption;
- improvement of the technology, temperature, and gas-dynamic regimes of heat treatment of the layer of pellets in order to improve the quality of the calcined pellets;
- the introduction of an automated process control system for the production of pellets in order to increase the efficiency of operational management, including diagnostics of the operation of the machine and its individual components.

The thermal scheme of the roasting conveyor machine of the new generation is presented in Fig. 2.43.

To prevent softening of raw pellets during their drying, the drying zone (Fig. 2.43) is divided into three sections: drying I with heat carrier supply (air) from below with a temperature of 250–350 °C; drying II—with the flow of coolant with a temperature of ~300 °C from above; drying III—supply of heat carrier with a temperature of ~700 °C from above.

Dried pellets fall into the heating zone, heated by a coolant, the temperature of which lies in the range of 800–900 °C (when roasting pellets for blast furnace smelting) or 800–1100 °C (at roasting pellets for metallization).

The pellets are strengthened in the burning zone: the temperature of the heat carrier, depending on the type of pellets, lies in the range of 1200–1350 °C. To equalize the temperature over the height of the pellet layer and ensure the proper

duration of the high-temperature treatment, a recuperation zone is provided behind the roasting zone, where the air from the cooling zone with a temperature of 1100–1150 °C is partially supplied.

The cooling zone with the aim of the most efficient use of heat from the cooled pellets is divided into three autonomous sections: cooling I—with a temperature of refrigerant not higher than 250 °C; cooling II—air coolant; cooling III—refrigerant air. Hot air from the cooling zone I with a temperature of 1050–1150 °C is divided into two streams: most of it enters the drying and heating zones, and the smaller part goes to the recovery zone; internal recirculation is carried out due to the pressure drop through the overflow system consisting of three lined gas ducts—central and two lateral.

The resulting hot air is used when burning in the burner of the burning zone.

The final cooling of the pellets takes place in cooling zone III; in this case, the atmospheric air is heated to a temperature of ~350 °C and supplied to drying zone II.

Due to the high degree of recirculation, the flue gas volume is limited to 1500–1600 m³/t, the consumption of natural gas is reduced to 8.4 m³/t, and the power consumption is less than 20 kWh/t.

2.8 Environmental Aspects of Pellet Production

2.8.1 *General Characteristics of Emissions to the Environment in the Production of Pellets*

The impact of the production technology of calcined iron ore pellets on the environment is due to the specifics of this process:

- the circulation of dusting charge materials;
- the circulation of the fragile in nature of the finished product (pellets);
- the presence of high-temperature zones (the temperature of the torch in the heated zones of the roasting unit reaches 1450 °C), where the combustion processes of the fuel (as a rule, gaseous) take place.

The nature of the impact on the environment in the production of pellets, associated with emissions into the atmospheric air, discharges into surface water bodies, the formation of waste, can be summarized by the scheme shown in Fig. 2.44.

As well as during sinter production, emissions to the atmosphere in the production of pellets arise during the preparation of charge materials (dosing, crushing, grinding of charge components), during the processing of finished products (calcination and sorting of finished pellets), as a result of burning natural gas (or other fuel) in the heated zones of the roasting machine, as well as the course of physicochemical reactions in the pellet and the calcined layer under the oxidizing conditions of the process.

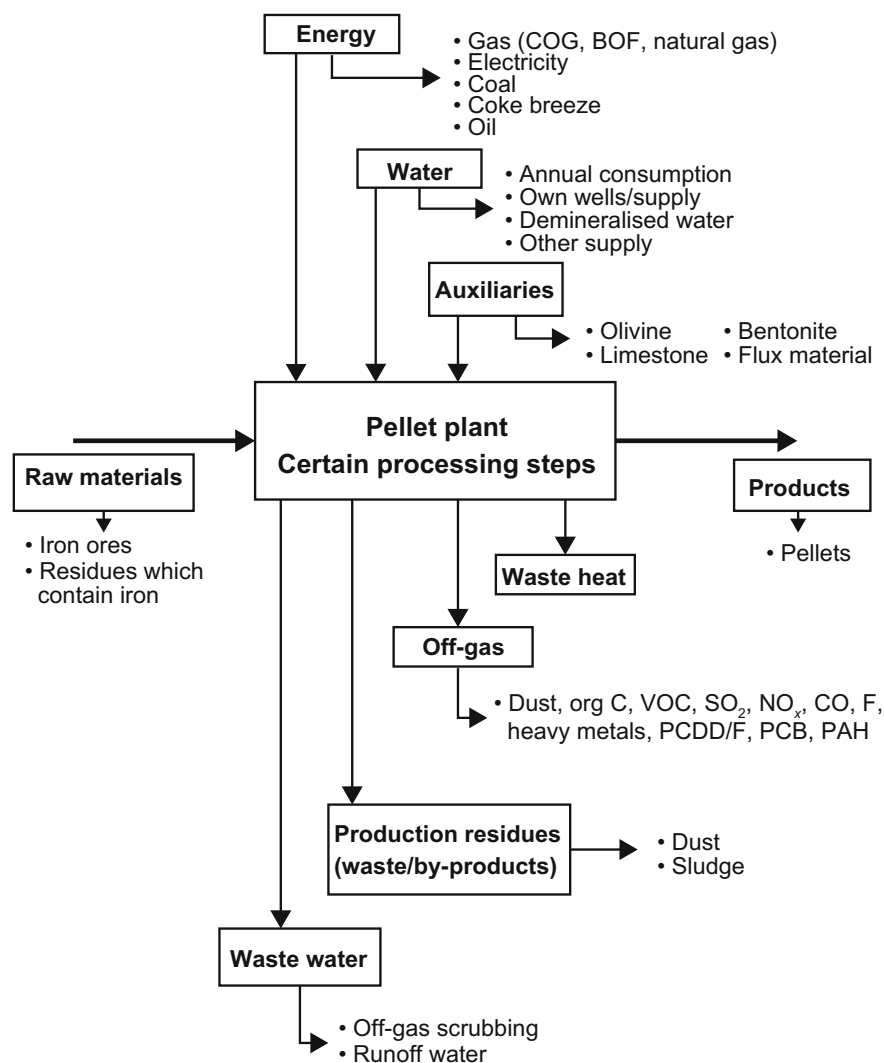


Fig. 2.44 Sources and nature of the environmental impact of the production of calcined pellets [15]

The priority components of emissions from pellet production plants are:

- dust emissions caused by the mechanical removal of the dispersed particles from the layer, arising from the destruction or deformation of the pellets when loaded on the roaster, or formed during the unloading of finished pellets from the roaster, subsequent overloads and sorting;
- gas components of emissions from natural gas combustion processes: emissions of nitrogen oxides NO_x (mainly formed at high temperatures from air

- components); insignificant emissions of carbon monoxide; to a small extent polyaromatic hydrocarbons (benzo(a)pyrene); depending on the composition of the iron ore material and additives, there may be some heavy metal contents of manganese (Mn), chromium (Cr), nickel (Ni), mercury (Hg), lead (Pb), cadmium (Cd), zinc (Zn);
- emissions from physicochemical interactions: emissions of sulfur dioxide SO_2 , depending on the presence and content of sulfur in the fuel (fuel oil, coal, natural gas), but mainly on the sulfur content in the charge components (primarily, iron ore) concentrate); HF and HCl emissions due to the composition of the gangue of iron ore concentrate (presence of chlorides and fluorides); PCDD/F emissions, mainly due to de Novo synthesis when chlorine-containing components are present in the blend.

The amount of heat carrier for heat treatment (exhaust gas volume) is determined by the type of iron ore raw materials, quality requirements for pellets depending on their technological purpose, peculiarities of the roasting unit and is within 1940–2400 Nm^3/t .

Quantitative characterization of emissions to the environment in the process of production of pellets, reflecting the best European practices, according to [113], is presented in Table 2.28.

As follows from Table 2.28, the best practices for the production of pellets (without the stage of enrichment of iron ore with the production of concentrate) do not include discharges into water bodies. The water consumed in the production of pellets is spent on equipment cooling (as a rule, the circulating cycle functions, therefore water is consumed solely to feed it), in wet dust-cleaning systems (also as part of circulating cycles); in some cases, water is spent on moistening the charge during its pelletization (evaporates during heat treatment).

Due to the fact that the collected dust corresponds to the composition of the components or the charge, it is sent to the process stream and therefore is not a waste.

The total amount of emissions to the environment in the production of pellets is in accordance with best practices [113] in the range of 230–1327 g/t.

2.8.2 Sources of Emissions from Technological Operations in the Production of Pellets

Schematically, technological operations for the production of pellets, demonstrating the main sources of emissions, are shown in Fig. 2.45. In general, the sources of atmospheric emissions from technological operations are described in Table 2.29. [15].

In the operations of charge preparation, on the lines of crushing of lumpy materials, as well as when dosing the crushed charge components, cyclones, electrostatic precipitators, bag filters are used to trap dust emissions.

Table 2.28 Characterization of emissions to the environment in the production of pellets in the aspect of the material balance of the process^a

Input			Output		
Raw materials			Products		
Iron ore concentrate	kg/t	935–965	Pellets	kg/t	1000.0
Bentonite		4.1–6.8	Emissions		
Olivine (1)		0–27.6	Exhaust gases	nm³/t	1940–2400
Limestone		0–5	Dust	g/t	14–150
Dolomite (2)		0–13.5	Dust	mg/nm³	7–70
Quartzite		0–20	Cd	g/t	0.02–2.2
Energy			Cr	g/t	5.1–22.4
Natural gas	MJ/t	14	Cu	g/t	1.5–6.7
Gas coke oven/blast furnace (3)		306	Hg (4.11)	mg/t	0.4–24.2
Coke breeze (3)		342	Mn	g/t	5.1–64.3
Coal (5)		223	Ni	g/t	6.5–17.2
Oil (5)		43–186	Pb	g/t	15.6–70.0
Power		54–99	Tl	g/t	0.6–3.0
			V	mg/t	13.4–15.1
Water	m³/t	0.11–1.25	Zn	mg/t	3–1300
			CO₂	kg/t	17–193
Compressed air	nm³/t	6.2–12.8	NO _x	kg/t	150–550
			NO _x	mg/nm³	73–283
			SO _x (7, 8, 11)	g/t	11–213
			CO		<10(5)–140
			VOC (9)		5(5)–40(3)
			HCl (6, 7, 11)		4–41
			HF (6, 7, 11)		1.8–5.8
			PAH (10)	mg/t	0.7–1.1
			PCDD/F (11)	ng I-TEQ/t	8.2–196
			PCDD/F (11)	ng I-TEQ/ nm³	0.005–0.1
			Waste and by-products		
			Dust	kg/t	–

^aData cover 63% of pellet production in the European Union

1—in the production of pellets for blast smelting; 2—for the production of pellets for direct reduction; 3—for plants with a full metallurgical cycle; 4—mercury mainly in elemental form; 5—for stand-alone installation (Sweden); 6—lower value when removing acid gases; 7—calculated on the material balance; 8—lower value if the technology of flue gas desulfurization is used; 9—measurement method is not known; 10—information on the Borneff 6 method; 11—education and yield for depend on the composition of the processed iron ore material

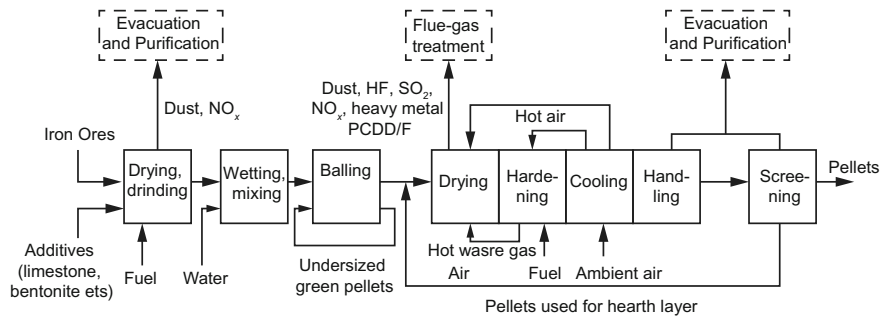


Fig. 2.45 Technological operations and sources of emissions to the environment in the production of pellets on a roasting conveyor machine

Table 2.29 Sources of atmospheric emissions from technological operations in the production of pellets

Input stream	Stage of the process	Output stream	The basic technological equipment	Emissions
<i>Charge preparation</i>				
Bentonite clay Limestone Chalk Bauxite Dolomite Olivine Polymer	Grinding lump bentonite, flux, hardening additives	Powder bentonite class <71 μm	Hammer Crusher Drying drum Ball mill	Inorganic dust containing SiO ₂
Concentrate with moisture content <10%, ground bentonite with moisture content ≥ 4%, crushed limestone, chalk, dolomite, bauxite, olivine, polymer	Dosing, mixing	The mixture (mechanical mixture of components in a given ratio of components and their consumption)	Dispenser-tape disk; mixers–rotary, drum, intensive mixing	Inorganic dust containing SiO ₂
<i>The production of raw iron ore pellets</i>				
The mixture is a mixture of iron ore concentrate with binder and flux-hardening additives	Pelletizing to obtain granules >5 mm	Raw pellets	Granulators (drum, disk, bowl)	Inorganic dust containing SiO ₂
Raw pellets	Classification by size class: <5 mm, 5–16 (18) mm, >16 (18) mm	Conditional raw pellets of a size of more than 5 mm and less than 16 (18) mm	Roller screens	Inorganic dust containing SiO ₂

(continued)

Table 2.29 (continued)

Input stream	Stage of the process	Output stream	The basic technological equipment	Emissions
Raw pellets of size class 5–16 (18) mm	Laying on the roasting machine	Raw pellets of size class 5–16 (18) mm laid in a layer	Pendulum or shuttle stacker; roller stacker	Inorganic dust containing SiO ₂
<i>Pellet heat treatment</i>				
Raw pellets of size class 5–16 (18) mm laid in a layer	Heat treatment: drying, heating, high-temperature hardening, cooling	Calcined pellets with the required physical, mechanical, and metallurgical properties	Roasting machine	Inorganic dust containing SiO ₂ , gaseous SO _x , NO _x , CO, CO ₂ and others. Sludge ^a
<i>Sorting and shipment</i>				
Calcined pellets	Sorting by size class: <5 mm, 5–16 (18) mm, >16 (18) mm; the allocation of pellets for the “bed”. +10–16 mm	Conditioned calcined pellets of size >5 mm; Pellets of the “bed” class. +10–16 mm; Fines class <5 mm	Vibrating screens	Inorganic dust containing SiO ₂ , sludge ^a
Conditioned calcined pellets of size >5 mm	Shipment in cars or transportation by a conveyor path to the subsequent technological processing; warehousing	Conditioned calcined pellets of size >5 mm	Loading hopper; conveyor tract, stacker	Inorganic dust containing SiO ₂
Calcined pellets of the “bed” class 10–16 mm	Return to the roasting machine	Layer “bed” on the roaster machine to protect the grate field	Hopper of the “bed” pellets	Inorganic dust containing SiO ₂

^aIn the presence of wet dust collection systems

Dust emissions in operations with wet materials (production of raw eyes) are quite limited.

A significant level of dust emissions in the unloading area of the roasting machine, sorting and subsequent shipment to the consumer requires equipping these zones with local aspiration installations or trapping devices that are part of the aspiration system.

Emissions of dust from high-temperature zones of the roasting machine are captured and sent for cleaning in electrostatic precipitators and/or bag filters or in wet gas cleaning systems using the Venturi scrubber–droplet separator device.

The established cleaning efficiency of dust emissions generated in the production of pellets, depending on the type of device lies in the range of 95–99%.

Schematic diagrams of the operation of dust-cleaning devices used in metallurgical technologies are discussed in Chap. 1 (Sect. 1.9.4).

2.8.3 The Best Available Technology in the Production of Pellets

The best available technologies in the production of pellets, aimed at reducing the negative impact, are associated both with activities in the main technological operations and “at the end of the pipe.”

The main solutions for the best available technologies in the production of pellets are shown in Table 2.30 [113].

Table 2.30 Best available technologies in the production of pellets

No.	Impact factor	Event (cleaning machine)	Parameter ^a	Note
1	Grinding of lump materials, their transportation, dosing, mixing			
1.1	Dedusting	Electric filters	<20 mg/m ³	
		Bag filters	<20 mg/m ³	
		Wet scrubber	<20 mg/m ³	
2	Getting raw pellets			
2.1	Dedusting	–	–	Special devices are not required due to limited dust emission, only as part of the general aspiration system of the site
3	Exhaust process gases (technologies “at the end of the pipe”)			
3.1	Dedusting ^b	Moistening the finished pellets (up to 3% moisture)	–	
		Multicyclones	–	95% efficiency
		Bag filters	<10 mg/nm ³	With restrictions on gas temperature and humidity
		Electric filters	<10–15 mg/nm ³	
		Wet gas cleaning system	<10 mg/nm ³	Along the way, it is possible to remove SO ₂ , HF, HCl

(continued)

Table 2.30 (continued)

No.	Impact factor	Event (cleaning machine)	Parameter ^a	Note
3.2	Reduce sulfur emissions (and other acid gases)	The use of charge materials with low sulfur content (fluoride, chloride)	–	
		Wet scrubber with NaOH addition	<30–50 mg/nm ³	<1–3 mg/nm ³ for HF, HCl
		Fluidized bed reactor with Ca(OH) ₂ spraying	6 mg/nm ³	Combined cleaning method; HF < 0.1 mg/nm ³ , HCl 0.6 mg/nm ³
3.3	Nitrogen oxide emissions reduction ^c	Reducing peak temperatures in high-temperature zones	–	
		Reducing the excess oxygen in the burning air	<82 mg/nm ³	Cumulative effect with low power consumption
		The use of burners with low emissions of nitrogen oxides	–	
		Selective Catalytic Reduction (SCR)	–	
4	<i>Aspiration emissions (unloading and sorting of finished pellets)</i>			
		Combination of devices: shelters and/or fencing and bag filter	<10–15 mg/nm ³	
		Combination of devices: shelters and/or fencing and electrostatic precipitator	<10–15 mg/nm ³	

^aDetermined as daily average^bAccording to [15], the indicator of the best available technology in terms of total dust emissions in the production of pellets <530 g/ton of pellets^cAccording to [15], the indicator of the best available technology for total emissions of nitrogen oxides <530 g/t pellets

A wet scrubber with the addition of NaOH is used to trap SO₂, HF, and HCl; residual gas concentrations will be 30–50 mg/Nm³, HF or HCl 1–3 mg/Nm³. For the purpose of flue gas desulfurization, technology is used with treating the gas with Ca(OH)₂ slurry in a “fluidized bed” reactor (GSA method). Slaked lime slurry, Ca(OH)₂, is sprayed into the exhaust gas, water evaporates, and lime particles absorb SO₂. The high concentration of dust contributes to an increase in the absorptive capacity of the reactor due to an increase in the reaction surface. After the reactor, the exhaust gas is treated in a cyclone to remove trapped dust and the reaction

product (part of which is recycled to the reactor). Finishing gas cleaning is carried out in an electric precipitator. The projected lime consumption is 264 kg/h; water is 10.6 m³/h. The effectiveness of the GSA method to minimize emissions of pollutants into the atmosphere is given below [113]:

Component	Before GSA (mg/nm ³)	After GSA (mg/nm ³)	Cleaning efficiency (%)
SO ₂	3009	6	96.8
HF	78	<0.1	99.8
HCl	133	0.6	99.5
Dust	1400	2	99.9

The main technological measures to reduce the emission of nitrogen oxides NO_x are the reduction of peak temperatures and excess oxygen concentration in the combustion air (in the heated zones of the roasting machine). The measures “at the end of the pipe” in relation to nitrogen oxides NO_x should include the method of selective catalytic reduction (SCR).

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Chapter 3

Briquetting



3.1 General Information on Briquetting of Natural and Anthropogenic Raw Materials

The creation of a dense mass of dispersed material is a favorite occupation of man, starting from the new Stone Age (the Neolithic, from 7000 BC). Almost as often, a person has to resort to the opposite effect—grinding a solid material. The most important branch of economic activity, in which both of these processes are extremely important, is metallurgy, which originated in the so-called Iron Age (from 1200 BC to 340 AD). And by the way, in which century we live now? Judging by the role that iron and steel play in our life, we can confidently consider the modern era of the information civilization as another period of the Iron Age.

The desire to obtain the most valuable raw materials for smelting iron leads to the need for deep enrichment of iron ore to produce concentrates so thin that their introduction into the mixture, for example, a blast furnace without preliminary agglomeration, would simply disrupt its operation. It is well known that a decrease in the fine fraction (5–0 mm) in the iron ore charge of a blast furnace for every 1% leads to a decrease in coke consumption by 0.4–0.7% and to an increase in furnace productivity by 1% [1]. The agglomeration accompanied by the heating of the iron-containing material is considered in detail in the previous sections. In this chapter, we study the so-called cold agglomeration.

The question is whether it is possible in some way to deliver fine material to the furnace without agglomerating it at all, but, say, to pack it into a container made of a material that would ensure the integrity of such a container to temperatures sufficiently high to metallize the concentrate? Indeed, in this case, the very need for sintering of the dispersed raw material would disappear. More recently, it was on this path that the specialists of one of the ferroalloy enterprises intended to go. It was suggested to pack concentrates in tin cans. And even laboratory experiments seemed to confirm the fundamental possibility of introducing un-agglomerated material into the charge of the ore-smelting furnace, but a simple calculation

showed that for a similar recycling of the resulting dispersed material would require construction, next to the ferroalloy plant, a separate cannery. When experts tried to introduce a concentrate into the charge of such a furnace without agglomerating or packaging it, it led to a deep disorder of the technology, to a significant increase in the formation of dust from gas treatment plants, to a sharp increase in the accident rate of furnaces and their failure. And the most important thing is that the use of raw concentrate has led to a deterioration of technical and economic indicators and, consequently, to an increase in production costs.

It is clear that for traditional metallurgical furnaces and reactors, agglomeration is an inevitable stage in the preparation of charge materials. Nevertheless, the search for methods of smelting metals using non-agglomerated raw materials in ferrous metallurgy practically does not stop.

In the monograph published in 2013 with the original name “The incongruities of metallurgy” [2], it is proposed, in particular, to metallize a dust–gas suspension from a fine or dustlike concentrate mixed with coal dust in a recuperator. According to the author, when “such a dust–gas suspension of concentrate and coal dust will come to a zone with a temperature above 720 °C, an intensive reduction of iron oxides by carbon will begin. Gases (CO, CO₂), heated in a recuperator, will react with pulverized solid reagents in 5–10 s, during the residence time of the dust–gas slurry in the recuperator. At the outlet of the heat exchanger, a suspension of fine iron powder in metallization gases (CO) will be obtained. Metallization will take place due to cheap recuperative heat. Further, such a dust–gas suspension of iron powder in CO can be blown into the blast furnace.” Unfortunately, the author of this concept confined himself to general considerations and did not confirm them with either a laboratory experiment or full-scale industrial test. In addition, he also suggests feed metallized material “to the charge of the steel-smelting unit in cans, bags, or in the form of briquettes.” But what about the desire to avoid agglomeration in general?

The author also did not mention the well-known experience of the Magnitogorsk Metallurgical Combine (MMK), where in 1953 they developed various methods for the direct production of iron and even patented a method of producing metal by reducing melted ores and a continuously operating unit for its implementation [3, 4]. The essence of the method of MMK lies in the idea of a straight-through two-chamber unit, including vertical and horizontal cameras with the organization of the torch from top to bottom in a vertical chamber. Fine iron ore concentrate is fed into the torch. The principle of “flow through” allowed excluding the stages of agglomeration and pelletizing of the charge for the production of pellets.

The 30 heats carried out in 1962 showed that the metallization of iron ore concentrate takes place in the conditions of an experimental furnace. The experience of operation of the furnace showed a low resistance of the lining, made of fireclay, carbon, zirconium blocks, and magnesite brick. When switching to intensive cooling of working areas with coils, refrigerators, they were covered with a layer of skull, the slag corresponded to the calculated one, but the heat loss from the water increased. Iron ore fines, obtained by grinding lumpy iron ore in an amount of

135–170 kg to a fraction of 0–0.5 mm, were used for each melt. Coke and coal fractions of 5–40 mm were mixed, and accordingly, 30 and 60 kg were consumed for smelting.

It is noted that the use of larger fractions of coal (coke) slows down the process of FeO reduction in the melt, and smaller fractions are removed from the furnace by the gas stream. Experiments confirmed that the temperature in the vertical chamber on the lining with intensive cooling and combustion of natural gas is sufficient to melt the iron ore part of the charge, reheat the carbon of coal (coke) to 900–1000 °C, and reduce iron oxides by 80–85% to FeO. However, in the horizontal chamber on the lining with intensive cooling to create a skull and when burning natural gas through arch burners to complete the recovery process and heating the melt to 1400–1450 °C heat was not enough. In some heats, due to large heat losses, the degree of FeO reduction did not exceed 70%. The identified problems did not allow at that time to go to the stage of practical implementation of the patented MMK method. This has not been implemented to date.

If we talk about commercialized metallurgical processes in which the metallization of non-agglomerated raw materials is used, we should first of all mention fluidized bed apparatus [5]. In such units, in contrast to shaft furnaces, the charge particles randomly move in a certain volume and, with correctly chosen values of the gas flow rate, do not leave the working chamber. And if in the shaft furnace the charge particles are in direct contact with each other, which determines the specificity of heat and mass transfer processes in a dense layer, then in a fluidized bed conditions such processes occur individually for each particle. Let us note at once that the practice of operating known installations of metallization in a fluidized bed has shown that there are restrictions on the grain size distribution of iron ores. In the well-known Finmet process [6], the proportion of ore particles with a size of less than 0.15 mm should not exceed 20%. The degree of metallization achieved on plants commissioned in 1999 and 2000 in Australia and Venezuela based on this process reached 92% with an average carbon content of 1.3%. Natural gas consumption was 13–16% higher than in shaft furnaces. In 2005, the plant in Venezuela ceased to exist, and the plant in Australia has not yet reached its design capacity. Another, worthy of mention, is the process of metallization of iron in a fluidized bed Circored, developed by Outokumpu (former Lurgi Metallurgie) [7]. However, this process has also used agglomeration. For effective metallization of fine materials (gas cleaning dust), their preliminary agglomeration was necessary, for which the company Outokumpu developed and patented a process for the production of micro-granules. The only industrial installation operating under the Circored process was commissioned in May 1999 in Trinidad. The actual annual production of the metallized product was 360 thousand tons, with the project capacity being 500 thousand tons. The plant was shut down in 2005 [8]. The Circored process has yet to prove its worth as a process working on ore fines. At least, it is not yet possible to talk about its economic attractiveness.

There are also attempts to avoid the agglomeration of raw materials in the smelting of ferrochrome in a fluidized bed reactor. What did it lead to? An experimental study showed that with the restoration of fines of chromic ore with a

particle size of less than $75\ \mu$ in a laboratory fluidized bed furnace with a temperature of no more than $1200\ ^\circ\text{C}$, a complete reduction of chromium and iron to carbides was observed for 7 h. This result formed the basis for the creation in 2010 of a pilot line with a capacity of 1 ton/h, including a rotating kiln, a fluidized bed reactor to maintain the material temperature at $1150\ ^\circ\text{C}$, and a leaning electric furnace [9]. The further development of such a process and its commercialization have since nothing been reported. Studies of the metallization of fines of chromic ore in a fluidized bed continue to this day, but, unfortunately, the authors do not bring them closer to the cherished goal of obtaining an attractive market metallized material from un-agglomerated raw materials.

An example illustrating the above is the well-known construction project of shop No. 4 at Aktobe Ferroalloy Plant (Aktobe, Republic of Kazakhstan). The construction of the workshop was started in 2010. The new production consists of four DC furnaces of new generation with a total capacity of 440 thousand tons of high-carbon ferrochrome per year. In such furnaces, a different mechanism for the recovery of ore materials is implemented than in furnaces of alternating current carbon, namely mainly liquid phase. The total cost of the project is about 843 million dollars. During the operation of the furnaces, the following indicators were achieved—the consumption of fine chromium ore is 3850 kg/t of chromium, and the consumption of reducing agent (coal) is 950 kg/1 ton of chromium, which practically corresponds to the performance of the process on alternating current. Specific energy consumption was higher than on AC furnaces 7552 kWh/1 ton of chromium against alternating current furnaces versus 6640 kWh/1 ton of chromium, due to the open arc burning on the bath surface and, consequently, large heat losses from the walls and roof of the kiln. Unfortunately, so far, the furnaces have not reached their design capacity, which indicates the absence of convincing arguments in favor of working on unfocused raw materials.

An attempt to avoid agglomeration as part of the reduction smelting process was undertaken in connection with the development of the well-known Romelt process [10], developed in 1979 by employees of the Moscow Institute of Steel and Alloys (Romenets V. A. and others) and implemented in 1985 as large-scale pilot plant at the Novolipetsk Steel Company (NLMK). This technology, unfortunately, did not receive wide distribution as well.

So, it is clear that the level of development of new metal-smelting processes using pre-metallization of raw materials without agglomeration achieved so far does not allow them to be considered as a serious alternative to blast furnaces and ore-smelting furnaces. The performance of the majority of well-known installations that implement such processes does not reach the declared design levels that justified their commercialization.

According to the World Steel Association, the total production of hot metal and directly reduced iron by the methods other than blast furnace smelting is only about 7.3% of the total iron produced by blast furnaces [11].

Thus, the agglomeration of dispersed iron-containing raw materials, natural and man-made, for its subsequent use as a charge component is a necessary step in preparation for the charge for blast furnace and ferroalloy furnaces, which in the near foreseeable future will remain the main metallurgical units for smelting iron

and ferroalloys. But is it possible to do without roasting during agglomeration; are there alternatives to the methods described in previous chapters? Yes, such methods exist, and moreover, historically they preceded sintering and pellet production. This is the so-called cold or unburned briquetting. It is necessary to clearly understand that, like any modern technology, briquetting combines “hardware” and “software.” The first, obviously, is the equipment itself, which allows you to create a solid-state structure from fine material, and the second is a set of methods for preparing and processing charge materials (with or without a binder), which ensure that the briquette properties comply with the requirements of one or another metallurgical process. Such properties have received the name “metallurgical” in the literature. Pursuing the goal to give the reader an idea of the technology in question from a scientific point of view, we will focus on the mechanism of gaining strength by a briquette, both at the stage of its creation in one way or another, and in the metallurgical unit itself. Therefore, we briefly describe the physical nature of the main industrial briquetting technologies and focus on the above-mentioned metallurgical properties.

3.2 History of the Industrial Briquetting in Ferrous Metallurgy

Acquaintance with briquetting could begin with reference to the most extensive modern information resource—to Wikipedia. But the inquisitive reader will be disappointed. In the English version, the use of briquette in metallurgy is not paid attention at all, and in the Russian version there are only 15 lines on briquetting in ferrous metallurgy. On the Cambridge Dictionary Web site (<https://dictionary.cambridge.org>), the word briquette is explained as—a small block of coal dust or peat, used as fuel. No mention of metallurgical briquetting applications. Here, echoes of the Second World War are heard, when in England briquettes from a mixture of coal dust and cement, molded into blocks of $15 \times 15 \times 5$ cm, were used for heating homes.

Well, let us try to fill this gap. So, what is the briquette? The word briquette (from the French “brique”—brick) means a pressed product. Indeed, as we will see later, the history of briquetting is closely intertwined with the production of bricks and some other building materials. And even the first commercially successful project of briquetting iron ore fines for blast furnaces was based on the equipment used at that time for the production of bricks.

Let us make a small excursion into the history of brick business. It is known that the brick business originated in ancient Egypt. During the period of the so-called Middle Kingdom (twenty-first century—early nineteenth century BC), when economic conditions no longer allowed the construction of giant pyramids, the raw brick became the building material for their construction. So, mainly from such a brick, the pyramid of Senusret was built (the base length is 107 m, and its height is

61 m). The brick, but already burned, was also used for the facing of the famous Tower of Babel (Etemenanki ziggurat—"House of the foundation of heaven and earth," second millennium BC). This is stated even in the Bible itself (Genesis, Ch. 11-3): "And they said to one another: "Come, let us make bricks and bake them thoroughly"". So they used brick instead of stone, and tar mortar. "Come", they said, "let us build for ourselves a city with a tower that reaches to the heavens, that we may make a name for ourselves and not be scattered over the face of all the earth..."".

Archaeological excavations on the Indian subcontinent allowed proving that as far back as the third millennium BC dwellings were built of raw brick. The most famous monument of antiquity, during the construction of which used raw and burnt bricks, is the Mohenjo-daro Citadel. A part of the Great Wall of China, which has survived to the present day (third century BC), was also built of baked bricks.

In ancient Russia, brick appeared only in the tenth century. The first Russian building of this material was the Tithe Church in Kiev. A striking example of the use of brick construction in Russia of the times of John III was the construction, beginning in 1485, of the wall and church of the Moscow Kremlin, which was led by Italian masters: "... and they made a brick stove outside the Andronikov monastery, in Kalitnikovo, what to burn brick and how to do, our Russian brick is already longer and harder, when it needs to be broken, it is soaked with water. Lime is densely tied up with tillers, it dries in the morning, and it is impossible to break the knife out." The main element from which the walls and towers of the Moscow Kremlin were erected is the so-called two-handed brick with dimensions up to $31 \times 15 \times 9$ cm and weighing up to 8 kg.

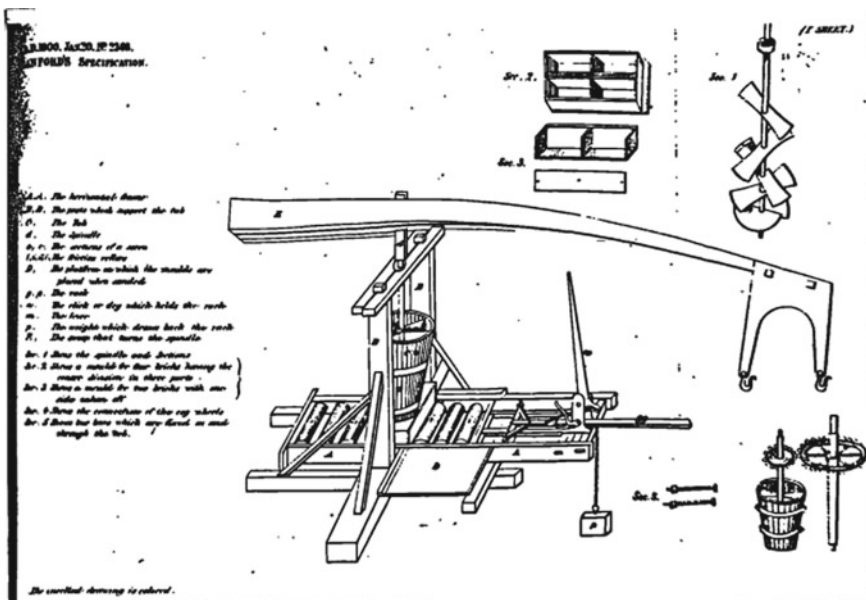
In the Middle Ages in Western Europe, urban growth and the risk of fire were one of the reasons for limiting the use of wood in construction. After the Great Fire of 1666, the English Parliament approved the famous "An Act for rebuilding the City of London," according to which it was forbidden to build wooden houses and houses on the basis of a wooden frame. The brick of the familiar modern form appeared in the sixteenth century in England. The most famous medieval brick buildings in England are Hampton Court near London (beginning of construction in 1514), several college buildings in Cambridge, and Herstmonceux Castle in Sussex (mid-fifteenth century). From twelfth century, brick spread to Holland, Denmark, Northern Germany, and other parts of Northern Europe, where there was a shortage of natural stone. Examples of brick structures can be: the Church of Mary (Marienkirche) in Lübeck (Germany), the Basilica of San Ambrogio in Milan (Italy), etc. The brick was also popular in Moorish Spain.

Until the nineteenth century, bricks were made by hand, and the process remained primitive and time consuming. Skilled molders filled the raw clay tins (special forms), which were then dried and then burned in floor kilns. They dried the bricks exclusively in the summer and burned them in kilns made of dried brick raw. One of the first patents on the molding machine was granted in 1741 to William Bailey from Taunton (England, UK patent number 575, 1741). Like other early machines, it was a molding machine largely imitating a manual molding procedure, but with a significantly higher productivity. Bailey's invention included

a separate mill to give the clay uniformity prior to molding; brass or iron molds containing five or six bricks that were filled with a homogenized clay, molded into a brick with a stamp or plunger press; and return device for cyclic repetition of the process. Half a century later (March 7, 1792), a patent for a molding machine was granted to David Ridgeway from Philadelphia (USA). A year later, with an interval of 5 days, Christopher Colles and Apollo Kinsley from New York received patents for similar inventions [12]. Historical sources preserved only a description of the device and the principle of operation of the machine, presented by Apollo Kinsley. In 1800, British patent No. 2368 was issued to Isaac Sanford, former Apollo's countryman, who resettled at Covent Garden. Figure 3.1 shows the image of the scheme of the machine, invented by Apollo Kinsley [13].

The mixed clay was fed under great pressure. Such a machine, successfully operating in Washington in 1819, had a capacity of up to 30,000 bricks/day, while the strength of freshly formed bricks made it possible to do without drying them and send them directly to the kiln. It is interesting to note that, despite the efforts of Isaac Sanford, these machines did not enjoy success in England. Nevertheless, many researchers consider Kinsley's invention to be the progenitor of modern belt-pressing technology.

The concept of a belt press was developed by a molding machine, invented by Joan George Degerlein in England in 1810 (Fig. 3.2, [14]), which made it possible to produce semisolid clay bricks.



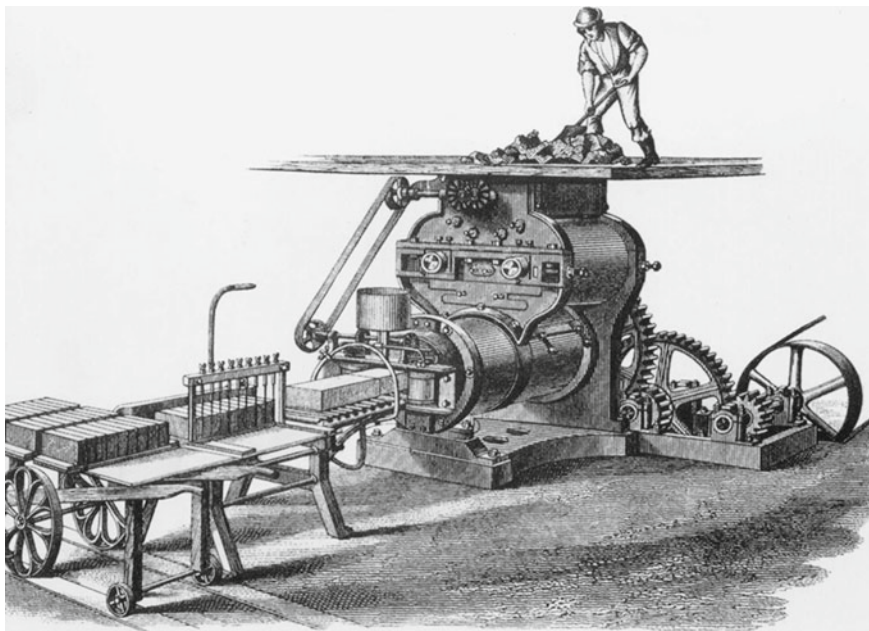


Fig. 3.2 Degerlein molding machine (England, 1810, [14]) <http://www.binfieldheath.org.uk/the-village/binfield-heath/history/brickmaking>

The wet clay mass entering the machine was forced through a special mold in the form of a bar, which was then cut into individual bricks. These first inventions served as the basis for widespread belt pressing, which will play an important role in briquetting.

For the first time, the idea to use a press for the production of briquettes was expressed by the Russian inventor A. V. Veshnyakov in application to the briquetting of charcoal and hard coal [15]. With the priority of July 7, 1841, he was granted a “privilege” for a new type of fuel, called “carbolyne.” Veshnyakov proposed to subject the charcoal (coal and coke) to grinding and sifting, then add vegetable or animal oil to it, load the resulting mass into bags (made of bast or strong canvas), tightly wrap with ropes or strong canvas, and compress them in the hydraulic press. The obtained pieces were proposed to be further dried. Later, Veshnyakov proposed replacing the bags with cast-iron boxes with holes. A year later, in 1842, Marsais, a Frenchman, invented a coal-fuel briquette with coal tar as a binder [16]. In 1843, a similar patent was granted to Wylam in the UK [17]. The first patent for coal briquetting in the USA was granted in 1848 by William Easby (Fig. 3.3, [18]).

In 1859, the first coal briquette factory was built by Sahut Conreur in Raismes in France, where in 1860 a roller press was used to produce coal briquettes. The essence of the concept of such briquetting was forming with the help of two

UNITED STATES PATENT OFFICE.

WILLIAM EASBY, OF WASHINGTON, DISTRICT OF COLUMBIA.

METHOD OF CONVERTING FINE COAL INTO SOLID LUMPS.

Specification forming part of Letters Patent No. 5,739, dated August 29, 1848.

To all whom it may concern:

Be it known that I, WILLIAM EASBY, of the city of Washington and the District of Columbia, have discovered a new and useful method of converting fine or powdered coal or refuse coal, either anthracite, bituminous, or charcoal, into solid lumps or blocks or prisms for the use of steam vessels or any other purpose in which fuel is required, which method is described as follows:

I take the fine coal and put it into a strong mold of the form and size of the intended blocks, lumps, or prisms to be formed, and of sufficient depth to remove the necessary quantity of fine coal. To form the required block, lumps, or prisms and subject the mass to sufficient pressure to cause the particles to adhere and form a solid mass, which may be effected by a piston of a size corresponding to that of the mold to be operated upon by any suitable mechanical means, and when the fine coal shall have been thus pressed into a solid body it will be discharged from the mold by any convenient mechanical means. The fine coal, being thus formed into solid cubes or other suitable forms, will be in a convenient state for packing, for transportation, or for burning.

The utility and advantage of the discovery

are that by this process an article of small value and almost useless can be converted into a valuable article of fuel for steamers, forges, culinary, or other purposes, thus saving what is now lost. The fuel thus prepared will be equal to any now in use. It will be highly advantageous for steam-vessels, as when formed into hexagonal prisms it can be stowed in a smaller space than other fuel. Its specific gravity being greater than that of the natural coal will also contribute to this advantage. For culinary purposes it will have an advantage over any other fuel. Its compactness renders it less liable to break or fall to pieces. It is contemplated to form the fuel for the last-named purpose into oval or egg-shaped lumps, thereby leaving no angles to be worn off by abrasion.

What I claim as my invention, and desire to secure by Letters Patent, is—

The formation of small particles of any variety of coal into solid lumps by pressure, in a manner and for the purposes substantially as herein described.

WM. EASBY.

Witnesses:

H. N. EASBY,
J. W. EASBY.

Fig. 3.3 Title page of William Easby patent (1848, [18]) <http://www.briquettepress.com/News/History-Of-Coal-Ball-Briquetting.html>

cast-iron rolls, the surface of which was covered with submerged ellipsoidal cells, which, while simultaneously rotating the rolls, should ideally coincide with each other, forming a container for forming the briquetted mass held in it. One of the first patents for the design of a roller press was obtained only in 1884 by J. M. Wilcox in the USA (Fig. 3.4, [19]). The inventor was able to significantly simplify the design of the roller press through the use of dividers, grooves, and lifts, which cheapened the production of such presses and contributed to the growth of their use for the production of briquettes.

In the literature, there is an erroneous idea that the first roller press was invented in 1865, which is illustrated by a drawing from a report on briquetting peat dated to the same year (Fig. 3.5, [19]).

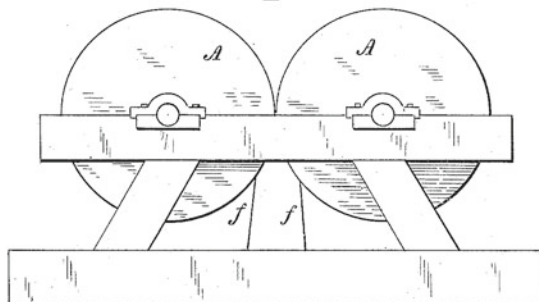
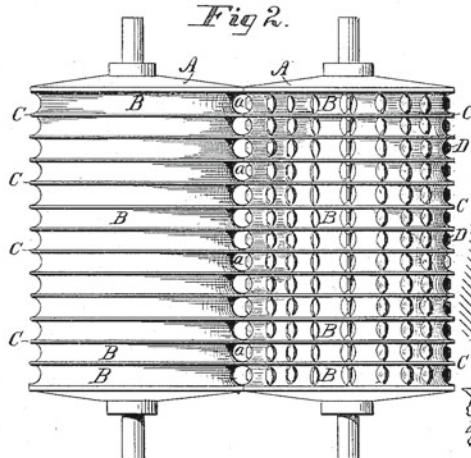
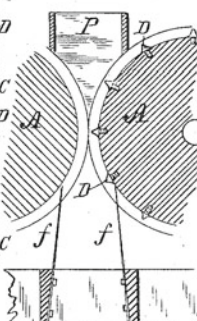
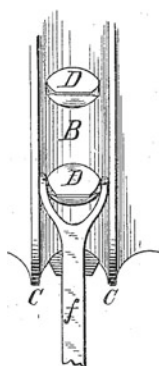
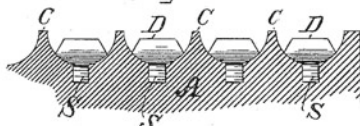
However, it can be seen that the figure shows a piston press, not a roller press. Since 1901, Köppern began to use the roller press for coal briquetting.

(No Model.)

J. M. WILLCOX.
MACHINERY FOR COMPRESSING AND MOLDING POWDERY AND
PASTY SUBSTANCES.

No. 309,117.

Patented Dec. 9, 1884.

Fig. 1.*Fig. 2.**Fig. 3.**Fig. 5.**Fig. 4.**Fig. 6.*

WITNESSES:

A. H. Leuker
John H. Leuker

INVENTOR

James M. Wilcox

N. PETERS, Photo-Lithographer, Washington, D. C.

Fig. 3.4 Title page of J. M. Wilcox patent (1884, [19])

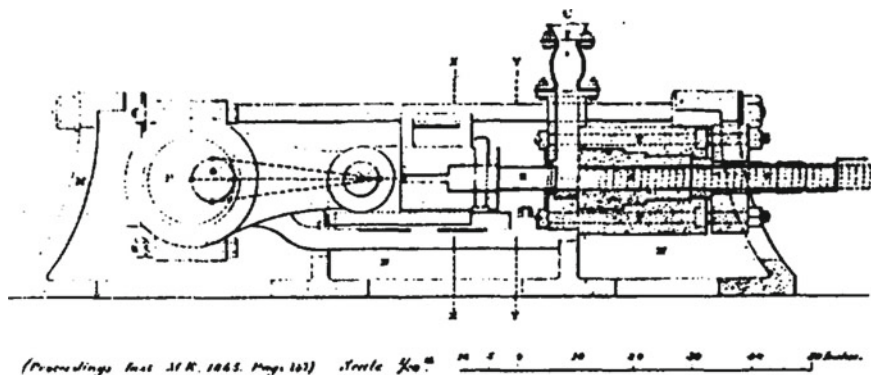


Fig. 3.5 Piston press for peat briquetting (1865, [20])

The history of industrial briquetting can be divided into the following periods:

- beginning of the twentieth century—the 1900–1929 of the twentieth century;
- 1930–1959 of the twentieth century;
- 1960–1979 of the twentieth century;
- 1980–1999 of twentieth century;
- 2000–Nowadays.

3.2.1 *Beginning of the Twentieth Century—The 20s of the Twentieth Century*

At the beginning of the twentieth century, metallurgists were faced with the need for the agglomeration of fine iron ore, and it was decided to try to apply the technology used at that time for the production of bricks for these purposes.

It is safe to assume that industrial briquetting originates from the first commercially successful project to produce briquettes from small magnetite iron ore, implemented at the beginning of the last century in Sweden and Finland, thanks to the talent and efforts of Gustav Gröndal (Fig. 3.6). In Herrang (Sweden) and in Pitkaranta (Finland), briquette factories were built and put into operations as part of the blast furnace units.

For the production of briquettes, stamp presses of Sutcliffe design (Fig. 3.7, [21]) with a pressure of 30–50 MPa were used. A patent for such a press was received by Edgar Sutcliffe from Lancashire (England) on March 31, 1925. The patent number 1531631 was issued in the USA on May 31, 1925, and was called “press for the production of bricks, briquettes, blocks, and the like.” Sutcliffe himself defined his invention as “presses of the mold and plunger type for the production of bricks, briquettes, blocks, and like consolidated masses from coal or like carbonaceous



Fig. 3.6 Johan Gustav Gröndal (February 11, 1859–March 16, 1932) <https://www.geni.com/people/Gröndahl/6000000041491719847>. Gröndal Johan Gustav was born on February 11, 1859 in Fröslunda (Sweden), died on March 16, 1932 in Stockholm (Sweden). His energy and inventive talent in metallurgy began to emerge with the beginning of his work in 1880 as an engineer at the Pitkäranta Copper-Tin Plant on Lake Ladoga in Finland near the Russian border. Gustav introduced a number of improvements, which soon led to an increase in the company's profits. He invented new methods of enrichment of iron ores, which were previously considered unsuitable for processing. These methods included magnetic separation, briquetting of new kiln designs. Of particular importance was the practice of its ore separators and ball mills, which were distinguished by a high degree of safety in operation. Gröndal became widely known in the 1910s and 20s due to its numerous inventions in the mining industry and fuel technology. Between 1894 and 1932, he issued a total of 65 patents, of which 62 were national. Thanks to his world-patented inventions and new designs, he occupied a special place among metallurgists and industrial entrepreneurs. He has implemented a number of projects in Russia, Germany, Austria, England and Manchuria. A number of well-known companies such as Herrängs Gruf AB, Luleå Ironworks AB and Totherhätte electrothermal AB are associated with his name. He also founded The Gröndal Kjellin Co. Gustav Gröndal was distinguished by simplicity and personal charm, sense of humor. He always remained an optimist and kept youthful enthusiasm throughout his life.

substances, concrete, clay, or other substances or mixtures capable of being consolidated by pressure.” A feature of the Sutcliffe press was the possibility of pressing the wetted material. The mixture for briquetting, for example, coal “may consist of one part coal to one and a half to two parts of water or may be a mixture containing say 25% of water.” The molded mass was fed into the receiving funnel of the press. The molding of the briquette was carried out with the progressive advance of the plunger that pushed the briquette out of the mold. Electricity consumption for the production of a ton of briquettes was 5 kWh.

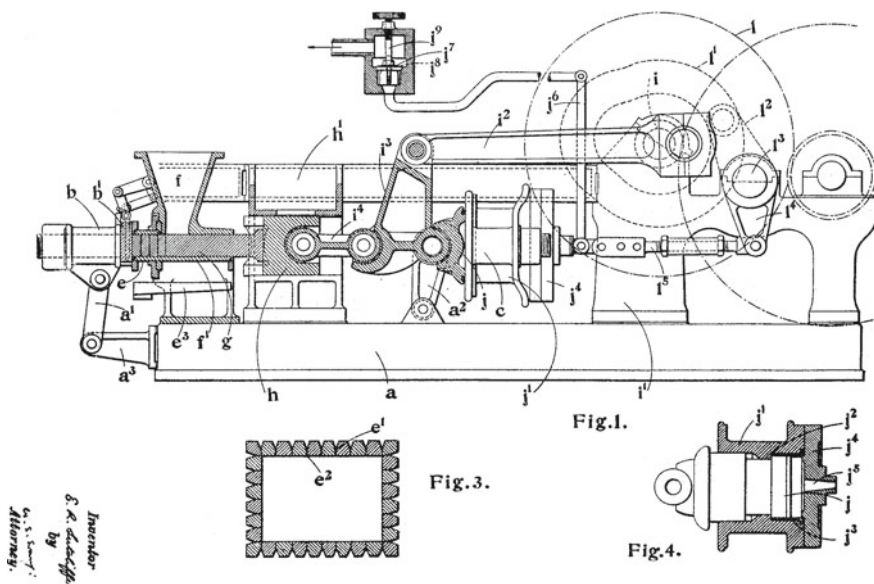


Fig. 3.7 Design of Sutcliff stamp press for the production of bricks and briquettes (patent No. 1531631, England, 1925, [21]); **a** base plate; **b, c** parts of the crank–slider mechanism; **e** mold; **f** receiving funnel; **g** plunger; **h** slider; **i** operating shaft; **j** plunger)

The fine concentrate was pressed into briquettes without the use of a binder material, and the moisture content in the concentrate was adjusted to obtain briquettes with strength sufficient to remove them from the press and load them on special carts for delivery to Gustav Gröndal's kiln furnaces. On December 28, 1903, he received a patent for the design of a briquette kiln (patent No. CA85977A). The necessity of burning briquettes to give them the strength required for blast furnace smelting was due to a number of reasons. Achieving the required mechanical strength without binder and roasting would require the application of ultrahigh pressures (over 200 MPa), as, for example, in the famous Ronay press, which made it possible to obtain dense and durable briquettes, the porosity of which, however, did not contribute to their good reducibility during heating. Adding organic binders also did not solve the problem. Firstly, most of the known organic binders are very expensive, and secondly, when heated, the organic material burns out or undergoes pyrolysis, which negates its astringent effect. The use of inorganic ligaments, in addition to the effect of “dilution”—reducing the iron content in the charge—significantly affects the composition of iron and slag, increasing the yield of the latter.

Gröndal's kiln was in the form of a tunnel, with a track leading down the center and a combustion chamber in the middle. The air required for combustion enters the gas-tight platform at the feed end of the furnace and, having passed the discharge end, returns above the platforms of the carts loaded with briquettes. The cold air

circulating under the platform keeps the wheels and carriage frame cool, heats up as it simultaneously cools the baked briquettes, and enters the combustion chamber hot; hot gases, in turn, heat the briquettes and cool themselves to exit the furnace. Such heat recovery increased the efficiency of the furnace. Coal consumption averaged 7% of the briquette mass; the main heat loss was associated with evaporation of water in briquettes. The temperature in the combustion chamber when burning gas reached 1300° or 1400 °C, and with this heating the particles were sintered enough to create a solid, strong briquette. It is important that during briquette roasting their desulfurization was achieved. The time spent on the operation depended on the type of ore and the required degree of desulfurization. When the total iron content in the ore is 38%, it contained 68.3% in the concentrate and 68% in the briquette. For sulfur content, these values were, respectively, 0.066%, 0.026%, and 0.006%.

The briquette manufacturing process at the factory in Herrang, kilns and briquettes on carts are shown in Figs. 3.8 and 3.9, courtesy provided, as well as Fig. 3.10, by David Michaud, the owner of the Internet resource 911Metallurgy Corp. [22]. The sizes of briquettes (150 × 150 × 75 mm), exceeding the generally accepted sizes of bricks, attract attention.

The carts had a frame structure lined with refractory bricks. Special devices at the front end, a groove at the rear end, and flanges on the sides, which were lowered

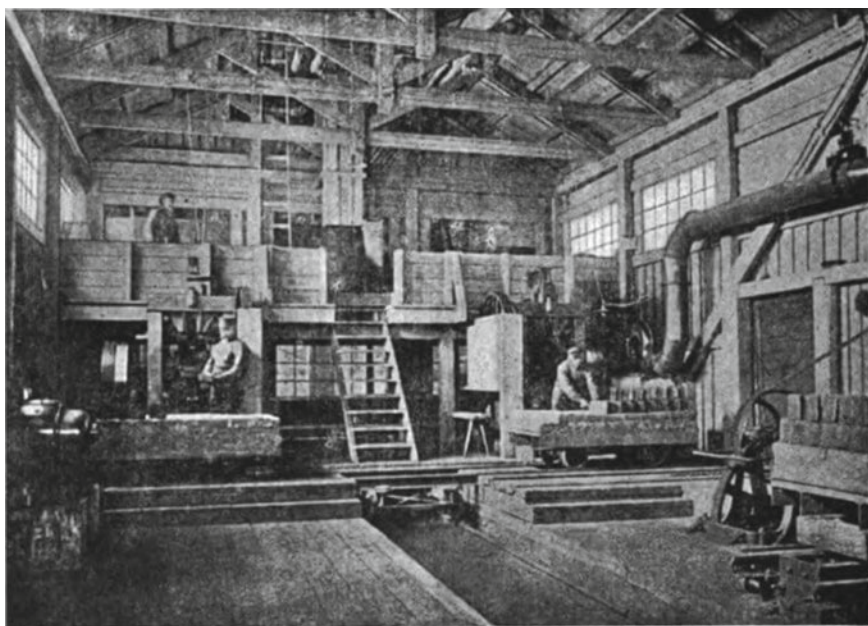


Fig. 3.8 Briquette factory at The Grondal Kjellin Co. in Sweden [21] <https://www.911metallurgist.com/magnetite-concentration/>

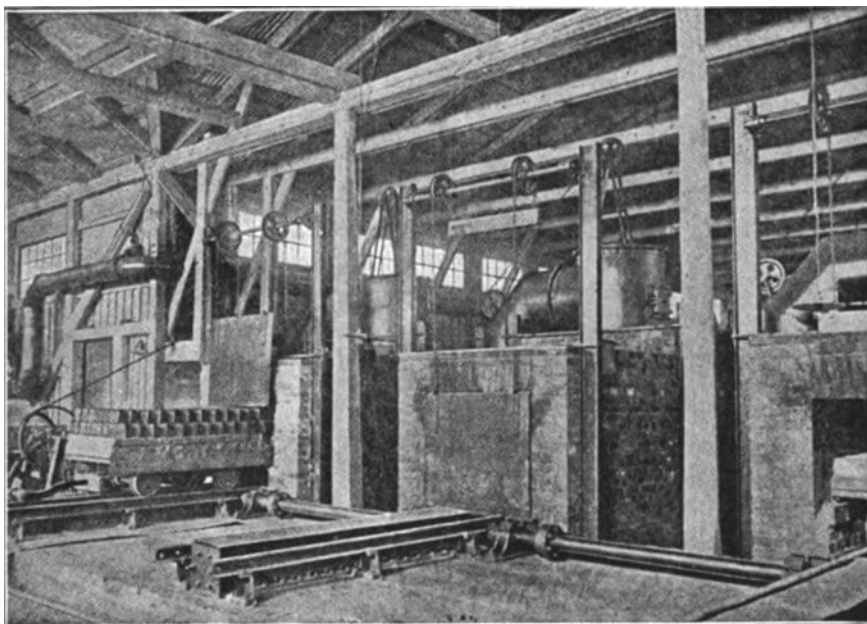


Fig. 3.9 Briquettes firing kilns at The Gröndal Kjellin Co. in Sweden [21] <https://www.911metallurgist.com/magnetite-concentration/>

into the oven in a groove filled with sand, allowed the column of such carriages to form, thus, an airtight platform.

Briquettes were made using the Gröndal technology and at a lower temperature due to the use of various binding materials. For example, in Pitkäranta (Finland), lime was used as a binder (3–5% of the mass of the briquette). After two weeks of curing, the briquettes were heated to 800 °C for subsequent hardening. At a briquette factory in Edison, USA, resinous substances were used as a binder. The cost of briquette at this factory was about 45 cents/ton. Interestingly, the equipment for iron ore dressing at this plant was designed by Thomas Edison himself.

A factory with a capacity of 60 thousand tons of briquettes per year was soon built in Guldsmidshyttan (Sweden, Fig. 3.10). Factory staff was only 14 people.

Similar factories with a capacity of 40–60 thousand tons of briquettes per year were put into operation in other Swedish cities (Strassa, Bredsjö, Hjulsjö, Luleå, and Uttersberg). The largest briquette factory in those days, which was based on the Gröndal technology, was built at Sydvaranger in Norway. The processing plant had a capacity of 1.2 million tons of ore per year and was equipped with 56 ball mills and 200 separators of the Gröndal construction, and at the briquette factory the briquettes were fired in 20 furnaces of the above-described construction of the same Gustav Gröndal. The capacity of the briquette factory was 600 thousand tons of briquettes per year. Briquettes were exported to Germany. A factory with a capacity

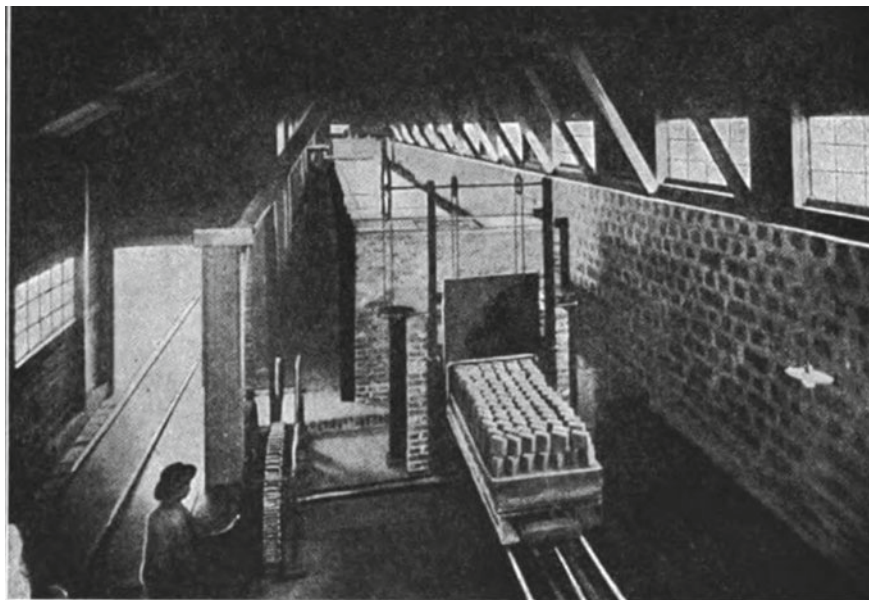


Fig. 3.10 Briquette factory at The Grondal Kjellin Co. in Guldsmeshyttan (Sweden, [21]) <https://www.911metallurgist.com/magnetite-concentration/>

of 100 thousand tons of briquettes, which were also exported to Germany, was built in another Norwegian city—Salangen.

Despite their large size, these briquettes were successfully used in a low-shaft blast furnace with a capacity of 50–140 tons/day at the plant in Pitkäranta. In the process of oxidative roasting, magnetite was oxidized to hematite, and sulfur was removed from briquettes (by 98%). Porous briquettes (40% porosity) had high mechanical strength (10 MPa) and high recovery, which led to a reduction in coke consumption and an increase in the productivity of the blast furnace. The success of the project contributed to the rapid spread of such technology. In 1913, there were already 38 such briquetting lines (16 in Sweden, 12 in England, 6 in the USA).

At about the same time, anthropogenic materials from the ferrous metallurgy, such as top dust and mill scale, were also subjected to briquetting. In Germany (Ilseeder Hütte), a pilot plant was created for briquetting these materials in mixture with clay slurry of brown iron ore washing. The mixture was heated and pressed at a pressure of 30 MPa. Briquettes gained strength indoors, reaching a compressive strength of about 10 MPa [22]. Clay iron ore fines, blast dust, and cinder were also briquetted without binders, plasticizing the mixture by grinding the components and moistening. Stamp presses were applied for briquetting. Ready briquettes were burned in a shaft furnace (capacity up to 40 tons/day).

The successes in the briquetting of iron ore fines and anthropogenic materials achieved at the very beginning of the twentieth century and the dominance of

briquetting as the only industrial sintering technology until the twenties of the last century allow us to consider this time as a kind of “golden age.” Along with the development and modernization of equipment for the production of briquettes, the ways of preparing and processing the charge for briquetting were developed and improved. The operating experience of the first briquette factories showed that the potential for agglomeration without bonding materials is limited due to the insufficiently high strength of raw briquettes and the need for costly roasting. In 1901, the Russian mining engineer L. Yuzbashev proposed to do without firing and use hydraulic cement as a binder for briquetting ore fines [23].

His idea was soon embodied in a number of Russian factories. As well as in the process of Gröndal, briquettes were made on ordinary brick presses. Coal or coke breeze, chopped straw, sawdust, and other materials were added to the charge, which, fading when briquettes were heated in a blast furnace, contributed to the growth of their porosity and, consequently, better recoverability. Briquettes were dried at ambient temperatures and, after curing, were sent to the stock yard of the blast furnace. The use of cement made it possible to remove part of the fluxes from the charge, in proportion to the content of CaO and MgO in it. The method of Yuzbashev, however, was not widespread due to the relatively high cost of cement at that time. In addition, the cement content in the briquette mass (3–6%) did not ensure the integrity of the briquettes in the zone of high temperatures of the blast furnace. “The first pancake is lumpy.” Unfortunately, this bad experience led to the emergence of a “myth” that cement in principle is not capable of providing the so-called hot strength to briquettes due to the fact that Portland cement loses its binding properties at 750–900 °C. It is true. Calcium silicate hydrates are destroyed at even lower temperatures (400–500 °C). But from the mineral phases formed at such temperatures, under certain conditions, a new liquid high-temperature bond can form. Modern experience in the use of cement as a binder for blast furnace briquettes confirms the validity of this conclusion.

At the same time, at the very beginning of the last century, V. Schumacher (Germany) proposed to use crushed quartz sand (1–5% by weight of the briquette) and quicklime (3–10% by weight of the briquette) as a binder. This powder was thoroughly mixed with ore after wetting and then pressed at a pressure of 40–70 MPa. Briquettes were strengthened by steam treatment at a pressure of 1 MPa for 2–4 h in an autoclave at a temperature of 174 °C. By the way, Schumacher is credited with the authorship of the very principle of autoclaving [24]. In a nutshell, this is nothing more than the processing of the material at a pressure above atmospheric and at a temperature above 100 °C. With this steaming, a new binder of calcium hydrosilicates ($\text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$) was formed, which was obtained by the reaction $\text{Ca}(\text{OH})_2 + \text{SiO}_2 + (n - 1)\text{H}_2\text{O} = \text{CaO} \cdot \text{SiO}_2 \cdot n\text{H}_2\text{O}$. The compressive strength of such briquettes reached a value of 10–13 MPa. Briquettes maintained integrity when heated to temperatures of blast furnace smelting. The method was introduced at two steel plants in Germany. However, in the practice of briquetting Schumacher’s method was not rooted due to its complexity and high cost.

Thus, by the twenties of the last century, the achievement of the strength of briquettes required for smelting iron was mainly provided by firing or other

temperature treatments (steaming), and the productivity of briquette factories was limited by the productivity of equipment used at that time to make bricks.

The performance of such equipment did not meet the growing needs of blast furnace production for agglomerated raw materials. Briquetting was quickly replaced by the sintering technology developed by that time. High performance and manufacturability of the process, the possibility of utilization in it of the inevitable in the smelting of iron and steel dispersed iron-containing materials, led to its rapid spread. Sintering practically supplanted briquetting from ferrous metallurgy. Thus, for example, by 1923 almost all the above-mentioned Gröndal briquette factories were replaced by sinter plants.

The use of roller presses for briquetting natural and man-made yellow raw materials that began in the 20s of the last century did not save the situation with briquetting. It is important that roller presses were created specifically for briquetting; that is, they were not “borrowed” from the building materials industry. Roller briquettes at the beginning of the twentieth century found sufficient application in low-shaft blast furnaces and in blast furnaces of small volume. Briquettes were made of iron ore fines, limestone, and coke dust. In the blast furnaces of the Kushvinskyi plant, the proportion of briquettes in the charge reached 25%. Briquettes in the amount of up to 100 thousand tons per year were used in the charge of the Kerch blast furnace (the capacity of the briquette factory in 1915 was 35 thousand tons of briquettes) and the Taganrog metallurgical plants (the capacity of the briquette factory in 1906 was 30 thousand tons of briquettes) [25].

3.2.2 30–50s of the Twentieth Century

In the 1930s, the search for effective and affordable bonding materials continued. It is curious that such a search had its main purpose to reduce energy consumption for firing. One of the few attempts to turn briquetting into a real “cold,” unburned was associated with the name of the Soviet scientist–metallurgist P. P. Kazakevich, who in 1936 conducted research on the briquetting of flue dust with Portland cement as a binder. But, despite the generally satisfactory results of his research, the method was not widely distributed at that time, since obtaining mechanically strong briquettes required a very long time. Cement myth rooted.

Another noteworthy attempt to carry out briquetting without firing was undertaken in 1936 at the Krivoy Rog briquette factory. Briquettes were made from ore fines of rich hematite ore. To the ore fines were added 5–10% of crushed iron shavings and 0.5–1.0% NaCl in the form of a solution, which accelerated the process of formation of iron oxide hydrates. Briquettes’ strengthening was achieved as a result of corrosion and hydration of iron shavings. The hardening of briquettes for some ores was completed within a few hours after their production. For most ores, the curing period was 20–40 h. Briquettes did not need drying or firing. In the literature, this method of briquetting has received the name of the method of Yarkho, after the name of the author [26]. The same method of briquetting was used

at the briquette factory built in 1933 in Nizhny Tagil. However, this generally successful method did not become a landmark in cold agglomeration. The obvious disadvantage of the method was the high cost of the additives used and the content of alkaline compounds in the briquettes, which is highly undesirable for the blast furnace.

In 1932, Averkiev and Udovenko published an article entitled “Briquetting of flue dust and fine ores with alkali silicates,” in which they suggested using the so-called liquid glass—an aqueous alkaline solution of sodium silicates $\text{Na}_2\text{O}(\text{SiO}_2)_n$ [27]. Dissolved liquid glass was added to the briquetted ore, and the wetted mass was thoroughly mixed and pressed. The consumption of liquid glass for briquetting, for example, flue dust, was not less than 15–18% of the mass of the briquette. Compressed briquettes were dried and fired at 400–500 °C, after which they acquired good strength and water resistance. The disadvantages of the method revealed already at the first full-scale testing. Briquettes could not withstand high temperatures and differed low porosity. High cost of liquid glass together with its substantial consumption, markedly reducing the iron content in the briquette, made such briquetting economically unjustified and technologically inefficient because it required additional flux consumption and increased the amount of slag in the blast furnace smelting.

A method that allowed to significantly reduce the consumption of liquid glass for briquetting was soon proposed by Vegman [1]. The method was based on the binding properties of silicic acid gels of the general formula $n\text{SiO}_2 \cdot m\text{H}_2\text{O}$, which fall out of the liquid glass solution when treated with a weak solution of calcium chloride. To obtain such a gel, the ore was processed, before pressing, in succession with two solutions—first with a 1–2% solution of liquid glass and then with a 1.5–2% solution of calcium chloride—and then pressed. Freshly formed briquettes were dried and then burned at a temperature of 500–600 °C to dehydrate the resulting silica gel. The finished briquettes had high strength (18–22 MPa) and porosity up to 21% and met the requirements for blast furnace briquettes. The consumption of liquid glass in terms of the SiO_2 content decreased markedly (to 1.0–2.5%), but this decrease was compensated for by the need for costly roasting. And this method is not widespread.

In 1957–1958, a series of pilot industrial melts with briquettes in the charge of basic oxygen converters of the Petrovsky plant were held in Ukraine. Briquettes were made according to the method of Yarkho at the Krivoy Rog briquetting factory. The composition of the mixture—iron ore concentrate, limestone, bauxite and iron shavings fraction 0–3 mm. Raw briquettes gained strength during the week in a warmed warehouse. The supply of briquettes that gained strength was carried out along the path of bulk materials with the first addition of charge materials. Briquettes were also loaded into the converter during purging. In total, over 100 heats were held. In the first 60 heats, the content of calcium oxide in briquettes was 21.5%, and the missing amount of fluxes was injected into the converter in the form of lime. The melts performed confirmed the possibility of using ore–limestone briquettes to control the temperature of the metal bath. The process with briquette was more intensive, but emissions were not observed. The slagging process has

improved. For the next series of heats, the limestone content in briquettes was increased to 35.45% to achieve the required basicity ($\text{CaO}/\text{SiO}_2 = 10.74$). Experimental melts showed that briquettes are a useful and effective part of the charge of oxygen converters [28].

We will not dwell on the results of using briquettes in open-hearth furnaces, because this experience is only of historical interest, since this method of steel production is already in the past. Nevertheless, some of the results of using briquettes in open-hearth heats obtained in the late 50s in Ukraine continue to be relevant to the briquetting technology as a whole. By the way, for these heats briquettes were made all at the same Krivoy Rog briquette factory. The results of pilot industrial melts showed that the productivity of furnaces increased by 6.3% compared with the performance in the base period (when melting on the ore), while reducing the duration of melting when using briquettes by 2 h. The results made it possible to conclude that the use of briquettes in the charge of open-hearth furnaces is preferable to sinter and pellets.

In the 1950s, the first known attempt to produce iron ore briquettes was made using the vacuum extrusion technology well known in the ceramic industry. A wetted mixture of iron ore and bentonite was fed into the vacuum chamber and then into an extruder, from the die of which oblong cylindrical briquettes exited [29]. However, this method has not received its distribution at that time. Unsuccessful attempts to use extrusion for the agglomeration of raw materials in the iron and steel industry were also made in the USSR in the 60s. At the same time in Germany, the production of a tape-vacuum press was mastered, which included two screws and a vacuum chamber located between them. The first screw mixed and homogenized the mixture, and the second molded the briquettes, forcing the mixture through the holes of the die. The press was used for briquetting of ore and coal charges and concentrates of poor iron ores; however, its low productivity (10 tons of briquettes per hour) limited its use in metallurgy.

In the absence of new, breakthrough developments in briquetting in the 30–50 s of the last century, its suppression by sintering continued. In addition, since the 1950s, the industrial production of pellets began to develop rapidly—a technology that effectively pelletized fine concentrate. As of the middle of the last century, only about 0.5% of all iron-containing natural and man-made materials of ferrous metallurgy were briquetted [1]. Nevertheless, interest in briquetting has not waned, which was reflected in the creation in 1953 of the International Briquetting Association—a public organization uniting metallurgists and manufacturers of briquetting equipment [30], later renamed the Institute for Briquetting and Agglomeration. The progress of briquetting in the world was facilitated by the IBA science and technology conferences held in the USA every two years. For many years, IBA was headed by Richard Komarek (President and Founder of K. R. Komarek—the largest manufacturer of roller presses in the world).

3.2.3 60–70s of the Twentieth Century

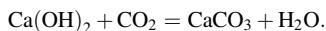
Interest in briquetting resumed in the 60–70s of the last century due to the complicated environmental situation in the areas of metallurgical production, associated mainly with harmful emissions from sinter plants. In 1961, the Donetsk Briquette Factory was built in the city of Donetsk (Ukraine). In the 1960s–1970s, briquetting factories at the Alchevsk and Magnitogorsk plants and the KMAruda plant were also commissioned. At Magnitogorsk Metallurgical Plant, mill scale was briquetted along with lime using a roller press, and the resulting briquettes were dried in a tunnel kiln. At the KMAruda combine, magnetite concentrate (Fe —59.68% and SiO_2 —5.5–14.0%) was briquetted together with quicklime. The mixture was mixed and maintained in silos, in which the lime was quenched with moisture concentrate. The lever press was used for briquetting. Raw briquettes were autoclaved at a pressure of 8 atm. and a temperature of 174 °C.

In Germany blast furnace, flue dust was briquetted with sulfite liquor as a binder (5–7% of the mass of the briquette). The briquetting factory, equipped with Humboldt roller presses (with a capacity of 10–15 tons/h), produced up to 200 tons of briquettes per day. To achieve the required mechanical strength, the briquettes were fired at a temperature of 600–900 °C. The resulting briquettes were melted in blast furnaces. The share of briquettes in the ore part of the charge reached 18%.

In the second half of the twentieth century, several experimental and industrial briquetting units for ore–fuel charges according to the Weber method [1] were also working in the Germany. Ore fines mixed with carbonaceous reducing agent (high-volatile coal and tar) and binders (sulfite-alcohol bard (SAB) concentrate—5% and hydrogenated coal tar or acetylene sludge—more than 20%) are mixed and briquetted in a roller press (20–70 MPa). Raw briquettes were dried at 250 °C and then subjected to semi-coking for one hour in retorts of the Humboldt company, where sand with a temperature of 700–800 °C was used as a heat carrier. Briquettes were used to smelt iron in low-pit furnaces with a capacity of up to 120 tons/day.

The production of ore and coal briquettes became widespread in the GDR. So at the Max Hütte enterprise, briquettes were produced from fines of poor iron ore (53% of the mass of the briquette, fraction 0–2 mm, total iron content 23–33%) with the addition of coke breeze (5% of the mass of briquette, 0–2 mm). Acetylene silt (42% of the mass of the briquette) was used as a binder, which also served as a fluxing additive. Briquettes were made with a roller press with a pressure of 50–70 MPa. Raw briquettes were carbonized by blowing off the exhaust gases from the blast furnace Cowper at a temperature of 120–150 °C for 30–120 min. The compressive strength of briquettes increased from 6–9 to 15–17 MPa after such processing.

The essence of the carbonization process as applied to briquetting is that calcium hydroxide ($\text{Ca}(\text{OH})_2$), the basic mineral of slaked lime, loses crystalline moisture when heated to 530–580 °C, as a result of which the binding properties are lost and the briquettes lose strength. Carbonization proceeding according to the scheme:



leads to the formation of secondary limestone, which is characterized by a dissociation temperature in the range of 860–920 °C, which determines the higher strength of the briquettes. Air carbonization is an extremely slow process and may require from a week to a month or more to achieve the required strengths of briquettes. To accelerate the carbonization process, the Weiss method is used, which consists in a two-stage treatment of briquettes with carbon dioxide under pressure. At the first stage, briquettes are treated with cold gas, and at the second stage, heated to a temperature of 90–100°.

Tests have shown that with an increase in the content of coke breeze, the strength of briquettes decreased, and with an increase in the iron content in the ore and pressing pressure, the sludge consumption decreased. Achieving the values of compressive strength of 20 MPa required the grinding of ore to the class—1 mm. With an ore fineness of 0–5 mm, the strength of briquettes averaged 17 MPa. When heated, the briquettes did not crack; till 400 °C their strength increased, and at a higher temperature—decreased. Full-scale testing conducted using such briquettes at two blast furnaces of the Max Hütte plant showed that the melting progress was improved both when replacing part of the traditional batch with briquettes and when melting 100% of the briquettes. The productivity of the furnaces increased by 20%, and coke saving was 14.7%.

At another metallurgical plant of the GDR in West Kalb, built after the Second World War, briquettes containing 75% of iron ore fines, 20% limestone, and 5% of coke breeze were smelted in 10 low-shaft furnaces of 78 m³. For hardening, briquettes used carbonization, as well as at the plant “Max Hütte” (see above). The share of briquettes in the charge of such furnaces reached 30–40%. The productivity of the furnaces, at the same time, increased by 4.1%, and the consumption of coke decreased by 11%. The furnace course was smooth, and the pressure of the top gas increased without increasing the pressure of the blast, which indicated a high gas permeability of the briquette layer of the charge.

One of the most important features of this stage in the development of the technology of briquetting was the emergence and wide distribution of the technology of so-called hot briquetting. By such was meant the molding of a softened, partially metallized mixture heated to high temperatures. The possibility of producing briquettes from metallized hot material was the result of the development and improvement of the design of roller presses. The interest in briquetting partially metallized material was due to hopes for increasing the efficiency of blast furnaces and steelmaking furnaces. The briquetted charge was distinguished by a higher iron content, uniformity of chemical and granulometric composition, resistance to secondary oxidation, etc.

One of the first successful projects of hot briquetting, which was important for the development of briquetting technology in general, was implemented in the UK

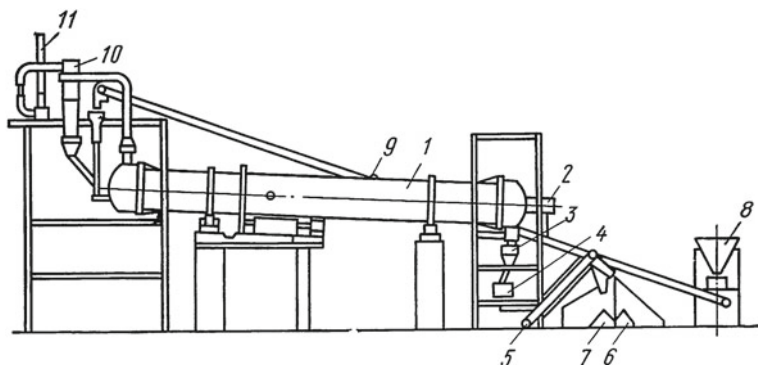


Fig. 3.11 Hot briquetting plant in Port Talbot (UK, [31]); 1—rotary kiln, 2—burner, 3—intermediate bunker, 4—roller press, 5—elevator, 6—briquettes, 7—screening of briquettes, 8—iron ore bunker, 9—secondary air supply, 10—cyclone, 11—exhaust pipe)

in the mid-60s. In a blast furnace with a volume of 1798 m^3 , briquettes made of iron ore concentrate by hot briquetting on a semi-industrial plant were melted. The hot briquetting unit was located at the Steel Company of Wales (now Tata Steel) in Port Talbot [31, 32]. It consisted of a rotary metallization furnace with a length of 25.6 m and a roller press (Fig. 3.11).

The share of briquettes in the blast furnace charge was 25%. The total number of the melted briquettes is 12 thousand tons. In fact, it was one of the first experiments using blast furnace briquettes. The operation of a large blast furnace did not deteriorate with the introduction of briquettes into the charge. However, coke consumption in the experimental period (25% of the briquettes in the charge) increased and amounted to 567 kg/t of pig iron versus 547 kg when operating without briquettes. Iron smelting also decreased from 2281 tons/day when operating without briquettes to 2234 tons with 25% of briquettes in the charge.

In the same years, the factory of hot briquetting was commissioned in the USA by United States Steele. Iron ore fines (particle size less than 0.635 mm) were heated in a rotary kiln and then fed to a roller press using a screw feeder. After sieving on the vibrating conveyor, the briquettes were supplied by a bucket elevator to the rotating refrigerator.

Hot briquetting was also applied by another American company—Dofasco. But in this plant, a mixture of iron ore fines, mill scale, and flue dust was heated to 1000°C in a fluidized bed reactor. The heated mixture entered the roller press of Komarek with a capacity of 10 tons/h. One of the important results was that the temperature dependence of the wear of the roller press tires was revealed. It turned out that at temperatures of the briquetted mass below 535°C , sleeves worked without replacement for a long time.

In the 1960s, several more companies in the USA commissioned hot briquetting lines—Dominion Foundries and Steel, Gray Iron Foundry, and others [33–35].

No less important achievement of the metallurgy of the 60–70s is the development and implementation of another method of briquetting associated with heat treatment. When briquetting ore–coal mixtures, the coal component of the charge, heated to a plastic state, played the role of a binder. In the modern literature, this method is also called hot briquetting, which often leads to confusion and embarrassment. More precisely, the essence of such a method is defined by the term “thermal briquetting” proposed at the Moscow Mining Institute (MGI), in which in the 60s of the last century the features of this method of briquetting and the properties of briquettes were fully studied [1, 36, 37].

The basis of the method known from the practice of continuous coking is the formation of a solid from coal of plastic mass upon reaching a certain temperature level. For example, hard coal is plasticized at 350–460 °C, peat—at 300–400 °C.

In experiments on thermal briquetting at MGI, various iron ore concentrates were used with an iron content of 65–68% and mixed with peat or black coal (Fig. 3.12). The prepared mixtures, with or without the addition of fluxes (from 5 to 15% hydrated and quicklime), were heated in electric molds to 300–430 °C. One of the main results of the research was that the quality of thermo-briquettes was mainly influenced by their fuel component. The chemical composition of iron ore concentrates practically did not affect the quality of thermal briquettes. The mechanical strength of such briquettes decreased with a decrease in the content of the fuel component in them. An increase in the pressing pressure from 20 to 120 MPa led to a noticeable increase in compressive strength and a less pronounced increase in abrasion strength.

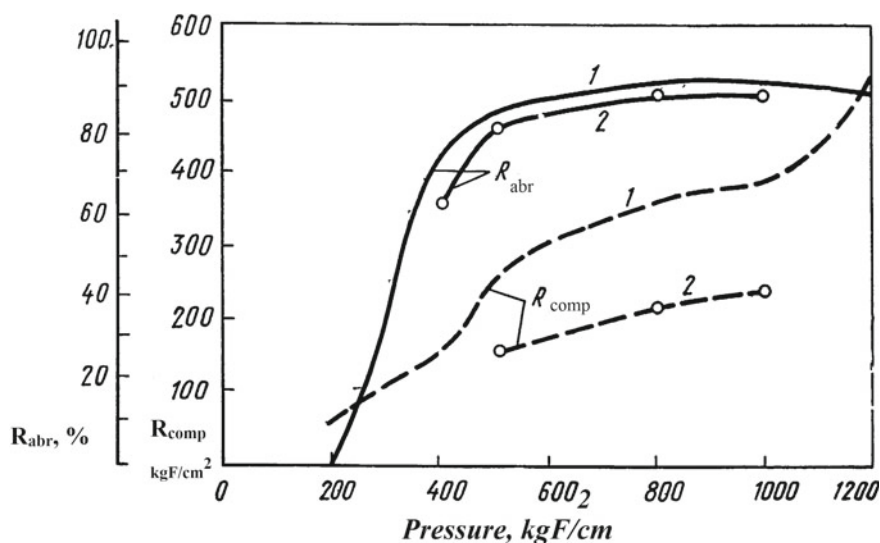


Fig. 3.12 Influence of pressure on the mechanical strength of thermal briquettes (1—briquettes with peat, 2—briquettes with coal, R_{abr} —abrasion resistance, R_{comp} —compressive strength) [38]

The addition of fluxes to the charge contributed to the growth of the mechanical strength of the briquettes due to the manifestation of the binding properties of lime. At temperatures of thermal briquetting, the formation of calcium hydrosilicates takes place, as in the Schumacher process described above. The content of calcium oxide in thermal briquettes was 1–3%, with 10–15% in the initial charge.

It was also found that the porosity of thermal briquettes depends on the particle size distribution of the charge components and the applied briquetting pressure. Porosity decreased with decreasing particle size and with increasing pressure. The absolute values of the porosity of thermal briquettes ranged from 19 to 39%.

The behavior of thermal briquettes during heating was studied in a resistance furnace with a graphite heater in a nitrogen atmosphere. The reduction of briquettes of two different compositions was studied—75% of ore and 25% of peat and 70% of ore and 30% of peat. For both compositions, the degree of reduction upon heating to 1500 °C reached values of 94–98% within 4.5 min. The high thermal stability of thermo-briquettes was explained by the formation of a framework of metallized phases.

Significant interest shown in those days to thermal briquetting in the UK, Germany, Holland, and Japan led to the emergence of a number of industrial plants in which the mixture heated to temperatures for plasticizing coal was briquetted with roller presses. Interest in such briquetting remains today.

Returning to the term “hot briquetting,” it should be noted that this concept should rather be referred to the processes of production of so-called hot briquetted iron (HBI), which is a product of direct reduction iron production processes, such as developed in the same time period (in 1966) the famous Midrex process [39]. Direct reduction iron briquetting is the only passivation method that complies with the standards of the International Maritime Organization (IMO) governing the rules of maritime transport. The fact is that, due to its high porosity, sponge iron exhibits a pyrophoric property, to combat which, its pressing in HBI is applied. The most popular in the world for the production of HBI received Köppern roller press [40]. Sponge iron after reduction in the Midrex reactor is fed at a temperature of about 700 °C to pressing with a specific force of up to 180 kN/cm. The continuous strip of briquettes coming out of the roller press is further divided into separate briquettes.

The historical picture of briquetting technology in 60–70 years would be incomplete without mentioning of another important milestone—the beginning of the use of briquetting for smelting ferroalloys. An interesting experience has been gained in the ferroalloy industry, showing the promise of using briquettes in the charge of ore-smelting furnaces. The first industrial experience of using briquettes based on manganese ore concentrates in the charge of the ore-smelting furnace was obtained in 1961, when 160 tons of roll briquettes made of manganese concentrate (30.9% Mn; 4% Fe; 0.577% P; 26, 95% SiO₂; P/Mn = 0.0018; 0.33% S; 1.9% CaO; and 4.05% BaO) was used in the charge of a 2500-kVA furnace of the Zestafoni Ferroalloy Plant (ZFP) [41]. The results of the heats showed that this type of charge component is quite effective. In 1966, pilot industrial studies on the smelting of ferrosilicon manganese in industrial ore-smelting furnaces were carried out at the

same plant using ore briquettes of manganese concentrate from the Chiatura deposit [42]. For industrial experiments, briquettes were obtained on a roller press with a capacity of 5 tons/h from ore with a particle size of 5–0 mm on a binder of sulfite-alcohol bards (SABs) with a density of 1.2 g/cm^3 . With an ore moisture content of 4% and an addition of 8% binder, the mixture was stirred for 15 min. And in this case, heat treatment was required. The fact is that the binding properties of SAB are caused by polymerization processes occurring in it, leading to the formation of long chains of molecules in the body of the briquette. The polymerization reaction in the presence of manganese is most fully realized at temperatures of 160–180 °C. For iron ore briquettes, the polymerization temperature reaches 200 °C. The achievement of the required strength values of briquettes required their drying at temperatures of 50–300 °C.

On the charge with ore briquettes, silicomanganese was smelted in a three-phase open ferroalloy furnace with a capacity of 16.5 MVA. The furnace worked normally and stably, the gas permeability of the charge was good, and the flame was distributed evenly throughout the furnace. After 112 h of experimental melting, it was concluded that sufficiently strong briquettes can be obtained from manganese ore of this size suitable for use in the charge of ferroalloy furnaces. When working on ore briquettes, the furnace productivity increases, the power consumption is reduced, and the reducing agent consumption is also reduced. In 1970, in the Dnepropetrovsk Metallurgical Institute, parameters of the smelting of marketable silicomanganese on a briquetted charge of a mixture of manganese oxide concentrates I and II of the Nikopol grade at 1: 1 and on sinter made from the same mixture were investigated [43]. For briquetting, the mixture of concentrates of a fraction of 10–0 mm was ground to a size of 3–0 mm. Briquettes were made on a semi-industrial roller press at a pressure of 500 kg/cm^2 , and the binder was a mixture of bitumen, fuel oil, and SAB in an amount of 10% by weight of the charge. The mixture was mixed in tanks with steam heated (to activate the polymerization of the SAB). Briquettes of two compositions were prepared and melted: with an excess of reducing agent (coal) in the amount of 50%, introduced to create a skeleton in the briquette and increase its strength (mixture of concentrates—54.5%, river sand—9.1%, coal—27.3%, a mixture of bitumen and mazut—3.6%, SAB—5.5%), with a stoichiometric amount of reducing agent necessary to reduce silicon and manganese (a mixture of concentrates—60.6%, river sand—10.1%, coal—20.2%, a mixture of bitumen and fuel oil—3.6%, SAB—5.5%). Laboratory tests showed that the physical properties of raw briquettes were superior to those for fired briquettes, so they refused to fire the briquettes.

The values of mechanical strength and heat resistance were higher for raw briquettes. Commodity silicomanganese was decided to be smelted on raw briquettes. Semi-industrial smelting on briquettes of the above composition and on sinter was carried out in a three-phase open ore-smelting furnace with a capacity of 1.2 MVA at a voltage of 81.60–85.89 V and a current of 6000–6500 A with a continuous process with a closed top chamber. Briquettes with an excess of reducing agent had a high electrical conductivity, and when penetrating they gave a significant increase in the current load, which led to the rise of the electrodes and

the opening of the top. To eliminate this phenomenon, 10% of manganese concentrate was added to the briquette sample. In this way, 14 tons of briquettes with an excess of reducing agent, 1.2 tons of concentrate, and 200 kg of dolomite were melted. The smelting of silicomanganese on briquettes containing a stoichiometric amount of reducing agent took place without any complications. The load was steady; in addition to briquettes, nothing was additionally introduced into the furnace. Comparative data of heats with different charges (briquettes and sinter) showed that smelting of silicomanganese on briquettes should be preferred to smelting on sinter.

The results of the pilot heats formed the basis for the construction and commissioning in 1976 of a briquette factory at the site of the Zestafoni Ferroalloy Plant. Manganese ore briquettes, in versions with the addition of gas cleaning dust and without it, were produced by roller presses Sahut Conreur (France). However, this first industrial experience was unsuccessful. Due to the increased wear of the bandages of roller presses, their high cost, and the impossibility of their independent production, this briquette factory was closed.

Briquetted charge was used also for smelting ferrosilicon. At the Zaporizhia plant of ferroalloys, briquettes were made from sand, coking coal, and iron ore concentrate. The mixture was heated and stirred in a steam mixer and then pressed with a roller press. Raw briquettes were burned at a temperature of 600–800 °C for 10–13 h to achieve a reduction degree of 70–80%. The smelting of ferrosilicon on the briquetted charge was carried out in a 3.5 MVA furnace. Briquettes were also used for smelting carbon black ferrochrome, ferrosilicochromium, and ferromanganese. When working on briquettes, the furnace productivity increased, and the power and reducing agent consumptions decreased [43]. The smelting of ferroalloys from briquetted charge became widespread in the USA, France, Japan, and Germany [44].

Summarizing the contribution of the 60–70s to the development of briquetting technology, it can be said that heat treatment of the charge or raw briquettes (in one form or another) remained in most of the implemented projects of briquette factories as a mandatory component of briquetting. The use of roller briquettes in blast furnace production did not lead to an increase in the scale of the industrial use of this technology in the iron and steel industry. The main reason for the low competitiveness of briquetting in those years was the low productivity of roller presses compared to the performance of sintering tape (1500–10,000 tons/day) and firing machines (2500–9000 tons/day). In the ferroalloy industry, where the requirements for productivity and for the strength of briquettes are much lower than in the blast furnace, growth in briquette production was observed. As a result, by the mid-70s, the production of briquettes was already about 2% of the total volume of agglomeration in ferrous metallurgy [45].

3.2.4 *The 80s—The End of the Twentieth Century*

In the last two decades of the last century, one of the main incentives for the development of briquetting technology was still the difficult environmental situation in the regions where metallurgical plants are located, primarily due to harmful emissions from sinter plants (more than 50% of all harmful emissions). In the structure of emissions of pollutants of the integrated metallurgical enterprise for all the most significant components of emissions (dust, carbon monoxide, sulfur dioxide, nitrogen oxides), sintering is dominated by 31.1% dust, 77.8% CO, 61% SO₂, 26% NO_x [46].

In addition, it turned out that not all types of fine anthropogenic materials of ferrous metallurgy can be considered as a full-fledged charge material for sinter production. First of all, this applies to blast furnace and converter sludge. The presence of zinc and lead in such materials prevents their use in sinter production. The use of dusts and sludge from electric furnaces for the production of sinter also poses serious difficulties due to fluctuations in the chemical composition of such materials, high dispersion, low iron content, and the presence of nonferrous metals. The “capricious” charge for sintering is also the flue dust due to its poor crumpling ability due to the presence of carbon. Much of the flue dust is carried away with sinter gases and repasses to the sludge. A separate problem in the sinter production was also the preparation of small fractions of the so-called return (sinter fines) to the sinter production.

A similar problem turned out to be relevant to another technology of agglomeration—the production of pellets. This problem arose most acutely in Sweden, where by the end of the last century blast furnaces worked exclusively on pellets. The last sinter plant in Sweden ceased to exist in 1995 [47].

The limited or inability to use the above materials for sinter production, the accumulation of reserves of iron-rich pellet fines together with the increased cost of waste disposal (up to \$10–15 per ton of waste) in the early 90s justified efforts to find effective methods of briquetting such materials. Briquetting was destined to become recycling technology—the “assistant” of sintering and pellet production. The search led to the emergence in the arsenal of briquetting a new method of forming briquettes—vibropressing.

Thus, in Germany, in 1982, in the framework of a project for the effective recycling of dust and sludge with a high zinc content, known as the “oxy cup,” a study was launched aimed at choosing the most efficient briquetting technology. The result of the research, which continued in 1995 in Aachen, was the choice in favor of the technology of vibropressing for the production of carbon-containing self-reducing briquettes (C-Brick, [39]). The possibility of using vibrations for agglomeration was well known by then. First, as early as 1902, vibration was used in the USA in the production of concrete, and in 1927 in France a patent was issued for a method of vibrating concrete compaction. In the same year, a method for producing agglomerated masses using vibration was patented in the USA (Fig. 3.13, [48]).

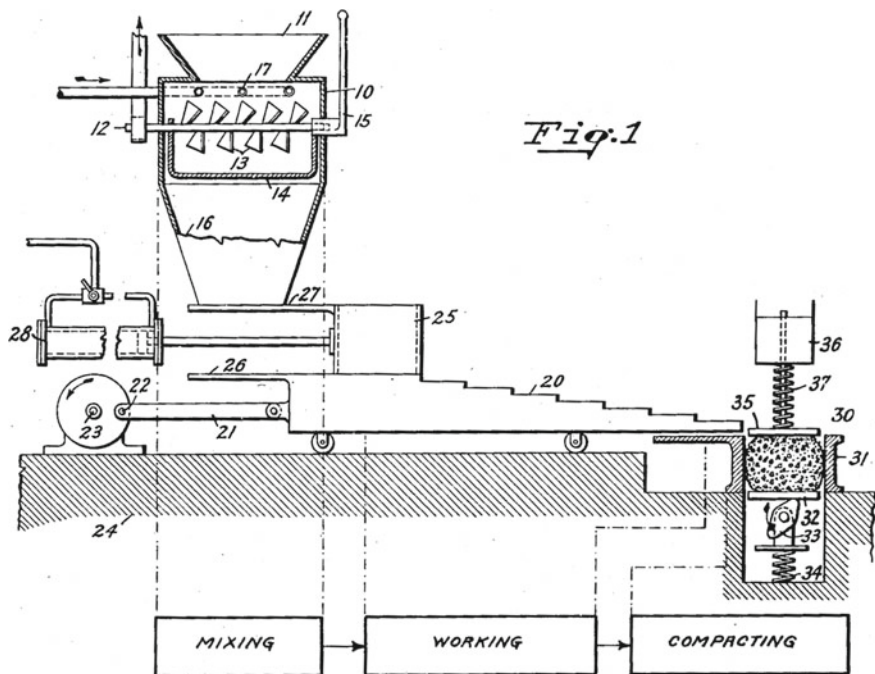


Fig. 3.13 Illustration for US patent No. 1647075 on the method of production of agglomerated mass using vibration [48]

In 1988, the first vibropress briquetting factory with a capacity of 110 thousand tons of briquettes for ferrochrome smelting was commissioned at Vargön Alloys in Sweden [49]. Since 1991, this method of briquetting has been used in France by Eurometa SA for the agglomeration of the ferroalloy fines [50]. Briquettes from ferroalloy fines were used in the foundry business.

According to this method, briquettes were produced at low pressures (0.02–0.1 MPa) and simultaneous exposure of the compression mixture to vibration (frequency 30–70 Hz and amplitude 0.2–0.6 mm). For molding, multi-die molds with sizes from $20 \times 20 \times 20$ mm to $500 \times 1500 \times 1500$ mm were used. The manufacturing cycle lasts no more than 30 s. Cement was used as a binder.

The components of the briquette were dust and sludge from the blast furnace production, converter and electric smelting production, oily mill scale, magnetic slag fractions after desulfurization, and other iron-containing materials. Carbon-containing components are—coal, coke breeze, anthracite, petroleum coke. Briquettes together with large-sized (up to 1 m in diameter) metallurgical slag scrap were then melted in a special cupola operating on an oxygen-rich blast. The share of briquettes in the cupola charge was up to 70%.

In 1999, a pilot cupola with a capacity of 210 thousand tons per year was built in Duisburg (Germany) at a loaded charge consisting of 75% of briquettes and 25% of

bucket skulls. The satisfactory metallurgical properties of the briquettes produced by this new method contributed significantly to the commercial success of the oxy cup process, which today is rightly regarded as providing a solution to the problem of recycling zinc-containing dusts and sludge. In the period from 2005 to 2011, 6 oxy cup process furnaces with briquette factories were built in the world (three each in Japan and in China). However, the high cost of the main equipment and engineering of oxy cup and the insufficiently high performance of the vibropress (up to 20 tons/h) restrain its further wide distribution.

The choice of vibropressing as a method of briquetting pellet fines also came from specialists of Merox Company (Sweden, [51]). One of the first industrial briquette lines of vibropressing was put into operation at the SSAB plant in Oxelösund (Sweden) in 1995 [52]. Briquettes 60×60 mm in size and hexagonal in cross section are used as a component of the blast furnace charge (60–100 kg of briquettes per ton of iron). The composition of the briquette is 25% top dust, 50% mixture of scrap metal, desulfurization scrap, converter sludge, pellet fines, and 5–8% aspiration dust. Binder, Portland cement (10–12%), has moisture content of briquettes 5–8%. The particle size of the briquetted mixture is 0–5 mm. The limitation for the proportion of briquettes in the blast furnace of SSAB is the zinc content in the sludge. By the way, as studies conducted at the Technical University of Lulea showed, briquettes from pellet fines showed abnormal swelling (volume increase by 20%), similar to swelling of the pellets themselves, when reduced in atmosphere of the CO and H₂ mixture [53–55].

The vibropressing briquetting technology debuted in this way turned out to be commercially successful, but still could not be considered 100% cold agglomeration technology, since the briquette's curing required their thermal treatment at temperatures of 80–120 °C. An important result of the above-described vibropressing experience was also the restored “reputation” of cement as a binder.

But perhaps the most important event of the last two decades of the last century in briquetting was the entry into the market of companies specialized in providing briquetting services for ferrous metallurgy materials on a so-called toll basis, when briquettes are made by the manufacturer at their own expense from the raw materials provided by the metallurgical enterprise.

The pioneer of such a business in briquetting was the company National Recovery System (NRS, USA), which in the early 70s began to search for a solution to the problems of utilization of oxide materials of ferrous metallurgy by briquetting. Several compositions of briquetted fluxing additives and various compositions of briquettes from materials with high iron content were worked out. These briquettes began to be widely used in the US recycling practice in the 90s of the last century. Since the end of the 80s, the NRS has been looking for efficient and inexpensive binders for briquetting in blast furnaces. The combined binder of molasses and non-gypsum cement, for which the patent was obtained, was used in the production of 15,000 tons of experimental blast furnace briquettes for smelting on blast furnace No. 8 by US Steel at Gary Works [56]. To achieve the required hot strength in blast furnace smelting, from 14 to 19.5% (mass) of such a binder was added, as indicated in the patent itself. For the composition consisting of mill scale

(41%), steelmaking slag (19%), and flue dust (40%), 11.5% of cement and 8% molasses were required, which considerably diluted the mixture. In addition, the briquetted charge had to be dried to a moisture content of 3%, since it is impossible to form a wet mass using a roller press. Such low moisture content turned into a lack of moisture for cement hydration. Cold strength of briquettes, measured according to ISO 3271-1985 E tumble testing, was not less than 70% (the proportion of pieces of briquettes with a size of more than 6.3 mm after the 200 turns of the drum at a speed of 25 revolutions/min). The share of briquettes in the blast furnace charge, which did not violate its operation, reached 10%. This level was quite enough for recycling anthropogenic materials. The success of the pilot campaign allowed the NRS to build four briquetting factories in the USA and one in the UK at the Port Talbot plant.

In early 1993, US Steel began working at the Edgar Thomson plant, the Bethlehem Steel Company in Pennsylvania, and the Inland Steel Company. The fourth factory in the USA began operations in 1996 at the National Steel Corporation's plant. In 1997, the factory began operation in the UK.

There was no sintering plant at Edgar Thomson's US Steel plant, and all the generated iron-containing wastes were buried or stored in dumps. The above-mentioned increase in the cost of waste disposal has provided an economic opportunity for their on-site processing by roller briquetting. Briquetting factory was designed to produce 200 thousand tons of briquettes per year. Productivity of the pressing equipment is 40 tons of briquettes per hour. A patented composition of molasses and cement was used as a binder. And it was with this mixture associated with the first problem faced by the blast furnace specialists. Starting from about the sixth month of operation, the smells emanating from the blast furnace gas cleaning system became a serious problem. The source of the smell has been identified. It turned out to be a protein that got into the system with molasses. It was decided to switch to a purely inorganic binder, as a result of which odors ceased. By 1998, up to 10% of briquettes were used in the blast furnace charge. For the converter briquettes, a combined binder from a mixture of lime and molasses was also used, but no odor problems were noted.

The briquetting factory at the Inland Steel plant had to solve the problem of recycling 100% of all iron-containing anthropogenic materials—current and previously accumulated. The need to eliminate dumps at the site of the enterprise and the rising cost of disposal outside of its borders stimulated the search for a suitable recycling method, which resulted in a choice in favor of roller briquetting. Factory capacity is 250,000 tons of briquettes. Briquettes were used in the charge of blast furnaces and oxygen converters. When using blast furnace briquettes at this enterprise, there was also a problem with odor. In addition, there were elevated levels of ammonia in the wastewater. As in case with Edgar Thomson's US Steel plant, it was also decided to abandon the combined binder.

Another briquetting factory built by NRS was located at the site of the National Steel plant. The sinter plant was closed shortly before that, all the anthropogenic materials were formed during the operation of the three blast furnaces, and two converters were accumulated or buried. The roller briquetting factory was designed

for production of 300 thousand tons of briquettes per year, of which 80% of briquettes were intended for blast furnace charge. Briquettes were made from blast furnace and converter sludge, top dust, mill scale, coke breeze, and other materials. The share of briquettes in the blast furnace charge reached 6.5%.

Roller briquetting was also used at the NRS briquette factory built in Port Talbot (UK). Rising costs for the disposal of waste was again the main incentive for their processing. Unlike the aforementioned briquetting factories, zinc-containing converter sludge was briquetted here. Other anthropogenic materials were added to the sintering mixture. Another feature of briquettes was the high content of coal (up to 30% by weight). The capacity of the factory is 180 thousand tons per year of briquettes per year.

In 1993, the NRS also built a roller press briquetting factory at the Lake Erie Works plant in Canada [57].

In the summer of the same year, the Bethlehem Steel plant built and put into operation a briquetting line based on stiff vacuum extrusion (SVE), a technology widely used in the USA for the production of bricks. The factory was intended for the agglomeration of converter dust that has been stored in the company's dumps for many years, and upon reaching a critical level of its accumulation, the owners of the enterprise were forced to recycle this material. Briquettes were used as a component of the blast furnace charge. The capacity of the line was 100 thousand tons of briquettes per year [58]. The performance of the extruder supplied by J. C. Steele and Sons reached 20 tons/h. The main attractive advantage of extrusion, which led to the choice of this technology for briquetting, was the very low cost of basic equipment. Cement was used as a binder, which added \$8 per ton to the cost of briquette. The cost of manufacturing tons of briquette ranged from 11 to 14 US dollars. In total, the line produced about 70 thousand tons of briquettes and was dismantled in 1996 after the liquidation of Bethlehem Steel. Disputes about the expediency of liquidation of the company have not yet subsided, and the blast furnace, where the extrusion line was located, is a gloomy monument to the once successful enterprise. The equipment of this line still functions as part of a Texas Instruments bauxites briquetting plant [59].

Thanks to the efforts of NRS, the scale of briquetting in the world has increased significantly. In essence, the company created a market for briquetting services, to which other service companies soon entered. Another important achievement of this legendary company was that the briquetting was finally cold. Preparation of briquettes for metallurgical processing did not require any heat treatment if you do not take into account the drying of the charge for a roller press.

It is also very important that the NRS Company became the “godfather” of a fundamentally new technology of briquetting—stiff vacuum extrusion. But, as often happens, this industrial extrusion briquetting debut went unnoticed and unappreciated by the metallurgical community, and the NRS Company, despite the undoubted success of the project at Bethlehem Steel, no longer used stiff extrusion in its projects.

However, in 1996, one of the largest briquetting factories for the production of extrusion briquettes made from aspiration dusts of ferronickel production and

Fig. 3.14 Extrusion briquette manufacturing in Colombia



lateritic nickel ore fines with an annual production of 700 thousand tons was put into operation at a ferronickel plant in Colombia (Fig. 3.14). Initially, this enterprise, which has been operating since 1992, used pelletizing and roller press briquetting to agglomerate the fines of lateritic nickel ore and gas cleaning dust of electric furnaces. In 1996, after carrying out a series of comparative tests of various methods of agglomeration and processing of these materials (pelletizing, agglomeration, plasma furnaces, and SVE), the final choice was made in favor of the SVE technology, which made it possible to obtain an agglomerated product of the required size and shape with cold and hot strength sufficient preserving the integrity of briquettes when they are processed in rotary kilns and when melted in electric furnaces. This technology allowed to achieve high performance with a minimum cost of the resulting product. The company installed three Steele-90 extruders to produce 700 thousand tons of briquettes per year. A characteristic feature of the briquetting of the lateritic nickel ore using the SVE technology is the possibility of obtaining strong briquettes without the use of a binder. The main equipment of extrusion lines has been operating for 20 years without replacement. Nickel production in ferronickel in Cerro Matoso is 50 thousand tons per year, of which 10 thousand tons are brought in by briquettes. Nickel content in commercial products is 35%.

An equally important event in the history of briquetting in the ferroalloy industry is the development of the technology for smelting low-phosphorus carbon ferromanganese with a 100% briquetted charge [60]. In 1987, an experimental test of this technology was conducted under the conditions of the Nikopol Ferroalloy Plant in comparison with the traditional technology (Table 3.1). A three-phase ore-smelting furnace with a capacity of 3600 kVA was used as a melting unit.

The essence of the technology was to smelt carbon ferromanganese with the required low phosphorus content using the fluxless method with the charge, the ore part of which, in addition to graphite concentrate, contains a concentrate obtained by chemical enrichment of sludge. Low-phosphorus manganese slag produced by smelting carbon-free ferromanganese by flux-free method is used as a raw material

Table 3.1 Main indicators of the process of smelting low-phosphorus carbon ferromanganese

Parameter	Traditional technology	Briquetted charge
<i>Mass share in metal, %</i>		
Mn	78.10	80.55
C	5.26	5.24
Si	3.34	1.37
P	0.140	0.053
S	0.013	0.019
<i>Mass share in slag, %</i>		
Mn	11.66	40.16
SiO ₂	33.01	25.26
CaO	39.70	15.90
Slag basicity CaO/SiO ₂	1.20	0.63
Slag rate	2.21	1.15
<i>Mn distribution, %</i>		
In metal	65.75	55.38
In slag	21.77	32.88
LOI	12.48	11.74
Useful use of manganese, %	65.75	88.26
Capacity, base tons per day	4.10	6.44
Specific energy consumption, kWh/b.t.	5556.5	3485.5

in the smelting of low-phosphorus silicomanganese, refined ferromanganese, and metallic manganese.

Analysis of the results of the experimental melting showed that the briquetted charge provided an economically acceptable solution to the problem of smelting high-quality ferromanganese from highly phosphorous manganese ores.

Important results that contributed to the development of briquetting in the ferroalloy industry were obtained in the process of developing and commercializing technologies for producing dust briquettes and smelting manganese ferroalloys from them at the Zestafoni Ferroalloy Plant [61]. The need to dispose of dust and sludge from furnace gas cleaning was due to the large volume of its formation (50 thousand tons annually). Taking into account the metallurgical evaluation of waste, their dispersed state, and physicochemical properties, it was proposed to make briquettes from the mix of the dry dust, previously dehydrated sludge, and third-grade manganese concentrate. It has been established that to obtain mechanically strong briquettes (8–12 MPa), the optimum briquetting parameters are: moisture content of the charge 4–6%, binder content (SAB) 6–8%, amount of the fine component (dust and sludge) 30%, and minimum compacting pressure of 19.6 MPa. The comparative kinetics of the recovery of sludge briquettes and manganese sinter was investigated. It was found that briquettes gave the greatest degrees of reduction at different temperatures. The use of manganese and silicon from waste was increased due to the presence of bound carbon in them and the low

intensity of silicate formation, which is inevitable when using sinter. The results of high-carbon ferromanganese heats showed that the capacity of the furnace in the case of using briquettes increased from 73.33 to 75.67 tons/day, and the specific consumption of electricity decreased by 90 kWh/ton. Coke consumption decreased by 34 kg/t.

Thus, by the end of the last century, the main competing industrial technologies of briquetting were defined: roller press briquetting, vibropressing, and stiff extrusion. The market of manufacturers of equipment and services of briquetting according to the “toll” scheme has been formed. Briquetting has become firmly established in all branches of the steel industry. It is also important that, by this time, the success of technological developments was largely ensured by specialized scientific institutions (universities and laboratories). The role and importance of the Institute for Briquetting and Agglomeration (IBA) has increased, which contributed to bringing together the efforts of scientists, metallurgists, equipment manufacturers, and the growing popularity of briquetting. In 1999, the 26th IBA Conference took place, which was opened by Wolfgang Pietsch, author of the encyclopedic monographs on agglomeration in industry published in the 1990s [62].

3.2.5 *Twenty-First Century*

These trends also manifested themselves at the beginning of our century.

NRS continued to dominate the briquetting market. In 2004, another factory was built in the USA at the site of AK Steel, and since December 29, 2005, the NRS became a structural unit of Harsco Metals [57]. By 2011, Harsco Metals already owned a dozen briquetting factories around the world. Without exception, these briquetting factories were used for the production of briquette roller pressing. Seven briquetting factories, of which five with the capacity from 150 to 250 thousand tons of briquettes a year, were working in North America at the sites of the company's customers (US Steel Edgar Thomson Works, US Steel Lake Erie Works, ArcelorMittal—IH East, US Great Lakes Steel, AK Steel—Ashland), and two more with a capacity of 100 thousand tons of briquettes per year were located at the sites of Harsco Minerals. Several briquetting factories operated in Europe (two in the UK—at Port Talbot and Scunthorpe; three in France; and one in Slovakia) and in Asia. Briquettes were used in the charge of blast furnaces and oxygen converters. Blast furnace briquettes were produced in five factories—US Steel Lake Erie Works, US Steel Great Lakes, AK Steel—Ashland, US Steel's Mon Valley, and ArcelorMittal—IH East. Briquette charge included mill scale, blast furnace, converter sludge, and bag filter dust. ArcelorMittal—IH East used bauxite and flue dust briquettes. The share of briquettes in the blast furnace charge averaged from 3 to 6% (the maximum value is 12%). Fresh oily mill scale briquettes were added to the charge of converters, for example, at the Harsco Metals factory in Fort-sur-Mer (France). The share of briquettes in the charge was 1%. The briquetting factory in Ugine (France)

produced 10 thousand tons of mill scale and aspiration dust briquettes for steel-smelting electric arc furnaces (EAFs).

The business of Harsco Metals was promoted by the changed prices for charge materials. When comparing the prices of coke and iron ore fines in the late 80 s and by 2011, it was clear that the briquette began to be a valuable component of the charge of metallurgical aggregates and not just a means of recycling anthropogenic materials. In fact, the cost of coke breeze increased over this period from 45–60 to 350–400 US dollars per ton (almost 8 times), and the cost of iron ore fines—from 20–25 to 170–180 US dollars per ton (more than 7 times), while the cost of waste disposal increased from 10–15 to 30–35 US dollars per ton (twice). The total volume of briquettes produced by Harsco Metals exceeded 1.5 million tons per year in 2011.

In 2010, the company made an unsuccessful attempt to enter the market of briquetting services in Russia. It was planned to carry out a project for the production of almost 800 thousand tons of briquettes for blast furnaces from a mixture containing flue dust, aspiration dust, converter, blast furnace sludge, and sinter fines. A mixture containing additives developed by Harsco Metals was recommended as a binder (the composition was not disclosed). The proportion of binder in the briquette mass exceeded 17%, which would lead to a substantial “dilution” of the blast furnace charge. This project was never implemented.

A similar picture began to take shape at other briquetting factories of the company, which led to the fact that Harsco Metals completely ceased production of blast furnace briquettes, and the production of briquettes for converters was preserved only in the factories in Fort-sur-Mer (France) and in both factories in Great Britain. The Harsco Metals briquetting factory in Kosice (Slovakia) changed owners in 2015 and currently briquettes for converters are manufactured by the Phoenix Services [63] service company, founded in 2003.

Thus, roller compaction was almost completely superseded from the blast furnace segment of the briquetting market. However, roller press briquettes are still successfully used in steelmaking processes (in converters and in EAF).

Roller presses continued to be used in the ferroalloy industry. In particular, roller presses are used for agglomeration of metallized, and, therefore, abrasive, fines of crushing of ferroalloys [64]. In recent years, the efforts of many manufacturers of ferroalloys have been directed toward the development of efficient technology for the briquetting of crushing ferrosilicon fines [65, 66].

Nowadays, one more application of roller briquetting is the agglomeration of dispersed oxide and metallized materials of direct reduction iron (DRI) production processes.

In 2002, POSCO launched a rolling briquette factory to produce 500 thousand tons of briquettes per year from coal fines as a replacement for expensive coking coal in the FINEX process [67].

In 2011, a roller briquette factory was built in Brazil as part of an industrial demonstration plant operating according to the Tecnored process [68]. Briquettes are used in the charge of low-shaft furnaces of the process, as an alternative to

cold-bonded pellets. In 2015, the plant successfully reached a design capacity of 75 thousand tons of pig iron per year.

In 2016, Qatar Steel put into operation a roller press factory equipped with a South Korean-made press (Jeil) to agglomerate metallized dusts and sludge formed during the direct production of iron in the Midrex reactor. By 2018, the factory produced 200 thousand tons of briquettes, which were successfully smelted in the company's electric furnaces.

Primetals completed a series of studies that confirmed the viability of using roller press briquettes as components of the Midrex process charge and in 2015 announced plans to build a briquetting factory in Corpus Christi (Texas, USA) as part of a DRI reactor construction project (Midrex). The factory, commissioned in 2016, produces 160 thousand tons of briquettes from dust, sludge, and pellet fines per year.

Emirates Steel has announced the construction of a mill for the production of briquettes for the agglomeration of metallized and oxide materials generated in the Midrex process. Briquetting services will be provided by Phoenix Services [63].

Another interesting application of roller press briquetting, unfortunately not crowned with success, is associated with the pig iron zinc oxide (PIZO) process developed by Heritage Technology Group, in which briquettes from a mixture of EAF dust and carbon were melted in induction furnaces. A pilot plant was built at the site of the Nucor plant in Blytheville (USA) [69]. The briquettes are fed into the molten iron bath, in which the reduction of iron oxides by the carbon of the briquettes takes place. Volatile metal oxides (zinc, lead, cadmium, etc.) evaporate at the operating temperature of the furnace (1300–1500 °C) and are collected by bag filters. The zinc-rich material obtained in this way can then be used as a raw material in zinc plants. The zinc content in this material reaches 67%. Commodity products of the PIZO process are, in addition, cast iron and slag. Since the construction of the pilot plant in 2006, neither the technology developer company nor the customer has announced a transition to the full-scale project stage.

In general, for well-known reasons, the use of briquettes made of iron oxides in the charge of induction furnaces is impractical. In the body of such a briquette, eddy currents will not be induced, leading to the heating of a traditional metal mixture of induction furnaces in an alternating electromagnetic field.

A method for efficiently melting such briquettes in induction furnaces was proposed in 2012 [70]. It is proposed to equip an induction furnace with a graphite electrode and a plasma burner. Melting of the electrically conductive mixture at the bottom of the crucible is carried out by arc energy, followed by switching on the inductor and adding briquettes in portions with the formation of a protective charge layer between the arc and the crucible wall with a decrease in discharge power as the briquette is metallized with hard carbon and hot slag is formed. The proportion of briquettes can reach 90% of the mass of the charge.

The melting in induction furnaces of metallic wastes from foundry and engineering (grinding cuttings, iron and steel chips, etc.) was successfully implemented in Western Europe as part of the BRICETS project in 2004. For smelting iron and steel using such waste, an induction crucible furnace is recommended. Two types of

lumpy charge materials were tested—briquettes and pellets. Balance smelting on briquettes made from metallic materials implemented at a number of Scandinavian enterprises showed their acceptable efficiency. At the same time, research in the framework of the BRICETS project [71], conducted in the UK with pellets, showed the futility of their use as an additive in an induction furnace charge. Currently, the results of the BRICETS project are implemented in commercialized projects in the Swerea Group and SKF (Mekan and Gothenburg, Sweden). Reducing (or completely eliminating) the cost of disposal of waste (grinding sludge) contributes to the success of the process. The SKF plant in Mekan used cast-iron briquettes with the addition of grinding sludge (5%) and aspiration dust (2%). The quality of cast iron does not cause any complaints.

As for briquetting in iron metallurgy, until 2011 the lion's share of blast furnace briquettes was produced by the method of vibropressing.

In Russia, the first vibropressing factory was commissioned at the enterprise JSC Tulachermet in 2003 [72].

A series of campaigns on the use of vibropress briquettes of different component compositions on a cement binder in a 1000 m³ blast furnace charge was carried out in 2003 at NLMK [73–75].

In 2004, Progres Ecotec (Czech Republic) began to produce vibropress blast furnace briquettes for ArcelorMittal.

In 2010, the Kosaya Gora Iron Works put into operation a vibropress factory with an annual capacity of 120,000 tons for the production of briquettes from a mixture of concentrate, ore fines, flue dust, and a binder—Portland cement (not less than 10% of the mass of the briquette) [76].

In March 2012, a vibropressing line for the production of briquettes for blast furnaces was put into operation at the enterprise of the SSAB Company in Finland (Raahe Works) [77].

The results of full-scale testing and industrial use of vibropress briquetting technology show the fundamental possibility of achieving the required level of metallurgical properties of agglomerated products. However, this method of briquetting creates some significant technological limitations, overcoming of which either is difficult or leads to a significant increase in the cost of briquette. As of the beginning of 2016, briquettes in this way in industrial volumes are not produced in Russia.

The ferroalloy industry has also maintained an interest in vibropressing, aided by the success of the factories mentioned earlier, Vargön Alloys and Eurometa. Since 2001, Aaltvedt Betong AS's vibropress factory has been operating in Norway, producing briquettes for Eramet [78]. Manganese ore fines and gas cleaning dust are briquetted. Binder is the Portland cement (10–12% of the mass of the briquette).

An example of the successful application of vibropress briquetting technology for the agglomeration of manganese-containing anthropogenic materials, including ferroalloy fines, is the experience of the South African company Assmang at the plant in Cato Ridge [79]. Vibropress briquettes made of silicomanganese on a “toll” basis were also produced in the USA for the Felman Company [80].

In 2006, the technology of stiff vacuum extrusion briquetting again entered the “arena.” In Brazil, a briquette factory for the production of extruded briquettes from lateritic nickel ore fines and aspiration dusts of ferronickel production was commissioned—a complete analog of the factory previously built in Colombia with a capacity of 700 thousand tons of briquettes per year. The factory was built on the site of the company Vale. Thus, the total annual production of briquettes using stiff vacuum extrusion was 1.4 million tons, comparing with the total production of briquettes at Harsco Metals factories.

Despite such obvious commercial success, until 2009, stiff extrusion technology remained terra incognita for the steel industry. The choice in its favor could be based more on risk than on the results of a systematic study of the metallurgical properties of extrusion products. This gap was eliminated as a result of research carried out by Bizhanov A. M. and others [59, 81–90]. In the period 2009–2013, stiff extrusion has been systematically studied and adapted to the conditions of most industrial processes for smelting iron, steel, ferroalloys, and direct iron production. The choice in favor of this technology became conscious and scientifically grounded. For the designation of extrusion products, the term BREX (extrusion briquette) was proposed, for which a trademark registration certificate was issued [91].

Let us compare some parameters of roller and vibropress briquetting with briquetting using a stiff extrusion method (Table 3.2).

Table 3.2 Comparison of briquetting technology

Process characteristics and properties of briquettes	Briquetting units and their characteristics		
	Vibropress	Roller press	Stiff extrusion
Maximum performance	30 t/h	50 t/h	100 t/h
Service life (cost of parts to be replaced, US \$/ton)	1 year (n/d)	1 year (1.5)	1.5 year (1.0)
Compaction pressure	0.02–0.10 MPa	40–150 MPa	3.5–4.5 MPa
Cement share in briquette, %	8–10	15–16	4–6
Heat treatment of raw briquettes	80 °C (10–12 h)	Drying of charge	Not required
Returns	Absent	30% of production	Absent
Briquette shape	Prism, cylinder	Pillow	Any shape
Briquette size, mm	80 × 80	30 × 40 × 50	5–50
Charge moisture content, %	Less than 5%	Less than 10%	12–18%
The ability to store raw briquettes in a pile	Absent	Possible	Possible
<i>Utilities</i>			
Electricity	42.6 kWh/t	45.0 kWh/t	33 kWh/t
Natural gas	47 m ³ /t	0	0
Heat	0.3 GCal/t	0	0
Compressed air	90 m ³ /t	0	0

The high performance of stiff extruders, the possibility of agglomeration without pre-drying the charge, and the lower consumption of binder caused a growing interest in extrusion briquetting technology.

In April 2011, an industrial briquetting line was commissioned at the Suraj PL plant in Rourkela (West Bengal, India), producing brex for their use in a blast furnace. The management of the company decided to implement a project for the production of brex from a mixture of converter sludge, blast furnace dust, Portland cement, and bentonite. The main objective of the project was to increase the economic efficiency of a small blast furnace by replacing the purchased ore with cheap brex.

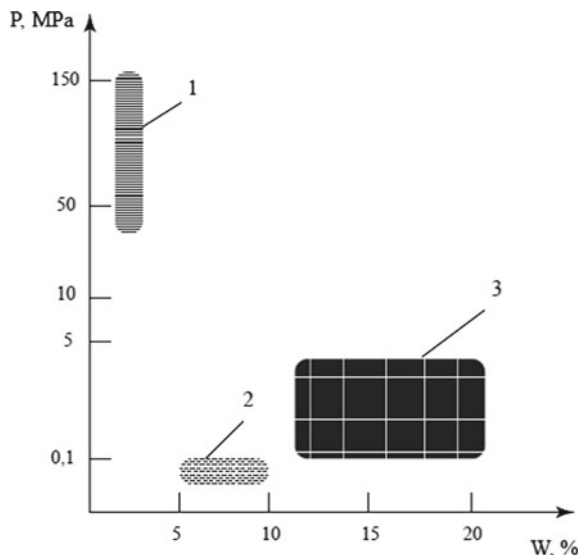
In the period from 2011 to 2018, 5 more briquette factories were commissioned, producing brex. Among them are two factories for the production of blast furnaces, two for the smelting of silicomanganese and ferromanganese, and one factory for the production of brex for the smelting of ferrochrome. A distinctive feature of projects carried out in the interests of ferroalloy companies was their pronounced environmental focus. Extrusion agglomeration made it possible to effectively utilize gas cleaning system dust accumulated over decades, significantly improving the ecological situation in the area of ferroalloy production.

The world's largest factory for the production of blast furnace brex was built in 2018, Lipetsk (Russia), at the site of NLMK. Its capacity is 700 thousand tons of brex. With its commissioning, the total annual production of brex will exceed 3 million tons.

The first experience of the operation of SVE lines in comparison with the experience of roller press and vibropress briquetting factories made it possible to designate some specialization of the known methods of briquetting. Namely, for the briquetting of dry materials with organic binders, when the achievement of high hot strength of briquettes is not required, roller press briquetting allows to obtain mechanically strong briquettes due to the application of high pressure (up to 150 MPa). Vibropressing allows agglomeration of a mixture containing a substantial part of large fractions (up to 10 mm and more), but requires special measures to preserve the strength of raw briquettes (moving on pallets, heat, and moisture treatment) and does not allow moisture of the briquetted mixture to exceed 12–15%. Stiff extrusion is irreplaceable when agglomerating thin materials and is able to agglomerate mixtures with a moisture content of up to 20% at compacting pressures an order of magnitude lower than in a roller press (3.5 MPa). In particular, this technology allowed the agglomeration of EAF dust and gas cleaning dust of ferroalloy production, which practically could not be briquetted with either roller presses or vibropresses. The possibility of agglomeration of wet materials allows either to completely abandon the drying of raw materials or to significantly reduce the cost of such drying. A comparison of these technologies in parameters such as the applied pressure and moisture contents of the agglomerated mixture is given in Fig. 3.15.

The success of briquetting as an industrial technology was largely promoted by the results of scientific research aimed at improving and extending the service life of equipment, as well as studying the metallurgical properties of briquettes and the

Fig. 3.15 Comparison of technologies of briquetting according to the parameters of briquetting (applied pressure and moisture content of the charge). 1—Roller pressing, 2—vibropressing, 3—stiff vacuum extrusion



search for new methods of sintering. Specialized studies of the characteristics of briquetting and the behavior of various briquettes in metallurgical aggregates were carried out at the University of Lulea (Sweden), at the Moscow Institute of Steel and Alloys (MISIS), and in scientific laboratories of the largest metallurgical companies. Research by Swedish scientists substantiated the expediency of using vibropressing to produce blast briquettes with high metallurgical properties. The results of research carried out at MISIS made it possible to determine SVE as the best available technology in the production of agglomerated metallurgical raw materials and as the only briquetting technology alternative to sinter production.

Another major trend in the modern stage of development of the technology of briquetting is the emergence of a global market for product briquettes. Mining enterprises began to receive significant commercial benefits from the sale of briquettes, including export.

It should also mention the entry into the market of briquetting chemical companies offering polymer binders that have been successfully tested for mechanical and hot strength. BASF announced the commercialization of several of its products and supplies binders for a number of briquette factories [92]. A similar product is also being offered by Legacy Hill [93]. Despite the very high cost of such binder materials necessary to achieve the required strength, the proportion of such a binder is so small (0.2–0.3% by weight of the briquette) that its use can be economically justified. The importance of increasing the content in the briquettes of the main element (iron, manganese, chromium, etc.) due to a decrease in the proportion of binder should be taken into account. In particular, it is very important for the market of commodity manganese briquettes.

3.3 Basic Materials for Briquetting

The most important metallurgical properties of the briquettes are: cold strength, porosity, reducibility, softening, and hot strength.

Cold strength allows the briquettes to maintain integrity and not to collapse with the formation of fines during transportation, handling and loading into the furnace. The porosity of briquettes affects the reaction surface of the interaction of the oxides of its components with a gaseous reducing agent. Reducibility is the ability of the components of the briquette to give oxygen to the gaseous reducing agent. Good reducibility of briquettes allows to reduce the degree of development of direct reduction and the specific consumption of coke for iron smelting. Softening of briquettes can affect the gas permeability of the charge column in the furnace; therefore, the higher the temperature of the beginning of the softening of the briquette, the less the contribution of this part of the charge to the increase in resistance to gas flow. The metallurgical value of briquettes increases with a decrease in the temperature difference between the beginning and the end of their softening. Hot strength is the ability of briquettes to preserve integrity as much as possible without destruction in the process of heating and phase transitions. Before we consider examples of the manifestation of these properties of briquettes in various metallurgical furnaces and reactors, we will focus on the analysis of the basic materials used for briquetting in ferrous metallurgy.

Dispersed materials of natural and anthropogenic origin, which can be used as components of the briquette mixture, are formed at all stages of the metallurgical process from the extraction and enrichment of ores, in the production of sinter and pellets, in the preparation and introduction of the charge in metallurgical furnaces and reactors, during gas cleaning of exhaust gases, and shipment of the finished product to the consumer.

3.3.1 *Mining and Beneficiation of Ores*

For the majority of furnaces and reactors of ferrous metallurgy used today, there is a lower limit for the size of the charge pieces. For example, for blast furnaces, the allowable size of the charge pieces is at least 10–12 mm. With the extraction and further enrichment of brown iron ore and hematite iron ore, the yield of fractions larger than 10 mm does not exceed 30% and the formation of a fine fraction is large, with particle sizes less than 0.05 mm, which makes the direct use of such materials in the charge (without preliminary agglomeration) economically meaningless due to the gas flow from the working space of furnaces and ore particle reactors.

Iron ore fines and concentrates are suitable charge components for briquetting. Depending on the iron content, there are rich iron ores (Fe content 60–65%), ores with average iron content (45–50%), and poor ores (less than 45%). With increasing iron content in the briquette, its metallurgical value also grows. It is known that with an increase in the iron content in the blast furnace charge by 1%, the productivity of the blast furnace increases by 2–2.5%, and the specific coke consumption decreases by 1–1.5%.

The properties of briquettes are also influenced by the features of the crystal structure of iron ore minerals, the content of gangue and impurities. The difference in the mineralogical structure manifests itself predominantly at the stage of heating briquettes due to the restructuring of the crystal structure of iron oxides (as, e.g., when hematite is reduced to magnetite). On the briquetting of iron ore fines and concentrates, such features, as a rule, are not affected.

Moreover, poor lump-forming capacity, which negatively affects the quality of sinter, is not a limitation during briquetting. In [94], the metallurgical properties of ore-coke briquette based on hematite ore (ore—79%, coke fines—15%, Portland cement—5.55%, bentonite—0.45%) were studied, which confirmed the prospects for the use of such briquettes in blast furnace charge. Durable briquettes were also obtained from Kovdor iron ore concentrate. The structural features of the magnetite ores of the Kovdorsky deposit are associated with its heterogeneity, which does not allow to obtain high-quality sinter on its basis [95]. At the same time, the strength of briquettes from Kovdor iron ore concentrate during drop tests from a height of 2 m onto a steel base exceeded 98% (the proportion of pieces with sizes greater than 4.75 mm). Binder is a mixture of molasses and hydrated lime (3% by weight of the briquette).

The composition of gangue of iron ore fines and concentrates may include iron-free quartz minerals, aluminosilicates, garnets, pyroxenes, and calcite. The main components of the gangue are silica (SiO_2), alumina (Al_2O_3), lime (CaO), and magnesium oxide (MgO). When melted in a furnace, gangue forms slag, whose properties are largely determined by the so-called basicity— $(\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$. For example, the so-called self-melting ore with a basicity of about 1 is considered the most valuable for blast furnace smelting.

Impurities, which are usually found in iron ores, can significantly affect the properties of briquettes. It should be noted that, in contrast to sintering and the production of pellets, which imply mandatory high-temperature processing of iron-containing materials, which allow to remove harmful impurities, in cold briquetting the chemical composition of the charge remains unchanged. Harmful impurities include—S, P, As, Zn, and Pb. Mn, Cr, Ni, V, W, Mo, and other elements are considered useful.

The characteristics of other types of ore fines and concentrates (manganese, chromium, and nickel) will be considered when studying the properties of briquettes based on them in the following sections.

3.3.2 Sinter and Pellet Production

Disperse materials of interest for briquetting are formed in the processes of sinter and pellet manufacturing, crushing, handling, and transportation. These include dust and sludge from sinter production and induration machines and screenings of sinter and pellets.

The specific yield of dusts from sintering machines can be from 10 to 24 kg/t of sinter. At the preparatory sites, 9 kg of dust per ton of sinter is formed. The output of dust in the production of pellets reaches 7–9 kg/t of pellets, in the preparatory areas—5–16 kg/t of pellets.

Dust consists of particles of sinter (pellets) and particles of raw materials for such industries (ore, coke, coal, limestone). The typical chemical composition of dust of sintering machine is: iron content—45–55%; SiO_2 —5–10%; sulfur—6–10%; CaO —10–20%; and Al_2O_3 —1–2%. Particle shape is spherical with a granular surface (magnetite) or oblong (hematite). More than 46% of such dust particles have a size in excess of 40–50 μ . The size of the dust particles of roasting machines is smaller. About 40% of particles are larger than 40–50 μ .

The small fraction of the sinter (the fraction of the finished sinter with size smaller than 5 mm) is formed when it comes off the sintering belt, after sieving the return from the cooled sinter and when it is loaded into the skip of the blast furnace. This material has the chemical composition and mineralogical composition of the finished sinter.

The indurated pellet fines are formed during classification, transportation, unloading, storage, and subsequent loading of pellets into the blast furnaces and metallization reactors. The typical granulometric composition of pellet fines is—8% of particles are larger than 6.30 mm, 60% have sizes in the range of 0.15–6.30 mm, and 32% of particles are smaller than 0.15 mm. The iron content in the pellet fines is 65% on average. Some features of the mineralogical composition of iron-containing phases of pellet screening can lead to an abnormal swelling of briquettes on a cement binder when they are heated in a reducing atmosphere.

3.3.3 Coke Production

In the process of coking coals, coke breeze, coke dust, and other dispersed materials are formed. The output of dust in the production of coke is 2–4 kg/t of coke. When furnaces are loaded, about 0.4 kg of dust per ton of coke is produced, and in the production of finished coke—0.7–0.8 kg of dust per ton of coke. The chemical composition of dust and fines corresponds to the composition of coke. Coke breeze and dust are among the most popular reducing agents used in briquetting.

3.3.4 Blast Furnace Production

The most promising dispersed materials for briquetting generated in the blast furnace production include flue dust, wet gas cleaning sludge, sludge, and dust generated in the sub-bunker rooms of blast furnace. Flue gas dust is dust carried through the blast furnace top by blast furnace gas. It is formed as a result of the abrasion of pieces of the blast furnace charge during its movement in the shaft of the furnace. Dust in the sub-bunker rooms is formed during transportation and handling of the charge components. Sludge is generated as a result of hydraulic cleaning and wet cleaning of emissions of aspiration systems.

The total formation of flue dust and sludge is about 64 kg/t of iron. The output of sludge of wet gas cleaning of blast furnace gas is 26 kg/t of hot metal. The output of top dust is on average 38 kg/t of hot metal [96].

About 30% of flue dust particles have a size in the range of 150–250 μ . The iron content varies widely (40–50%) and depends on the type and properties of the main components of the blast furnace charge. An important distinguishing feature of flue dust is the presence in its composition of noticeable amounts of carbon introduced by particles of unreacted coke, which makes this material a promising component of self-reducing briquettes. The carbon content in flue dust can exceed 30% (mass). Hematite, magnetite, and calcium ferrite are the main iron-containing phases of flue dust. Iron ore grains have an irregular shape with sizes ranging from 0.5 to 150 μ . Fragments of coke are relatively large in size (from 350 μ to 1 mm).

The iron content in the sludge of the wet gas cleaning of blast furnace gas varies widely (20–55%), and there may be a significant presence of undesirable impurities such as zinc and lead.

Iron content in sludge of sub-bunker rooms of blast furnace is 33–35%, and its composition is close to the composition of the sinter charge. The granulometric composition of such sludge is close to the composition of the dust of sinter plants.

3.3.5 Steelmaking

In steelmaking processes in oxygen converters and electric furnaces, dispersed materials are formed, which can serve as valuable charge components of briquettes. These include converter sludge, dust, and sludge from electric arc furnace (EAF). In some cases, steelmaking slags can also be added to the briquette mixture; however, due to their low iron content, their use in briquetting is limited.

In the exhaust converter gases, the dust content is very high (on average, up to 30 g/m³, and in some cases up to 60 g/m³). The main minerals of such dust are maghemite, magnetite, and wustite. The material itself is a black powder with spherical particles. The average particle size is 0.08 μ ; 10–15% of the particles are larger than 10 μ . Large fractions of dust are particles of the charge materials, droplets of slag, and the shell of carbon monoxide bubbles carried by the gas

stream. Sludge is formed during wet gas cleaning of converter gases. In such materials, in the process of drying, sludge granules are formed, on the surface of which there is a tricalcium silicate ($3\text{CaO} \cdot \text{SiO}_2$), the granular structure of which prevents the strong adhesion of particles with cement gel during briquetting, which leads to low mechanical strength of briquettes based on converter sludge. Giving such a briquette, the required strength may require increased consumption of cement binder. The strength properties of briquette based on converter sludge are improved when using a combined binder consisting of equal parts of hydrated lime and molasses (3% by weight of the briquette). Converter sludge is preferably briquetted in a mixture with blast furnace sludge. The strength of the briquette consisting of a mixture of equal fractions of the converter and blast furnace sludge (47% of the mass of the briquette each), with such a binder, when tested for fivefold dropping from a height of 2 m onto a steel base, exceeded 95% (the fraction of particles with dimensions more than 4.75 mm), while the strength of the briquette on the basis of only converter sludge (85% by mass) with a cement binder (15% by mass) after similar tests did not exceed 89%.

The specific yield of the EAF dust is on average 8–10 kg/t of steel and can reach 20 kg/t with oxygen blowing. Dust is formed in the zone of arcs and is a vapor of metal condensing in the cold parts of the tract, condensed vapors of slag, and particles of the charge removed from the bath by a stream of exhaust gases. The content of Fe_2O_3 in such dust is 10–50%. The dust particles are predominantly spherical in shape. The bulk of the dust particles in the EAF dust have a size in the range of 0.2–20 μ [96].

A distinctive feature of EAF dust is its high content of zinc oxide (ZnO), which can exceed 20% of the mass of the material, which is unacceptable for blast furnace briquettes. The sale of dusts to the industrial enterprises of zinc-producing industry is possible with a content of at least 15% zinc (18.7% ZnO).

The structural features of the particles and the particle size distribution of the EAF dust create some difficulties in its briquetting with the method of vibropressing with cement as a binder associated with significant values of the specific surface of the particles (16,000 cm^2/g), which leads to a noticeable manifestation of the capillary effect and dewatering the briquette. Due to the lack of moisture, the hardening of the cement stone is impeded and the briquette does not gain strength. Such a feature of the EAF dust is not an obstacle for its briquetting with a roller press and the method of stiff vacuum extrusion.

3.3.6 Rolling Production

During the hot rolling process, scale is formed on the outer surface of the plates, sheets, and profiles. The output of mill scale of rolling production is about 2% by weight of the finished product. The shape of the particles is scaly. The size of the

main mass of particles does not exceed 0.2 mm. The chemical composition of scale is close to pure magnetite (65–72% Fe).

The scale may be contaminated with lubricating oils and cutting fluids (coolant) as a result of their leakage from the lubrication system of rolling mill equipment. The presence of oil determines the high hydrophobicity of the particles of scale surface.

The hydrophobicity of the surface of particles of oily scale reduces the effectiveness of the use of cement as a binder during its briquetting. The de-oiled scale can be used to produce washing blast furnace briquettes.

3.3.7 Ferroalloy Production

In the production of ferroalloys, various dispersed materials are also formed, which are suitable components of briquette charges (dust and sludge, fines of pellets and sinter, fines of crushing of ferroalloys). In the ferroalloy industry, dry (open and semi-closed ore-smelting furnaces) and wet systems (closed and sealed furnaces) are used. Open and semi-closed ore-reducing furnaces are equipped with a dry gas cleaning, and closed and sealed furnaces are equipped with a wet gas cleaning.

The specific dust emissions of ferroalloy furnaces are 8–30 kg/t of alloy. The total formation of dust in the areas of preparation of raw materials, warehouses of charge materials, and finished products reach a total of 1.1 kg/t of alloy. Particles of large fractions (about 10%) have an irregular shape, since they were formed outside the arc zone in the absence of phase transitions. Such dust contains particles of charge materials (ore raw materials, fluxes, and coke). The size of almost 90% of the dust particles of gas cleaning of ferroalloy furnaces does not exceed 10 μ . The particle shape is predominantly spherical.

The content of manganese oxides in dusty gas cleaning systems in the production of silicomanganese is 21–34% (mass) and in the production of ferromanganese is 20–25% (mass). The content of chromium oxides in the dust during the smelting of ferrochrome can reach 22–45% (mass). The content of micro-silica in the dust of gas cleaning production of ferrosilicon reaches 98%. Like flue dust, gas treatment dust from smelters can contain a significant amount of carbon (10–20% or more). The use of such dusts as components of the briquette mixture can help reduce coke consumption in the smelting of ferroalloys. Dust containing micro-silica can exhibit binding properties, resulting in lower consumption of binder materials.

Before shipment to consumers, ferroalloys are subjected to crushing and sieving on mechanized sieves to obtain the size of pieces required by the technology. When crushing using, for example, a jaw crusher with a slit width of 100 mm, up to 10–15% of the fines of ferroalloys with particle sizes less than 3 mm can be formed, direct recycling of which in the form of a charge component of the ore-smelting

furnace is impossible. The fine fraction of screenings of crushing of ferroalloys and dust, captured by systems of aspiration of sites of fractionation of ferroalloys, is promising components of the briquette mixture due to the high content of the metal phase.

3.3.8 Direct Iron Production

Sources of sludge formation in direct iron production processes are flue gas treatment systems (Venturi tubes); briquette cooling system; hydraulic washing of belt conveyors of the finished product transportation system; and dedusting scrubbers of the briquetting system.

The sludge is mixed in a common collector, and the mixture is then transported to a sludge collector. Moisture content of sludge reaches values of 30–40%. The total iron content in sludge can exceed 55% (total), and metallic iron content—22%.

Metallized fines are formed in the process of briquetting at the breaking of the briquette tape, at the destruction of the briquettes of hot briquetted iron (HBI). In part, it is represented by pellets that have not fallen into the gap between the sleeves of the roller press. The proportion of particles of such a metallized material with a particle size of less than 4 mm exceeds 92%. The total iron content in HBI fines exceeds 87%.

The variety of materials suitable for briquetting is not limited to the above list, which contains a brief description of the materials widely used in practice as components of industrial briquettes in ferrous metallurgy.

One of the most essential components in briquetting is a binder. The practice of industrial briquetting has shown that, of the variety of binding materials, cement, slaked lime (sometimes in combination with molasses), and some types of organic ligaments (lignosulfonate and starches) are most common in ferrous metallurgy. The use of such materials allows reaching a compromise between the cost of their acquisition and the level of briquette strength achieved with their help.

3.4 Basic Industrial Technologies of Briquetting in Ferrous Metallurgy

3.4.1 Briquetting Using Roller Presses

Before the advent of vibropressing and the technology of stiff vacuum extrusion, roller presses were most widely used for briquetting in ferrous metallurgy.

The principle of operation of such presses is that the briquetted mixture is fed into the gap between two rolls rotating toward each other, on the surface of which symmetrically located cells in the form of semi-briquettes are arranged in a

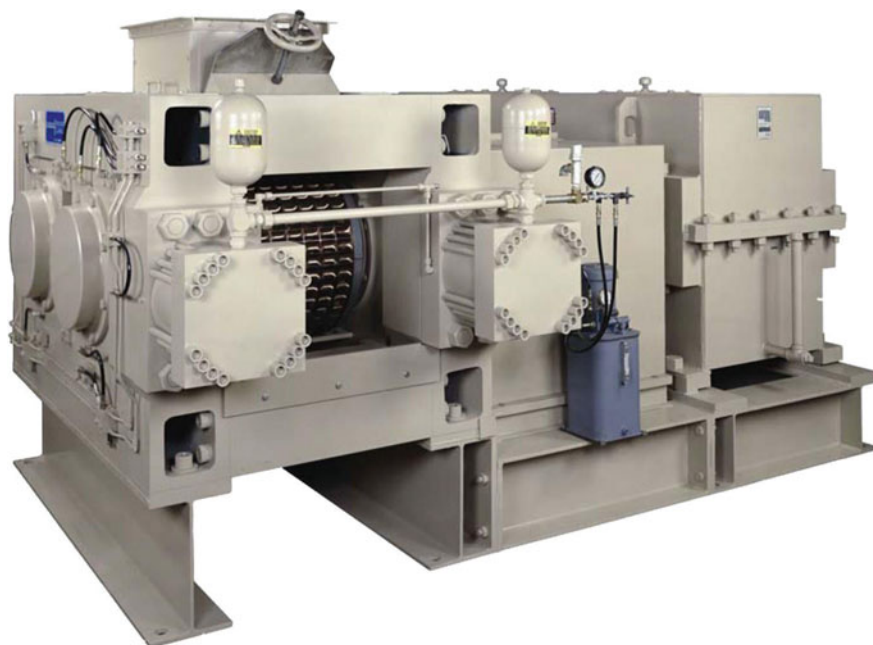


Fig. 3.16 General view of modern roller press (Komarek DH500). http://komarek.com/wp-content/uploads/2018/08/KOMAREK_DH500_Data_Sheet2018.pdf

checkerboard pattern. During the rotation of the rolls, there is a convergence of cells, the capture of the material, and its sealing compression. The briquetted material is subjected to bilateral compression, which contributes to a more uniform distribution of its density by volume. Then, as the rolls rotate, the cells diverge, and the briquette drops out of the cell under its own gravity. In some cases, in the designs of roller presses, pre-compressing dispensers are used for preliminary agglomeration of the briquetting charge in order to increase its bulk weight, which allows for an increase in the compressive load and the overall performance of the press. A general view of the modern roller press is shown in Fig. 3.16.

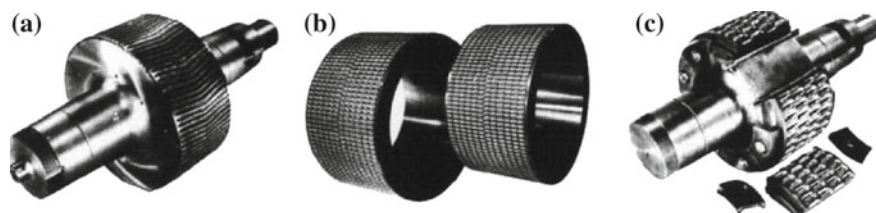


Fig. 3.17 Designs of rolls of roller presses: **a** one piece solid roll; **b** sleeve rings; and **c** segmented roll [97]

Fig. 3.18 Roller press sleeve

There are several types of press roll design: solid rolls, sleeve rings, and segmented rolls (Fig. 3.17, [97]). The main advantage of segment rolls (Fig. 3.17c), assembled from separate sections or segments, is the ability to quickly replace worn segments with minimal labor and time, which simplifies the operation of briquette equipment and increases its efficiency.

A variant of the sleeve ring is shown in Fig. 3.18.

The processes occurring in the briquetted mass in a roller press can, to a certain degree, be described by methods of the general pressing theory. The compaction process can be divided into three stages. The first stage is the reorientation of particles without changing their shape and size. In the second stage, the deformation of the soft and the destruction of brittle particles of material take place. At the last stage, plastic changes in the structure of the material occur, and its compaction occurs.

The strength of briquettes produced in this way depends on a number of factors: the particle size and component composition of the briquetted material, the magnitude of the applied pressing force, the moisture of the charge, the duration of the pressing process, the shape and size of the cells of the sleeves, and friction coefficients. Let us consider the influence of these factors on the effectiveness of roller briquetting.

The factor limiting the effectiveness of compaction of the material to be pressed is the presence of air, which is “trapped” inside the material during compression and is released after the external pressure ceases, thus leading to a softening of the briquette. The amount of pressed air can be 30–70% of the initial volume of air in

the material [98]. It is this factor that causes the frequent reduction in the strength of raw roll briquettes. Air displacement can also be difficult due to the presence of a binder that occupies a significant proportion of the pores. To avoid this phenomenon, it is necessary to ensure maximum removal of air from the briquetted mixture. Air removal can be facilitated by a reduction in the rate of material compression itself, facilitating the release of air from a decreasing pore space. Note that during vibropressing and in stiff vacuum extrusion, as we will see in the following sections, the removal of air from the briquetted mass is an important component of the technology and is achieved by displacing the air as a result of high-frequency vibrations in the vibropress and the complete removal of air from the stiff extruder's working chamber.

The maximum particle size for roller briquetting usually does not exceed 5–6 mm. At the same time, multi-fractionality is a factor favoring briquetting efficiency, since in this case the space between large particles is filled with smaller particles, which contributes to the displacement of air from the material.

When briquetting multi-component mixtures, one should also take into account the difference in the manifestation of the elastic–plastic properties of the individual components, leading to a significant difference in the degrees of compaction. Figure 3.19 [45] illustrates the degree of compaction of roll briquettes based on manganese ore fines with the addition of various carbon-containing materials (coal or peat). It is seen how significantly the degree of compaction of the mixture varies depending on the physico-mechanical properties of the components of the mixture.

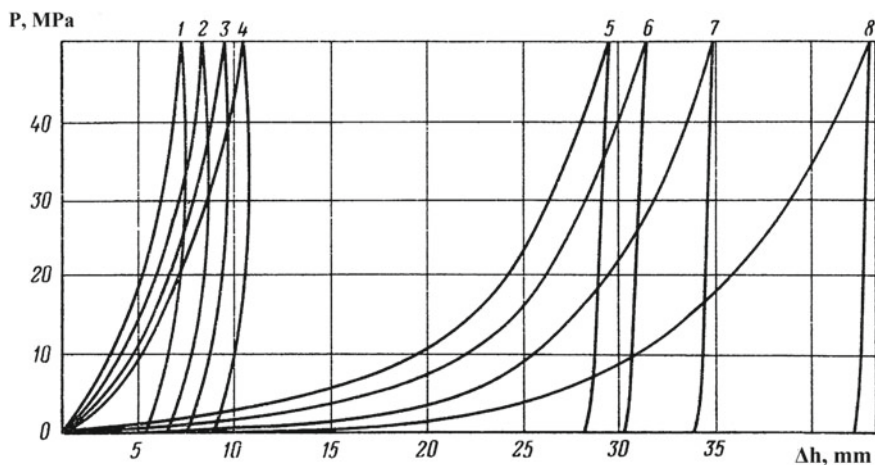


Fig. 3.19 Degree of compaction of the mixture with coal and peat components depending on the compression load (1–4—manganese ore fines and coal in proportions of 70:30, 60:40, 50:50, and 40:40, respectively; 5–8—manganese ore fines and peat in proportions of 70:30, 60:40, 50:50, and 40:40, respectively [45])

When briquetting loose mixtures that exhibit significant shrinkage (40, 50%, or more), it may be necessary to use a pre-compressing that allows to provide a specific preliminary pressure to 0.007–0.7 MPa, and the actual pressure to 68.9–690 MPa [45].

The growth of the applied pressure, which means an increase in the energy consumption for briquetting, leads to a decrease in the porosity of the briquette, which may reduce its metallurgical value in the reduction processes. Moreover, such a measure makes sense only for briquetting without a binder, since the application of high pressure can lead, for example, in the case of using organic binders, to squeezing the binder onto the surface of briquettes and sticking them together.

The structure of the material pressed in the rollers undergoes changes due to elastic and irreversible deformation, destruction of the particles of the pressed material, and the formation of cracks in it (at pressures above 10 MPa). Figure 3.20 shows the structure of a roller press briquette (manganese ore fines—47.6%, dust of the gas cleaning system—38.1%, coal—9.5%, and lignosulfonate as a binder—4.8%) in comparison with the structure of extrusion briquette (manganese ore fines—66%, gas cleaning dust—28%, cement—5%, and bentonite—1%).

It can be seen that as a result of high pressure (up to 100 MPa), the briquette structure is characterized by the presence of many large cracks and low porosity. The occurrence of such cracks may be due to elastic expansion after the finished briquette leaves the cells, which leads to a decrease in its strength.

A feature of roller briquetting is the limitation on the moisture content of the charge material (not higher than 5–10%). The required low moisture content of the charge limits the use of a binder that hardens by hydration, for example, cement, or requires the creation of combined binders with an increased content of cement in their composition.

The strength of the briquettes is significantly affected by the duration of the pressing process. For example, the duration of pressing for rolls with a diameter of

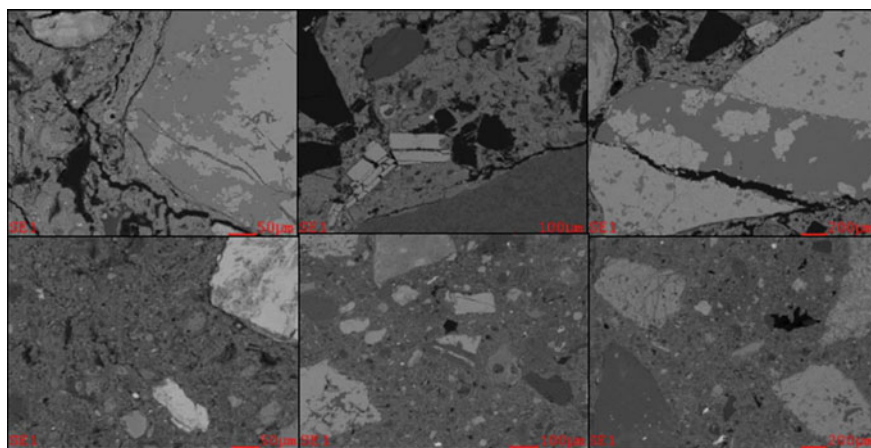


Fig. 3.20 Structure of the roller press briquette

1.1 m at a frequency of rotation of 8–11 revolutions/min is only 0.29–0.38 s. Exposure of the briquette under pressure allows not only more fully to force out the air from the narrowing pore space without the formation of pressed “air pockets,” but also to reduce the amount of elastic deformations that can lead to its softening. The increase in pressing time is achieved by restrictions on the speed of rotation of the rolls. For iron ore briquettes, usually no more than 6–8 revolutions of rolls per minute are recommended [45].

In 2003, a patent was obtained for the design of a roller press with a so-called extended compaction zone (ECZ) [99]. The developed design allows to intensify the process of removing the gaseous phase from the volume of the pressed material and to achieve high degrees of compaction of the material by a combination of static compaction of the material during its movement along the narrowing channel into the lower part of the space between the rollers and the subsequent dynamic compaction in the zone of action of the vibrating compactor pumping the material into the pressing zone. The scheme of a roller press with ECZ is shown in Fig. 3.21 [97]. The strength of briquettes increases by 10–15%, and the productivity of such a press increases by 15–20%.

The principle of the roller press with ECZ is as follows. Briquetted charge from the hopper (1) is fed into the extended sealing zone (2) through the loading openings made in the side walls of the press. In the channel of constant cross section formed by the working surface of the rolls, the side parts, and the surface of the tapes (5), the internal stresses relax in the charge layer and are pre-stabilized. Next, the mixture is forcibly injected into the lower space between the rolls due to the rotation of the rolls (3 and 4) and the movement of the belts and under the influence of the vibrating compaction device (6). The mixture is pressed by rollers into briquettes, which remain in the annular depressions—grooves, from which they

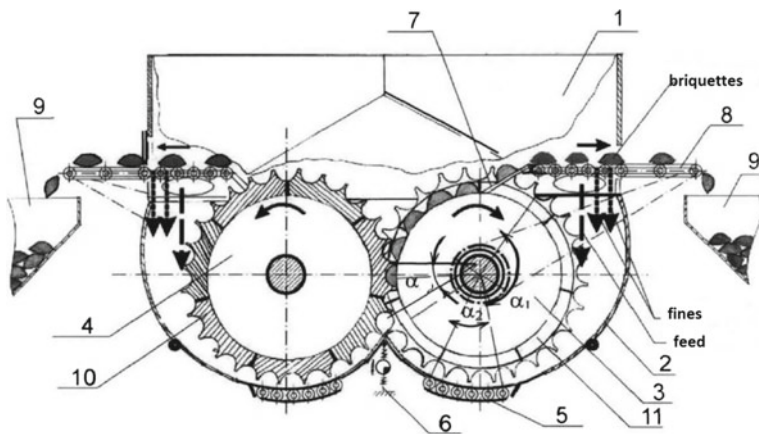


Fig. 3.21 Scheme of a roller press with an extended compaction zone: 1—loading hopper; 2—arcuate plate of the extended sealing zone; 3, 4—rolls; 5—endless tape; 6—vibrating device; 7—cleaning comb; 8—device for spillage recycling and removal of briquettes; 9—finished product bins; 10—removable forming elements of the gear type; 11—removable forming elements of the grooved type [97]

are removed by cleaning combs (7). Next, the briquettes come into the spillage selection device (8). The spillage and fines of the briquettes through the gaps between the rollers are returned to the loading zone of the roller press, and quality briquettes are transported to the bunkers of the finished product (9). To improve the performance characteristics, the roller press is equipped with removable forming elements (10 and 11), the use of which allows for the rapid restoration of the working surface of the rolls due to wear, as well as to obtain briquettes of various geometric shapes and sizes.

Figure 3.22 [45] shows the most common forms of the geometry of the cells of the roller press sleeves.

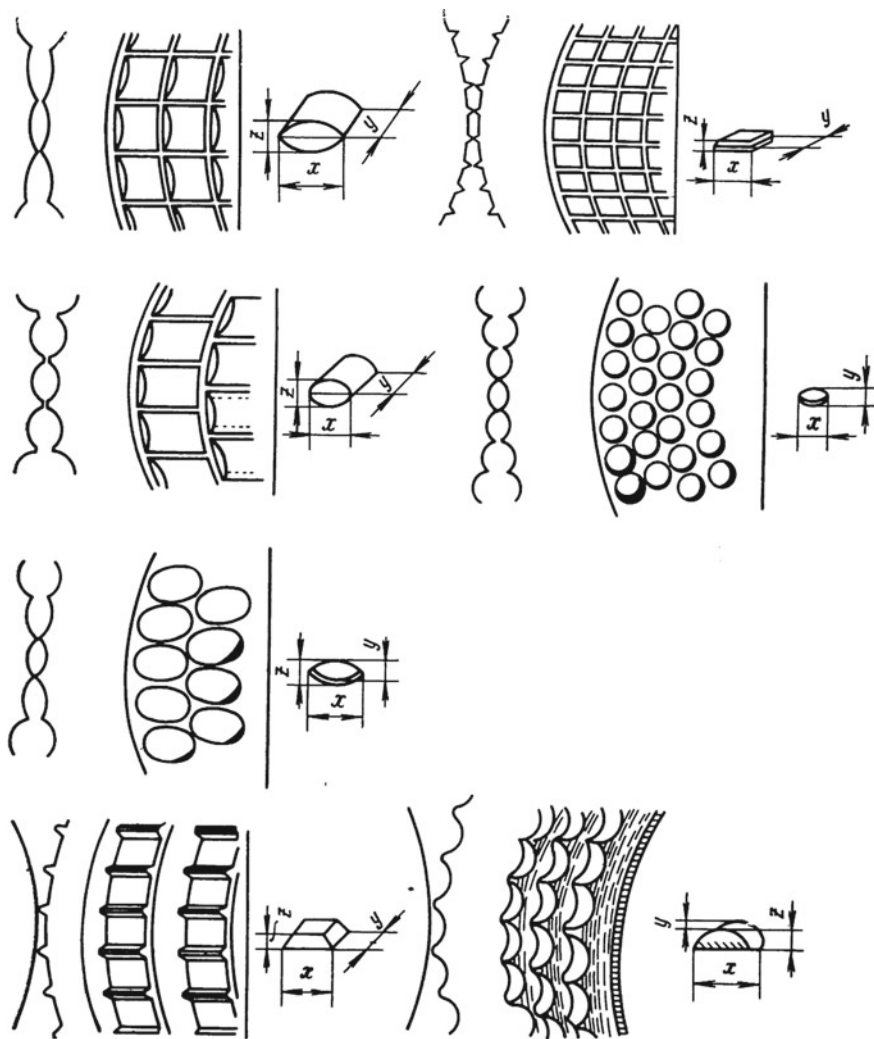


Fig. 3.22 Different types of cells of the roller press sleeves [45]

Operating experience of roller presses with traditional cell shapes showed that the displacement of the contacting cells resulted in the asymmetry of the briquettes formed, and the strength of the contact area of the halves of such a briquette is only 10–20% of the strength of the rest of the briquette mass. Due to the incomplete closure of cells of this type, a significant amount of return (up to 30%) may be formed when the roller press operates with the traditional form of cells.

In the design of a roller press, an open cell shape can be used, as, for example, in the ECZ press described above, the so-called grooved-toothed cell of the bandage (Fig. 3.23, [97]).

This form of cells does not require a combination of half-forms, allows you to double the amount of charge trapped by the cells in the sealing zone and to refuse preliminary pressing, and to simplify the manufacture of removable sleeves in the conditions of briquette plants as part of metallurgical enterprises.

The sizes of the briquettes manufactured by roller presses depend on the type of the metallurgical unit in which they are used as a charge component. One of the largest roller presses producer Köppern uses the following briquette sizes: $33 \times 30 \times 20$ mm for blast furnace briquettes and briquettes for direct iron production reactors; $46 \times 34 \times 20$ mm for electric arc furnaces, ore-smelting furnaces, and basic oxygen converters; and $62.5 \times 53 \times 34$ mm for cupola furnaces.

In roller briquetting, energy is expended on overcoming the friction forces between the particles of the material and the walls of the cells of the bandage and on the friction between the particles of the material themselves. The frictional forces in briquetting without a binder are important. If the magnitude of the adhesion force of the briquette with the surface of the cell exceeds the value of its tensile strength, the briquette is broken into two halves that remain in the cells.

Fig. 3.23 Grooved toothed cell shape [97]



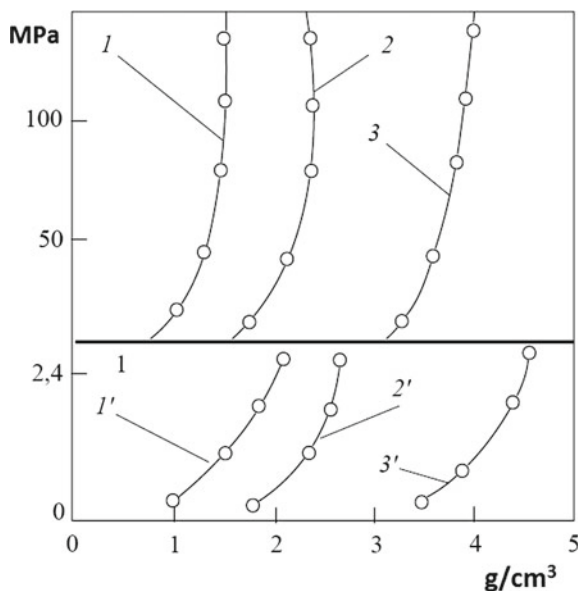
3.4.2 Vibropressing for Briquetting

3.4.2.1 The Physical Essence of Vibropressing and the Structure of the Briquette

The possibility of applying vibration for the agglomeration of natural and anthropogenic raw materials in metallurgy is due to a number of reasons. The very first experience of vibratory molding in powder metallurgy in the late 40s of the last century showed that the use of vibration when filling powder into a mold or in the process of compaction allows significantly reducing the required compressive load and homogenizing the distribution of its density over the volume. It was found that at vibrations with a frequency exceeding 50 Hz, the bonds between the particles in the compacted dry powder are destroyed and the internal friction in the compressible mass sharply decreases, which facilitates the convergence of particles and compaction of the mixture. In this case, a higher degree of compaction is achieved at lower than during compression, the values of the applied pressing pressures, which is well illustrated by Fig. 3.24 [98].

Another important physical process that occurs when vibration is applied to a formable mass containing gel phases is the so-called thixotropy (the word comes from Ancient Greek *thixis* “touch” and *tropous* “to turn”)—a decrease in viscosity (liquefaction) under mechanical action and thickening in state of rest. Manifestations of thixotropy underlie the process of vibration compaction of concrete [100]. Under the influence of vibration, the cement gel transforms into a sol, simplifying the movement (convergence) of solid aggregate particles under the

Fig. 3.24 Comparison of the degree of compaction of the material during static pressing (1–3) and vibropressing (1'–3'). 1, 1'—Boron carbide; 2, 2'—silicon carbide; and 3, 3'—titanium carbide [98]



action of its own gravity, which leads to compaction of concrete. Similar processes take place during briquetting with the use of cement binder, when, due to the reversible transformation of a cement gel into sol when exposed to vibration, at the stages of its liquefaction, particles of the briquetted charge approach each other under the action of their own gravity, which contributes to compaction of the briquette, and the air displaced by the approaching particles is released on the surface of the compressible mass in the form of bubbles. The thixotropy of the gel and the reduction of internal friction due to the oscillatory movements of the particles caused by vibration lead to the fact that the briquetted mass acquires some properties of the liquid, which simplifies the molding.

It is clear that thixotropy plays a key role in vibropress briquetting. It is no coincidence that almost all known vibropress briquette factories use cement as a binder. That is why the moisture content of the charge components plays an important role in briquetting with vibropressing. Its quantity should be sufficient to preserve the properties of the cement gel and for further hydration hardening of the cement. Usually, its content in the briquetted mixture is limited to 5–8% by weight of the briquette. The cycle of vibratory compaction lasts less than 30–40 s, which is obviously not enough for the cement to “set.” As a result, newly formed vibropress briquettes have a very low mechanical strength, which does not allow them to be transported and stacked like roll briquettes. Therefore, the equipment of the vibropress briquetting factories includes special mechanisms to transport and accumulate finished products on pallets. In addition, to speed up the curing of briquettes, their “steaming” is used—heat and humidity treatment at a temperature of 70–95 °C in an atmosphere of saturated steam. Movement of moisture and steam in a briquette that has not yet become strong may lead to its softening.

The requirements for the granulometric composition of the briquetted charge during vibropressing are not as rigid as for roller briquetting (less than 5–6 mm). An important advantage of this method of briquetting is the possibility of agglomeration of materials with a particle size of up to 10 mm. Figure 3.25 shows appearance of the briquette obtained by the method of vibropressing, showing the presence of large particles of material in the structure of the briquette.

The structure of the briquette produced by the method of vibropressing is highly homogeneous. Figure 3.26 shows an image of the structure of an industrial briquette sample (center and periphery), produced by vibropressing. The composition of the briquette is iron ore fines (61%), coke breeze (14.5%), flue dust (14.5%), and cement (10%). The uniform distribution of the main components of the briquette mixture (iron oxides, coke breeze, and cement) attracts attention. It can be seen that the largest grains are concentrated in the central part of the briquette.

The briquette porosity was determined using the STIMAN technique [101], based on the use of computer X-ray micro-tomography in combination with scanning electron microscopy. The porosity values obtained using micro-tomograph characterize a fraction of the total porosity, represented by macropores with a pore size (equivalent diameter) greater than 100 μ . For the considered vibropressed briquette, this value was 2.5%. The porosity determined by the electronic microscopy was



Fig. 3.25 Vibropressed briquette

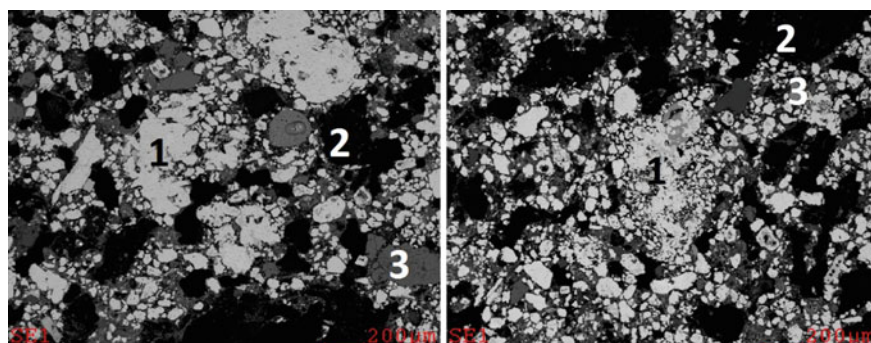


Fig. 3.26 SEM image of the vibropress briquette structure. On the left—the center of the briquette and on the right—the periphery (1—iron oxide, 2—coke breeze, 3—cement)

13.37%. The total porosity of the briquette is 17.87%. The morphological parameters of the structure of the briquette porosity are shown in Table 3.3.

Thus, it is clear that vibropressing allows forming a fairly dense structure of the briquette with low porosity values.

The properties of briquettes produced by the method of vibropressing are significantly influenced by the vibration parameters (duration, amplitude, and

Table 3.3 Morphological parameters of the porosity of the vibropress briquette

Sample	Micromorphological parameters	Pores category						$n, \%$	$K_a, \%$
		$D_1 < 0.1 \mu\text{m}$	$D_2 0.1-1.0 \mu\text{m}$	$D_3 1.0-10 \mu\text{m}$	$D_4 10-100 \mu\text{m}$	$D_5 > 100 \mu\text{m}$	$D_{\text{max}} \mu\text{m}$		
Vibropressed briquette	$N, \%$	1.9	15.9	35.8	46.5	—	91.4	13.37	19.07
	K_f	0.25–0.33; 0.42–0.50							
	K_f	0.33–0.42; 0.50–0.58							

where

1. n_{res} —total porosity calculated by SEM image
2. N —the contribution of pores of different size categories to the total porosity (n)
3. D_1, D_2, D_3, D_4, D_5 —various dimensional pore categories
4. D_{max} —maximum equivalent pore diameter
5. K_f —pore shape factor. It is calculated as the ratio of the minor and major axes of the ellipse inscribed at the time. For isometric pores, $K_f = 0.66-1.00$; for anisometric pores, $K_f = 0.1-0.66$; for slit-like pores, $K_f < 0.1$
6. K_a —anisotropy coefficient, or the degree of orientation of solid structural elements. Evaluated using the software “STIMAN.” For the samples studied, the presence of a medium-oriented microstructure is characteristic

frequency). Insufficient intensity of vibration may not lead to the manifestation of thixotropy, which will not allow achieving the required values of the density of the briquetted mass. Too intense vibration can lead to stratification of the briquetted mass and also degrade the density characteristics of the briquette. There is no theoretical basis for choosing a vibration mode. In each case, we are talking about the experimental testing of such modes on the bench models. To some extent, recommendations on the vibration modes developed in the technology of concrete vibration compaction may be useful. According to [102], the whole process of vibro compaction can be formally divided into two stages. The first is the rearrangement of large particles of a formable mixture and the formation of a macrostructure, and the second is a manifestation of the thixotropy of the cement gel and the formation of a microstructure. For the first stage, it is recommended to apply vibration, which causes low-frequency oscillations with large displacement amplitude to overcome the friction forces of the non-compacted particles. At the second stage, higher frequencies of vibration are advisable.

The methods of the theory of similarity and dimension [103] allow determining which factors influence the process of compaction of the vibrating mass. The main parameters that determine the process of vibro compaction are 10 values: N is the power of vibration exposure, $[Fl/t]$; A is the amplitude of oscillation, $[l]$; ω is the angular frequency of oscillations, $[1/t]$; t is the duration of the vibration; ρ is the density during vibro forming, $[Ft^2/l^4]$; τ_0 is shear resistance of the briquetted mixture, $[F/t^2]$; ν is mixture viscosity, $[Ft/l^2]$; l is the specific size of the forming zone, $[l]$; β is the linear damping coefficient of oscillations; g is gravitational acceleration. Here, F is force, t is time, and l is length. In accordance with the well-known π -theorem, the number of dimensionless combinations of defining parameters in the case of vibropressing is equal to 7. These combinations can be represented as:

$$\rho l^3 A^2 \omega^3 l^3 / N^2; \rho A^2 \omega^2 / \tau_0; \rho A \omega l / \beta \nu; \rho A \omega l / \nu; N t / \tau_0 l^3; N t^2 / \nu l^3; A \omega^2 / g$$

The dependence of the density of the mixture during vibropressing can be obtained from the equation in general:

$$\rho(A^2 \omega^3 l^3 / N^2; A^2 \omega^2 / \tau_0; A \omega l / \beta \nu) = f(N t / \tau_0 l^3; N t^2 / \nu l^3; A \omega^2 / g; A \beta)$$

The qualitative conclusions from the dependencies obtained in this way are reduced to the fact that the process of compaction of the mass during vibropressing is influenced by the acceleration of oscillations ($A \omega^2$), and the duration of the process is associated with the specific power of the vibration effect and with the properties of the briquetted mixture. The higher the vibration amplitude, the more effective the compaction.

3.4.2.2 Technology of Vibropressing, Transportation, Heat Treatment, and Storage of Briquettes

The process of vibropressing consists of several stages. The pallet is mounted on the vibrating table. The briquetted mixture prepared in the mixer with the addition of a binder is poured into a replaceable mold tooling—a matrix. Next, the mixture is compressed by the punch, a kind of “mirror” reflection of the matrix, ideally entering it exactly like a piston in a cylinder, and the vibration of the whole unit is turned on (Fig. 3.27).

The duration of the vibration cycle is 15–40 s. At the end of the molding cycle, the vibration is automatically turned off, the pressure in the hydraulic system decreases, the matrix rises, and the formed briquettes remain on the process pallet. The appearance of the briquetting vibropress is shown in Fig. 3.28.

The low strength of freshly formed briquettes does not allow them to be delivered to the zone of curing by the conveyor. Preserving the integrity of freshly formed briquettes requires special measures. Briquettes are transported, remaining on technological pallets.

Pallets with freshly formed briquettes along the conveyor (Fig. 3.29) are fed to a special hoist drive (Fig. 3.30), from where a stack of pallets is delivered to the heat treatment zone.

After accumulating the required number of pallets on the pallet stacker, they are removed and further transportation to the heat treatment chamber is carried out by an automatic stacked cart (Fig. 3.31) moving along the rails.

It is possible to transport a stack of pallets to the heat treatment zone and with the help of a transborder consisting of transfer and dispensing carts, which ensures the accuracy of the installation of pallets in the heating chambers. The appearance of the heat treatment chambers is shown in Fig. 3.32.

The duration of heat treatment can reach 24 h or more. The temperature in the chamber is 70–95 °C. The cost of heat treatment chambers can exceed 20% of the cost of equipment and engineering costs.



Fig. 3.27 Matrix (left) and punch (right)



Fig. 3.28 Vibropress for briquette production



Fig. 3.29 Transporting briquette pallets by conveyor



Fig. 3.30 Pallet stacker

After heat treatment, the briquettes on the pallets are moved to the stacker and further using a hydraulic pusher to the finished product conveyor for further unloading to the warehouse or loading onto a vehicle. The pallets freed from briquettes are returned to the vibropress. With a briquette line capacity of up to 130 thousand tons of briquettes per year, the number of formable pallets can exceed one million pieces. The cost of technological pallets may exceed the cost of the vibropress itself. In general, the cost of special mechanisms and devices for automatic vibrocompression lines, which ensure the integrity of raw briquettes before they are delivered to the heat treatment chambers and return the pallets, can be twice the cost of a vibropress. It is clear that in the absence of automation of these procedures, the capacity of the briquetting plant will be significantly lower. The cost of automation can be up to 50% of the cost of the vibropress.

In connection with the specifics of vibropressing, the productivity of a vibropress is usually understood as the number of units of products produced during an hour or eight-hour shift. First of all, productivity depends on the degree of automation, which affects the rate of removal of pallets with raw briquettes from the working area. Equipment productivity essentially depends on the sizes and volume of briquettes. Therefore, the performance is sometimes offered to compare the number of



Fig. 3.31 Stacked carts for transporting briquette pallets

pallets filled in a certain period of time. According to the results of operation of the known automated vibropress briquette factories, their productivity does not exceed 20–30 tons of briquettes per hour.

The size of briquettes is 60–100 mm; the most widely used form is a hexagonal prism. Such a size of vibropressed briquettes can lead to their “bridging” when unloaded into the bunker (Fig. 3.33). The smaller the size of the briquette produced, the lower the performance of the vibropress.



Fig. 3.32 Heat treatment chambers

Fig. 3.33 Unloading of vibropressed briquettes from the car



3.4.3 Stiff Vacuum Extrusion Briquetting Technology

Extrusion is a process used to create objects with a fixed cross-sectional profile. The material is pushed through the die of the desired cross section. This method has found a great distribution in the industry of the production of ceramic bricks.

Table 3.4 Types of extrusion

Type of extrusion	Low-pressure extrusion	Medium-pressure extrusion	High-pressure extrusion	
Designation used in structural ceramic industry	Soft extrusion	Semi-stiff extrusion	Stiff extrusion	
Extrusion moisture, % on dry	10–27	15–22	12–18	10–15
Extrusion pressure, MPa,	0.4–1.2	1.5–2.2	2.5–4.5	Up to 30

Vacuum is maintained in the working chambers of modern brick-making extruders, which contributes to achieving greater uniformity and density of the product. Stiff vacuum extrusion (SVE) technology is applied in the production of ceramic bricks in 64 countries around the world, including the USA, Britain, Germany, South Korea, and South Africa. The world's largest brick factory in Saudi Arabia produces a million bricks per day using SVE technology.

In accordance with brick industry terminology, the word “stiff” is used to describe the process of extrusion, which is carried out at pressures ranging from 2.5 to 4.5 MPa and moisture contents ranging from 12 to 18% (Table 3.4 [104]).

3.4.3.1 Preparation of Burden Materials for SVE Briquetting

One of the basic criteria determining the suitability of extrusion material is its plasticity—a trait that assures that it can be effectively pushed through the holes in die. A necessary condition for the status of plasticity is complying with the granulometric composition and moisture content requirements for SVE. In some cases, additional pulverization may be required in order to achieve the desired plasticity of material.

Unlike a roller press and vibropress briquetting, shear stress plays an important role in SVE agglomeration. Shear stress occurs when the mixture is processed in the screw feeder, in pug mills, and then in the extruder. In [105], based on a comparison of coal briquette porosity values in various pressing options (compression and its combination with torsion), it was found that more dense briquettes (less porous) are formed in the combined pressing option (under identical values of applied pressure). With full compression, a significant proportion of energy is expended on the elastic deformation of the particles themselves, while, in the presence of shear stress, the convergence of particles on the surface force activation distance is more effective. In full compression of close-packed particles, each particle only comes into contact with its immediate neighbors and is subjected to compression load. Under shear stress, the particles of the adjacent layers are subjected to abrasion due to contact with irregular surfaces, which can lead to crushing, the opening up of new surfaces, and, hence, to an increase in the number of contacts between particles of the mixture.

Table 3.5 Granulometric composition of brex components

Material	Fraction, mm/yield, mass%					
	−20... + 10	−10... + 5	−5... + 2	−2... + 1	−1... + 0.5	−0.5
Manganese ore concentrate, %	3.42	25.42	32.58	18.95	9.70	9.93
Bag house dust of SiMn production	Fine dust, size less than 0.063 mm					

Table 3.6 Composition of brex

Composition of brex	No. 1	No. 2	No. 3
Manganese ore concentrate	80	66	56
Bag house dust	14	28	38
Portland cement	5	5	5
Bentonite	1	1	1

The effect of shear stress can also be used to homogenize the mixture prior to its agglomeration by the SVE method.

Homogenization consists of souring of the mixture with the addition of a plasticizer and subsequent storing of such a mixture for some time before further processing. This method allows achieving a high degree of homogeneity of the mixture for subsequent agglomeration. The plasticizer consumption during the agglomeration of the homogenized charge, in comparison with the charge without prior homogenization, is markedly reduced.

In [106], it was proposed to pre-push the mixture through the shearing plate before homogenization. To demonstrate the effect of such an operation on the homogenization of the mixture, the values of compressive strengths of brex based on manganese ore fines and baghouse dusts of silicomanganese production in the versions with and without homogenization were compared. The granulometric composition of brex components is listed in Table 3.5. The composition of brex is given in Table 3.6.

A laboratory extruder has been used for brex sample production. The sheared mix was subjected to the souring over the course of 4 h. Table 3.7 shows the results of the measurement of the compressive strengths of brex No. 1–3 produced from this mix with and without souring. The increase in compressive strength a week after manufacturing was 14.2% for brex No. 1; 7.62% for brex No. 2; and 54.5% for brex No. 3.

Table 3.7 Compressive strength of brex No. 1–3

Strength/ brex No.	No. 1	No. 1—soured	No. 2	No. 2—soured	No. 3	No. 3—soured
Day 1 (MPa)	2.9647	2.7579	2.6890	5.7571	4.0955	6.1708
Day 3 (MPa)	4.8608	4.8608	6.0674	7.8255	6.1019	10.2042
Day 7 (MPa)	6.6741	7.6187	13.1345	14.3411	10.1698	15.7200

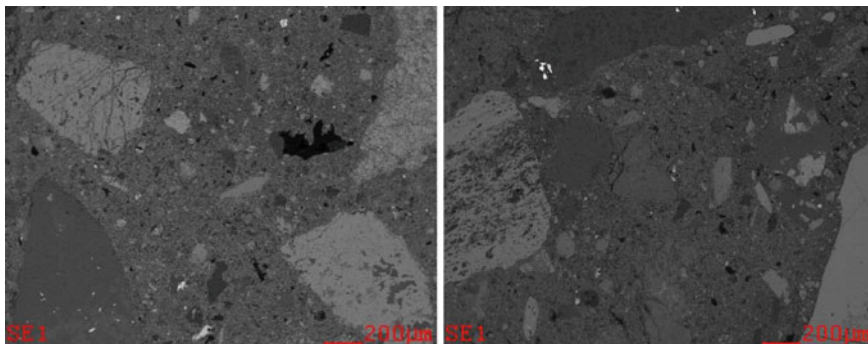


Fig. 3.34 Structure of the brex No. 2 structure. Left—without souring; right—with souring during 4 h after shearing

Study of the brex structure by means of scanning electronic microscopy revealed differences in the structure and distribution of pores. Figure 3.34 shows the structure of the brex No. 2.

One can see that pore size is significantly smaller in the brex made from a sheared and soured mix. The results suggest the use of a shearing extruder to prepare a briquetting mass for homogenization and have been used in the implementation of a number of briquette factory projects.

3.4.3.2 Technological Process of Briquetting by Method of Stiff Vacuum Extrusion

Typical layouts of the SVE briquetting line are shown in Fig. 3.35.

The mixture of raw materials is fed by a front loader to a J. C. Steele E Series Even feeder (Fig. 3.36), equipped with wear-resistant spiral cast-iron auger elements made of a chromium alloy.

Next, the prepared mixture with added binder and plasticizer is fed for mixing in the pug sealer. The line can also contain primary open pug mill. The pug sealer consists of a large open part and the sealing node. The open part (Fig. 3.37) consists of a trough and blades for mixing. The blades are fastened to the steel rod shaft by bolted clamps, making it possible to rotate the blades to adjust the angle at which the processing takes place and, thereby, change the machine's performance.

The pug sealer is combined in a single unit with the extruder and is positioned above it (Fig. 3.38).

The mixture enters the vacuum chamber partially agglomerated (Fig. 3.39), and due to the high vacuum inside the chamber the pieces of the mixture immediately crumble into isolated particles, which fall down on the blades of the auger. It is known [107] that air adsorbed by the surface of particles of plastic material in the form of polymolecular layers held by van der Waals forces slows down their

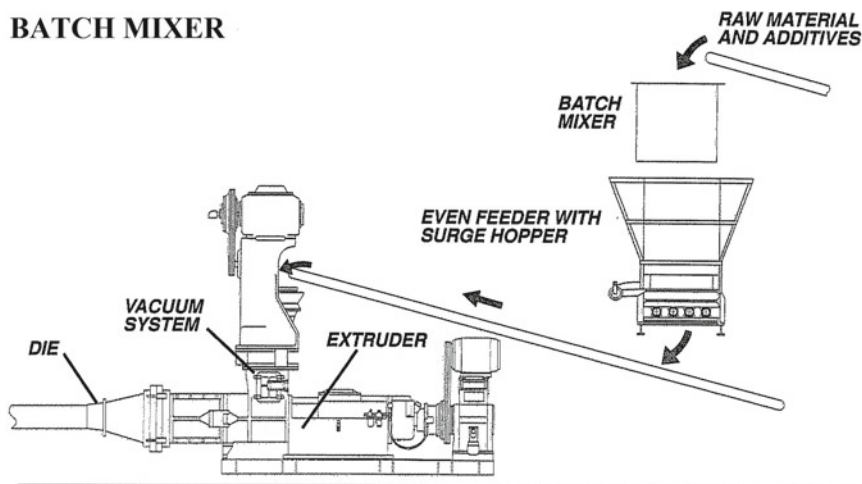
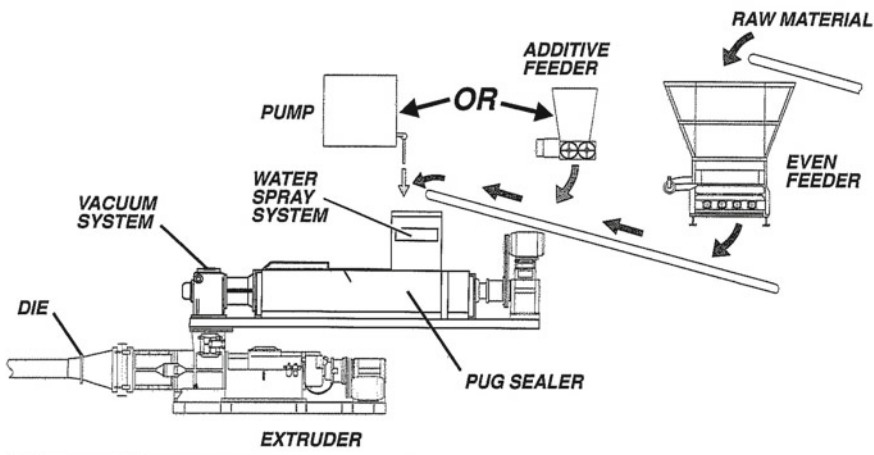
BATCH MIXER**CONTINUOUS MIXING**

Fig. 3.35 Typical layouts of SVE briquetting line

wetting with water, prevents the mass from being evenly compacted, and contributes to an increase in elastic deformations during plastic molding, forming delamination as well as micro-cracks. Filling the pores, the air also prevents the penetration of moisture into them and separates the particles of the mass, acting as a leaner. Evacuation leads to the removal of air from the pores and promotes closer contact of the particles.

The vacuum is maintained throughout the working volume of the extruder up to the die. The pressure of the vacuum is at least 100 mm Hg (in absolute value). The area of the vacuum in the working chamber of the extruder and pug sealer is shown in Fig. 3.40. The combination of mechanical pressure and vacuum in the working



Fig. 3.36 J. C. Steele E Series Even feeder



Fig. 3.37 Mixing in the open part of the pug sealer



Fig. 3.38 Appearance of extruder (bottom) and pug sealer



Fig. 3.39 Partial agglomeration of the mix in pug sealer

extruder chamber helps to remove almost all compressible air from the material before densifying, which allows them to be immediately transported by conveyors and stacked almost without the formation of a fine fraction. In addition, as is well known, the vacuum slightly decreases the viscosity of the cement paste, which facilitates its uniform distribution in the briquetting mass and improves its interaction with water [108]. This circumstance in combination with a higher density of

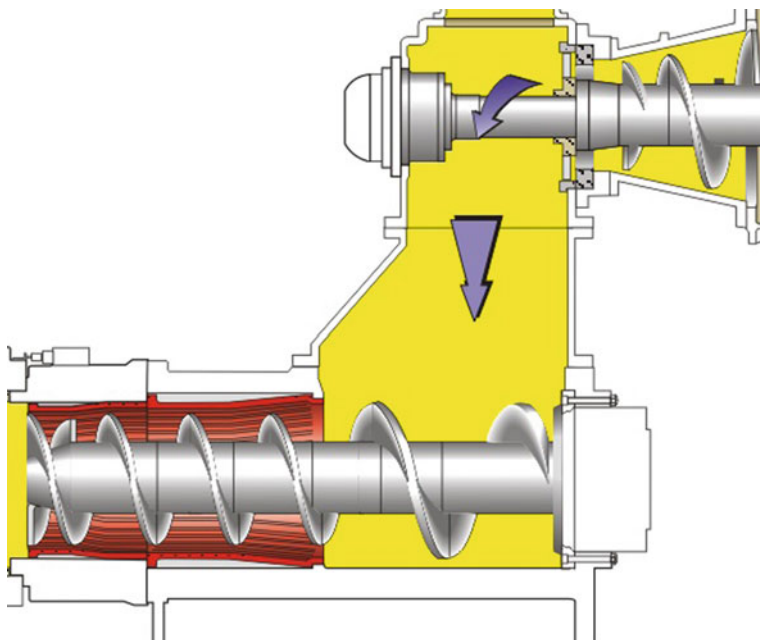


Fig. 3.40 Vacuum areas in extruder and pug sealer

the briquetting mass, due to the removal of air from it, leads to a decrease in the consumption of cement binder.

3.4.3.3 The Movement of the Briquetted Mass in the Extruder

Due to rotation of the auger blades in the working chamber of the extruder, formable mass performs translational and rotational motion, which is slowed by the walls (Fig. 3.41).

In the conveying zone, material is loose and moves along the barrel without densification. Bulk density remains unchanged. Zone 2 is the densifying region where the loose material is compacted. In zone 3, metering is achieved by way of the special geometry of the wings of the point auger. Zone 4 serves the purpose of distributing the pressure generated by the metering zone more evenly over the die, thus tending to yield a more even flow through it.

Mathematical modeling of the movement of the briquetted mass in an extruder in its full formulation continues to remain an extremely difficult task, requiring consideration of the rheological properties of the loaded materials. Most well-known studies use a simplified approach that combines mathematical and physical modeling. A review of the current state of modeling the formation of cast mass in an extruder is given in [104].

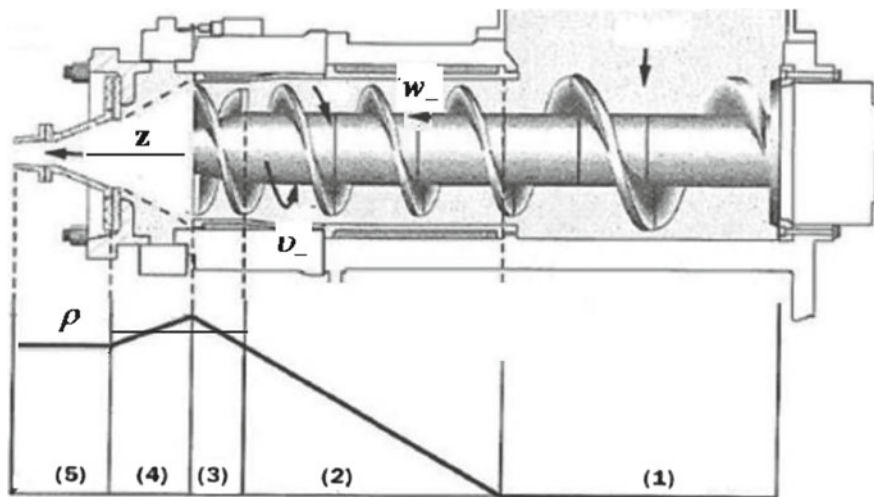


Fig. 3.41 Stages of densifying in the working zone of the extruder. 1—Conveying, 2—densifying, 3—metering, 4—pressure distributing, 5—die

Let us consider the movement of the briquetted mass in the working chamber of the extruder from the standpoint of the basic laws of continuum mechanics and with the intention of obtaining simplified qualitative dependencies that can serve as a basis for approximate calculations of the main parameters of the extrusion agglomeration process. The rotating mass of a wet, continuous medium has an isotropic molecular pressure field [109, 110] and is subjected to the fundamental laws of conservation of mass, momentum, and energy [111–113] with an appropriate rheology for the coefficient of dynamic viscosity μ [114–116].

First of all, as in [117], the motion of a particle, or point $\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$, will be measured in cylindrical coordinates r, θ, z ,

$$r = (x^2 + y^2)^{1/2} \text{ and } \theta = \arctg \frac{y}{x}, \text{ or } x = r \cos \theta \text{ and } y = r \sin \theta,$$

or in polar orts

$$\mathbf{I} = \cos \theta = \mathbf{i} \cos \theta + \mathbf{j} \sin \theta \text{ and } \mathbf{J} = -\sin \theta = \mathbf{j} \cos \theta - \mathbf{i} \sin \theta \text{ and } \mathbf{k}$$

preserving the sum of the double orts of the direct product and

$$\mathbf{ii} + \mathbf{jj} = \mathbf{II} + \mathbf{JJ},$$

“inheriting” the properties of the sine and cosine functions,

$$\mathbf{I}_\theta = \partial_\theta \mathbf{I} = \frac{\partial \cos \theta}{\partial \theta} = -\sin \theta = \mathbf{J} \text{ and } \mathbf{J}_\theta = -\partial_\theta \sin \theta = -\cos \theta = -\mathbf{I},$$

but otherwise remaining the same as the Cartesian orts $\mathbf{i}, \mathbf{j}, \mathbf{k}$:

$$\begin{aligned} \mathbf{I} \times \mathbf{J} &= \mathbf{i} \times \mathbf{j} = \mathbf{k}, \mathbf{J} \times \mathbf{k} = \mathbf{I}, \mathbf{k} \times \mathbf{I} = \mathbf{J}, \\ \mathbf{I} \cdot \mathbf{J} &= \mathbf{J} \cdot \mathbf{k} = \mathbf{k} \cdot \mathbf{I} = 0 \text{ and } \mathbf{I} \cdot \mathbf{I} = \mathbf{J} \cdot \mathbf{J} = \mathbf{k} \cdot \mathbf{k} = 1, \end{aligned}$$

so:

$$\mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k} = r\mathbf{I}(\theta) + z\mathbf{k}.$$

Like a given mass acceleration field,

$$\mathbf{g}(t, \mathbf{r}) = g^x \mathbf{i} + g^y \mathbf{j} + g^z \mathbf{k} = g^r \mathbf{I} + g^\theta \mathbf{J} + g^z \mathbf{k},$$

field velocities or flow

$$\mathbf{u}(t, \mathbf{r}) = u^x \mathbf{i} + u^y \mathbf{j} + u^z \mathbf{k} = u\mathbf{I} + v\mathbf{J} + w\mathbf{k} = \mathbf{r}_t,$$

receives three components of velocity, axial $w = z_t$, radial, $u = r_t$, and azimuthal, $v = r\theta_t$ from the polar orts

$$u^z = w, u^x = u \cos \theta - v \sin \theta, u^y = u \sin \theta + v \cos \theta,$$

will be considered further to be axially symmetric, or independent of the polar angle θ :

$$u_\theta = v_\theta = w_\theta = \rho_\theta = p_\theta = g_\theta^r = g_\theta^z = 0 \text{ for } g^\theta = 0.$$

In this case, the gradient

$$\nabla = \begin{pmatrix} \mathbf{i}\partial_x \\ +\mathbf{j}\partial_y \\ +\mathbf{k}\partial_z \end{pmatrix} = \begin{pmatrix} \mathbf{I}\partial_r + \mathbf{k}\partial_z \\ +\mathbf{J}\frac{\partial_\theta}{r} \end{pmatrix}, \partial_x = \cos \theta \partial_r - \frac{\sin \theta}{r} \partial_\theta, \partial_y = \sin \theta \partial_r + \frac{\cos \theta}{r} \partial_\theta,$$

and divergences

$$\begin{aligned} \nabla \cdot \rho \mathbf{u} &= \begin{pmatrix} \mathbf{I}\partial_r + \mathbf{k}\partial_z \\ +\mathbf{J}\frac{\partial_\theta}{r} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{I}\rho u \\ +\mathbf{J}\rho v \\ +\mathbf{k}\rho w \end{pmatrix} = \begin{pmatrix} (\rho u)_r \\ +(\rho w)_z \end{pmatrix} + \frac{1}{r} \mathbf{J} \cdot \begin{pmatrix} \rho u \mathbf{I}_\theta \\ +\rho v \mathbf{J}_\theta \end{pmatrix}, \\ \mathbf{I}_\theta &= \mathbf{J}, \mathbf{J}_\theta = -\mathbf{I}, \end{aligned}$$

and

$$\nabla \cdot \mu \nabla u = \begin{pmatrix} \mathbf{I} \partial_r + \mathbf{k} \partial_z \\ + \mathbf{J} \frac{\partial_\theta}{r} \end{pmatrix} \cdot \begin{pmatrix} \mathbf{I} \mu u_r \\ + \mathbf{k} \mu u_z \end{pmatrix} = \begin{pmatrix} (\mu u_r)_r \\ + (\mu u_z)_z \end{pmatrix} + \frac{1}{r} \mathbf{J} \cdot \mathbf{I}_\theta \mu u_r, \dots,$$

lead to the following mass, momentum, and viscous volumetric densities:

$$\begin{aligned} \nabla \cdot \rho \mathbf{u} &= \frac{1}{r} (r \rho u)_r + (\rho w)_z, \quad \nabla \cdot \rho u \mathbf{u} = \frac{1}{r} (r \rho u u)_r + (\rho u w)_z \\ \text{and } \nabla \cdot \mu \nabla u &= \frac{1}{r} (r \mu u_r)_r + (\mu u_z)_z, \dots, \text{ for } \mu = \mu(t, \mathbf{r}), \end{aligned}$$

respectively.

Furthermore, in order to save records let us represent the matrices by double vectors or more specifically by divectors: An identity matrix is the sum of the direct squares of the orts

$$\vec{\mathbf{e}} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix} = \mathbf{i}\mathbf{i} + \mathbf{j}\mathbf{j} + \mathbf{k}\mathbf{k} = \mathbf{\Pi} + \mathbf{J}\mathbf{J} + \mathbf{k}\mathbf{k},$$

Further, the matrix of momentum flow will be represented by the proportion $\rho \mathbf{u}\mathbf{u}$ of $\mathbf{u}\mathbf{u} = (u\mathbf{I} + v\mathbf{J} + w\mathbf{k})\mathbf{u}$ density of momentum flow

$$\nabla \cdot \rho \mathbf{u}\mathbf{u} = \left(\nabla \cdot \rho u \mathbf{u} - \frac{\rho v^2}{r} \right) \mathbf{I} + \left(\nabla \cdot \rho v \mathbf{u} + \frac{\rho v u}{r} \right) \mathbf{J} + (\nabla \cdot \rho w \mathbf{u}) \mathbf{k},$$

finally, the original for fluid mechanics the “matrix of the deformation rates” [117] by the matrix of the rate deformations, or fluid deformations $\mathbf{u}_r$ to be the sum of $\mathbf{u}_x \mathbf{i} + \dots$ of direct products $\mathbf{u}_x \mathbf{i}, \dots$:

$$\mathbf{u}_r = \begin{pmatrix} u_x^x & u_y^x & u_z^x \\ u_x^y & u_y^y & u_z^y \\ u_x^z & u_y^z & u_z^z \end{pmatrix} = \begin{pmatrix} u_x^x \mathbf{i}\mathbf{i} + & u_y^x \mathbf{j}\mathbf{j} + & u_z^x \mathbf{k}\mathbf{k} + \\ u_x^y \mathbf{j}\mathbf{i} + & u_y^y \mathbf{j}\mathbf{j} + & u_z^y \mathbf{j}\mathbf{k} + \\ u_x^z \mathbf{k}\mathbf{i} + & u_y^z \mathbf{k}\mathbf{j} + & u_z^z \mathbf{k}\mathbf{k} \end{pmatrix} = \mathbf{u}_x \mathbf{i} + \mathbf{u}_y \mathbf{j} + \mathbf{u}_z \mathbf{k},$$

with

$$\begin{aligned} \mathbf{u}_\theta &= (u\mathbf{I} + v\mathbf{J} + w\mathbf{k})_\theta = u\mathbf{I}_\theta + v\mathbf{J}_\theta = u\mathbf{J} - v\mathbf{I} = \mathbf{k} \times \mathbf{u} \\ u\mathbf{u}_{\theta\theta} &= \mathbf{k} \times \mathbf{u}_\theta = \mathbf{k} \times (\mathbf{k} \times \mathbf{u}) = \mathbf{k}\mathbf{k} \cdot \mathbf{u} - \mathbf{k} \cdot \mathbf{k} \mathbf{u} = \mathbf{k}w - \mathbf{u}, \end{aligned}$$

or

$$\mathbf{u}_r = \mathbf{u}_r \mathbf{I} + \frac{1}{r} \mathbf{u}_\theta \mathbf{J} + \mathbf{u}_z \mathbf{k},$$

with divergence

$$\nabla \cdot \mathbf{u}_r = \left(\frac{1}{r} (ru)_r + w_z \right)_r \mathbf{I} + \left(\frac{1}{r} (ru)_r + w_z \right)_z \mathbf{k} = (\nabla \cdot \mathbf{u})_r \mathbf{I} + (\nabla \cdot \mathbf{u})_z \mathbf{k} = \nabla \nabla \cdot \mathbf{u}$$

convolution, or point product

$$\nabla \mu \cdot \mathbf{u}_r = (\nabla \mu \cdot \mathbf{u}_r) \mathbf{I} - \frac{\mu_r v}{r} \mathbf{J} + (\nabla \mu \cdot \mathbf{u}_z) \mathbf{k},$$

with divergence

$$\begin{aligned} \nabla \cdot \mu \mathbf{u}_r &= \mu \nabla \cdot \mathbf{u}_r + \nabla \mu \cdot \mathbf{u}_r = \mu \nabla \nabla \cdot \mathbf{u} + \nabla \mu \cdot \mathbf{u}_r \\ &= (\mu (\nabla \cdot \mathbf{u})_r + \nabla \mu \cdot \mathbf{u}_r) \mathbf{I} - \frac{\mu_r v}{r} \mathbf{J} + (\mu (\nabla \cdot \mathbf{u})_z + \nabla \mu \cdot \mathbf{u}_z) \mathbf{k}, \end{aligned}$$

and the conjugate matrix is the sum of the corresponding reverse multiplications

$$\nabla \mathbf{u} = \begin{pmatrix} u_x^x & u_x^y & u_x^z \\ u_y^x & u_y^y & u_y^z \\ u_z^x & u_z^y & u_z^z \end{pmatrix} = (\nabla u^x) \mathbf{i} + (\nabla u^y) \mathbf{j} + (\nabla u^z) \mathbf{k} = \mathbf{i} u_x + \mathbf{j} u_y + \mathbf{k} u_z,$$

or

$$\nabla \mathbf{u} = (\mathbf{u}_r)_* \mathbf{I} \mathbf{u}_r + \frac{1}{r} \mathbf{J} \mathbf{u}_\theta + \mathbf{k} u_z, \quad \mathbf{u}_r = (\nabla \mathbf{u})_*,$$

with divergence

$$\nabla \cdot \mu \nabla \mathbf{u} = \left(\nabla \cdot \mu \nabla u - \frac{\mu u}{r^2} \right) \mathbf{I} + \left(\nabla \cdot \mu \nabla v - \frac{\mu v}{r^2} \right) \mathbf{J} + (\nabla \cdot \mu \nabla w) \mathbf{k}$$

so that

$$\nabla \cdot \mu (\mathbf{u}_r + \nabla \mathbf{u}) = \left(\begin{array}{c} \nabla \cdot \mu \nabla u - \frac{\mu u}{r^2} \\ + \mu (\nabla \cdot \mathbf{u})_r + \nabla \mu \cdot \mathbf{u}_r \end{array} \right) \mathbf{I} + \left(\begin{array}{c} \nabla \cdot \mu \nabla v \\ - \frac{(\mu v)_r}{r^2} \end{array} \right) \mathbf{J} + \left(\begin{array}{c} \nabla \cdot \mu \nabla w \\ + \mu (\nabla \cdot \mathbf{u})_z \\ + \nabla \mu \cdot \mathbf{u}_z \end{array} \right) \mathbf{k}.$$

Let us consider the motion of the particles in the wet mixture. If we follow Euler and add the strength of the molecular pressure p to Newton's law of dynamics, then, taking into account conservation of mass or the continuity equation

$$\rho_t + \nabla \cdot \rho \mathbf{u} = 0$$

add the buoyant force of Archimedes $-\nabla p$ (or the force of molecular pressure p) to the body force (or, to be exact, $\mathbf{g}\rho dV$) applied to mass ρdV with a given acceleration $\mathbf{g} = \mathbf{g}(t, \mathbf{r})$ in Newton's dynamic law that balances the inertial force $\rho \mathbf{a}$ of fluid acceleration $\mathbf{a} = \mathbf{u}_t + \mathbf{u} \cdot \nabla \mathbf{u}$ with the sum of $\rho \mathbf{g}$ and $-\nabla p$ refined subsequently by both the force $\nabla \cdot \mu \vec{\mathbf{b}}$ of Newton's dynamic viscosity $\mu = \mu(t, \mathbf{r})$ (supposed to be constant initially) and the matrix

$$\vec{\mathbf{b}} = \mathbf{u}_r + \nabla \mathbf{u} - \frac{2}{3}(\nabla \cdot \mathbf{u}) \vec{\mathbf{e}},$$

of Navier ($\nabla \cdot \mathbf{u} = 0$) and Stokes and the relevant pressure force $-\nabla(p - \zeta \mu \nabla \cdot \mathbf{u})$ with the second, or volume viscosity $\zeta \mu$, $\zeta = \text{const} \geq 0$ [111–113].

As a result, with appropriate contact (or applied to coordinate areas) forces to be tensions, stresses or components of the Euler–Navier–Stokes matrix

$$\vec{\mathbf{p}} = (p - \zeta \mu \nabla \cdot \mathbf{u}) \vec{\mathbf{e}} - \mu \vec{\mathbf{b}} = P \vec{\mathbf{e}} - \mu(\mathbf{u}_r + \nabla \mathbf{u}), P = p + \left(\frac{2}{3} - \zeta\right) \mu \nabla \cdot \mathbf{u},$$

with divergence

$$\nabla \cdot \vec{\mathbf{p}} = \nabla \cdot P \vec{\mathbf{e}} - \nabla \cdot \mu(\mathbf{u}_r + \nabla \mathbf{u}) = \nabla P - \nabla \cdot \mu(\mathbf{u}_r + \nabla \mathbf{u}),$$

and ensures the dynamic equilibrium of a continuous medium in the corresponding Navier–Stokes equations:

$$(\rho \mathbf{u})_t + \nabla \cdot (\rho \mathbf{u} \mathbf{u} + \vec{\mathbf{p}}) = \rho \mathbf{g} \text{ and } \rho_t + \nabla \cdot \rho \mathbf{u} = 0, \quad (3.1)$$

or

$$\begin{aligned} & (\rho u)_t + \left(\frac{1}{r}(r\rho uu)_r + (\rho uw)_z - \frac{\rho v^2}{r} \right) + P_r \\ & - \left(\frac{1}{r}(r\mu u_r)_r + (\mu u_z)_z - \frac{\mu u}{r^2} + \mu \left(\frac{1}{r}(ru)_r + (w)_z \right)_r + \mu_r u_r + \mu_z w_r \right) = \rho g^r, \\ & (\rho v)_t + \left(\frac{1}{r}(r\rho v u)_r + (\rho v w)_z + \frac{\rho w}{r} \right) - \left(\frac{1}{r}(r\mu v_r)_r + (\mu v_z)_z - \frac{(r\mu)_r v}{r^2} \right) = 0, \\ & (\rho w)_t + \left(\frac{1}{r}(r\rho w u)_r + (\rho w w)_z \right) + P_z \\ & - \left(\frac{1}{r}(r\mu w_r)_r + (\mu w_z)_z + \mu \left(\frac{1}{r}(ru)_r + w_z \right)_z + \mu_r u_z + \mu_z w_z \right) = \rho g^z, \\ & P = p + \mu \left(\frac{2}{3} - \zeta \right) \left(\frac{1}{r}(ru)_r + w_z \right) \text{ and } \rho_t + \frac{1}{r}(r\rho u)_r + (\rho w)_z = 0, \end{aligned}$$

Contact stresses of matrix $\mathbf{P}$ are naturally attributed to the source of liquid strains $\mathbf{u}_r$ for particles of the wet mixture in dynamic equilibrium [Eq. (3.1)], which replaces static equilibrium (Hooke's law) for small displacements in the solid particles of the dry material [118].

In this case, it is natural to estimate the distortions of the velocity field using a measure of liquid deformations [117],

$$D = D[\mathbf{u}] = \frac{1}{2} \|\mathbf{u}_r + \nabla \mathbf{u}\|^2 = \frac{1}{2} |\mathbf{u}_x + \nabla u^x|^2 + \frac{1}{2} |\mathbf{u}_y + \nabla u^y|^2 + \frac{1}{2} |\mathbf{u}_z + \nabla u^z|^2,$$

which is a familiar function measuring the dissipation of mechanical energy into thermal energy [112],

$$D = 2(u_x^x)^2 + 2(u_y^y)^2 + 2(u_z^z)^2 + (u_x^y + u_y^x)^2 + (u_y^z + u_z^y)^2 + (u_z^x + u_x^z)^2$$

or, in the axisymmetric polar variables

$$D = 2u_r^2 + 2\left(\frac{u}{r}\right)^2 + 2w_z^2 + \left(v_r - \frac{v}{r}\right)^2 + (v_z)^2 + (u_z + w_r)^2,$$

and systematically used, as shown, for example, in [119], the argument (or independent variable) of viscous rheology, suggesting the existence of an equation to measure the plastic state of the material [113–115]:

$$\mu = \mu(\gamma), \gamma = D[\mathbf{u}] \geq 0.$$

The geometric structure of the argument $\gamma = D$ reveals the identity of measure, as directly verifiable resolving D the sum of the proportions [117],

$$D = \frac{2}{3}A^2 + B^2 + \frac{2}{3}C^2$$

squares of local norms of inhomogeneity

$$A = \sqrt{(u_x^x - u_y^y)^2 + (u_y^y - u_z^z)^2 + (u_z^z - u_x^x)^2},$$

shear

$$B = \sqrt{(u_x^y + u_y^x)^2 + (u_y^z + u_z^y)^2 + (u_z^x + u_x^z)^2},$$

and compressibility

$$C = u_x^x + u_y^y + u_z^z$$

for liquid deformations, described by the matrix $\mathbf{u}_r$.

It is possible to show [117] that the power of deformations (work done per second) in an arbitrary volume V has the form

$$W = \int_V \mu \left(\frac{2}{3} A^2 + B^2 + \zeta C^2 \right) dV.$$

Let us simplify the initial problem. As already noted, in addition to transportation of the mass, the main purpose of the extruder is to compact the material in zone 2 (Fig. 3.41). We will limit ourselves to the portion (length) of zones 3 and 4, suggesting constant density of material, approximated by Newtonian rheology:

$$\rho = \text{const} > 0 \text{ (therefore, } \nabla \cdot \mathbf{u} = 0 \text{) and } \mu = \text{const} > 0.$$

We consider the flow of material in the space between two concentric infinite cylinders. Further, with the stationary external cylinder $r = a = \text{const} > 0$, we will maximize the auger operation for the transportation and shearing of mass in the extruder, or between cylinders

$$\varepsilon a < r < a, \varepsilon, a = \text{const} > 0, \varepsilon < 1,$$

shifting it to the inner cylinder $r = \varepsilon a$, that, due to conditions of liquid particles sticking to it, now moves this mass along the axis z , at the same time as rotating it around this axis with a constant velocity of boundary displacement $w_- > 0$ and torsion $v_- < 0$, as in Fig. 3.42:

$$\begin{aligned} w|_{r=\varepsilon a} = w_-, w|_{r=a} = w_+, v|_{r=\varepsilon a} = v_-, v|_{r=a} = v_+, \quad w_{\mp}, v_{\mp} = \text{const}, \\ \text{where } w_- > 0, \quad v_- < 0 \text{ and } w_+ = v_+ = 0. \end{aligned} \quad (3.2)$$

Finally, assume that the incoming mass is pushed further with a constant gradient of excess pressure or by the difference of its values $p_{\pm}$ at the ends of the chosen length:

$$-p_z = \frac{p_+ - p_-}{l} = \text{const} > 0, 0 < z < l, p_- = p|_{z=0}, p_+ = p|_{z=l}. \quad (3.3)$$

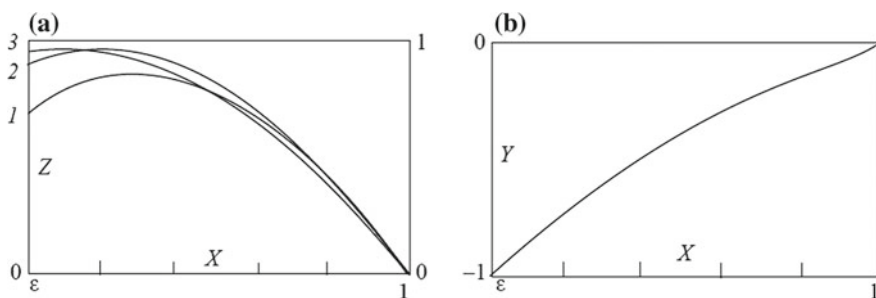


Fig. 3.42 Profiles of axial (left) and azimuthal (right) component of the considered spiral flow at two subcritical (1 and 2) and one supercritical (3) values of dynamic factor

In the absence of mass forces and radial displacements of the liquid material rotating and being moved longitudinally by the auger, and more precisely, under the assumption that

$$u = 0, v = v(r), w = w(r) \text{ and } g^r = g^z = 0, \quad (3.4)$$

the dynamic equilibrium (1) with conditions (3.2)–(3.4) is reduced to the proportions:

$$-\frac{1}{r}(rw_r)_r = \frac{-p_z}{\mu}, (rv_r)_r = \frac{v}{r}, p_r = \frac{\rho v^2}{r}, -p_z = \frac{p_+ - p_-}{l}, \varepsilon a < r < a, \\ 0 < z < l, w(\varepsilon a) = w_-, w(a) = w_+ = 0, v(\varepsilon a) = v_-, v(a) = v_+ = 0,$$

or to Hagen–Poiseuille’s flow between the pipes [110, 111, 120],

$$w(r) = w_+ - \frac{p_z(a^2 - r^2)}{4\mu} + \left(w_- - w_+ + \frac{p_z a^2(1 - \varepsilon^2)}{4\mu} \right) \frac{\ln \frac{r}{a}}{\ln \varepsilon} \text{ with } w_+ = 0,$$

at the same time spiral, as the Couette flow with azimuthal velocity

$$v(r) = \frac{\varepsilon a v_- - \varepsilon v_+}{r(1 - \varepsilon^2)} + \frac{r v_+ - \varepsilon v_-}{a(1 - \varepsilon^2)} = \frac{\varepsilon v_-}{1 - \varepsilon^2} \left(\frac{a}{r} - \frac{r}{a} \right) \text{ with } v_+ = 0,$$

and with pressure falling along the radius to the center of rotation, as in a centrifuge [117]

$$p(r, z) = p_+ - \frac{z}{l}(p_+ - p_-) - \int_r^a \frac{\rho v^2(r')}{r'} dr', \quad p_r = \frac{\rho v^2}{r} > 0, \\ \varepsilon a < r < a, 0 < z < l.$$

In Fig. 3.42 in dimensionless variables of the radius X and speeds of displacement and rotation of auger, Z and Y ,

$$\frac{4\mu w}{-p_z a^2} = Z = 1 - X^2 - \frac{1 - \varepsilon^2 - \delta}{\ln \varepsilon} \ln X, 0 < \delta = \frac{4\mu w_-}{-p_z a^2} < 1 - \varepsilon^2,$$

and

$$\frac{v(r)}{v_-} = Y = \frac{\varepsilon}{1 - \varepsilon^2} \left(\frac{1}{X} - X \right)$$

given the dependence of the latter from the first, i.e., dimensionless profiles $Z(X)$ and $Y(X)$ of the azimuthal $w(r)$ and axial $v(r)$ components of the velocity $\mathbf{u}$. The

latter depend on dimensionless parameters ε and δ : ratio of the inner radius $r_{\min}$ to an external a , or radial factor

$$\varepsilon = \frac{r_{\min}}{a}, \quad 0 < \varepsilon < 1,$$

and the ration of velocity of the boundary displacement w to the following speed viscous pressure w_p , or a dynamic factor

$$\delta = \frac{w_-}{w_p} = \frac{4\mu w_-}{-p_z a^2} > 0 \text{ at } w_p = \frac{-p_z a^2}{4\mu} \text{ and } -p_z > 0.$$

SVE extruders [119] are operated with the usually moderate values of $\varepsilon \approx 0.5$ and mostly at the subcritical value of $0 < \delta < 1 - \varepsilon^2$, rarely, at supercritical factor $\delta > 1 - \varepsilon^2$, that is illustrated by the dimensionless dependence $Z(X)$ in Fig. 3.42, left.

At the subcritical dynamic factor and the maximum possible speed of material transportation by the auger, $w(r)$ is limited by value

$$w_* = \max_{\varepsilon a \leq r \leq a} w(r) = w_p \max_{\varepsilon \leq X \leq 1} Z(X) = w(r_*),$$

close to the speed of viscous flow w_p , achieved within the field of flow: $\varepsilon a < r_* < a$. With the growth of the factor $\delta < 1 - \varepsilon^2$, this value approaches the speed w_p , shifting simultaneously on the internal radius of the cylinder $r = \varepsilon a$, and reaches w_p on the border of flow area, i.e., $r_* = \varepsilon a$ at $\delta = 1 - \varepsilon^2$, remaining maximum speed of the transported mass $w_* = w_p$ and at any superficial factor $\delta \geq 1 - \varepsilon^2$.

Thus, increasing the speed of displacement w_- at superficial factor δ does not increase the speed of transportation $w(r)$ in the flow area $\varepsilon a < r < a$, reaching the maximum value W_* on the border of this area $r_* = \varepsilon a$ and equal to the speed of viscous flow w_p .

The above concepts came from the central assumptions of continuum mechanics about the presence of the molecular pressure p in such materials and produced by its flow $\mathbf{u}$ liquid deformations $\mathbf{u}_r = (\nabla \mathbf{u})$, which together generate contact strain $\vec{\mathbf{p}}$, balancing the resulting acceleration of the particles in the Navier–Stokes equations (1). The original premise of the mechanics of viscoplastic deformation seems to be the opposite: There is a solid body, and the tension applied to its surface is defined as $\vec{\mathbf{p}}$ (shear stress), which produce deformation $\mathbf{u}_r$ (shear rate) upon reaching of a critical level—the so-called plasticity limit $\|\vec{\mathbf{p}}\| = \text{const}$ (yield stress). But details of the dependence between tension and deformation are reduced to the above classical formula for $\vec{\mathbf{p}}$. The same viscoplastic state of the material is described by the above-mentioned dependence of dynamic viscosity $u = \mu(\gamma)$ on measure of deformations $\gamma = D[\mathbf{u}]$, reduced to the constant $\mu = \text{const}$ at the superficial level of tension in well-known Bingham's model [111], which we also accept here for the flow of the material in extruder [121].

The extruded mass is not only mixed, but also compressed. Therefore, we will consider in the simplified variant that

$$\rho = \rho(r) \neq \text{const}(\nabla \cdot \mathbf{u} \neq 0) \text{ and } \mu = \text{const.}$$

Assuming that

$$u = u(r)_b, v = v(r), w = w(r) \text{ and } g^r = g^z = 0,$$

then the continuity equation in (1) leads to a permanent

$$r\rho u = m = \text{const, or } ru = m\varphi, \text{ where } \varphi = \frac{1}{\rho}$$

specific volume. When divided by dynamic viscosity,

$$\alpha = \frac{m}{\mu},$$

is a dimensionless value. Having in (3.1)

$$p_r = \frac{\rho v^2}{r} \text{ and } \frac{\alpha+1}{r^2} (ru)_r - \left(\frac{1}{3} + \zeta\right) \left(\frac{1}{r} (ru)_r\right)_r - \frac{1}{r} (ru)_{rr} - \frac{\alpha ru}{r^3} = 0$$

we solved for the values $\varphi_{\mp}$:

$$\varphi = \frac{\varepsilon^{\lambda_+} \varphi_+ - \varphi_-}{\varepsilon^{\lambda_+} - \varepsilon^{\lambda_-}} \left(\frac{r}{a}\right)^{\lambda_-} + \frac{\varepsilon^{\lambda_-} \varphi_+ - \varphi_-}{\varepsilon^{\lambda_-} - \varepsilon^{\lambda_+}} \left(\frac{r}{a}\right)^{\lambda_+},$$

$$\lambda_{\mp} = \frac{8+6\zeta+3\alpha}{2(4+3\zeta)} \mp \sqrt{\left(\frac{8+6\zeta+3\alpha}{2(4+3\zeta)}\right)^2 - \frac{3\alpha}{4+3\zeta}} \text{ at } \left(\frac{8+6\zeta+3\alpha}{2(4+3\zeta)}\right)^2 > \frac{3\alpha}{4+3\zeta},$$

Satisfying the conditions (3.2)–(3.3) and Eq. (3.1)

$$\frac{m}{r} v_r + \frac{mv}{r^2} - \frac{\mu}{r} (rv_r)_r + \frac{\mu v}{r^2} = 0, \frac{m}{r} w_r - \frac{mw}{r^2} - \frac{\mu}{r} (rw_r)_r = -P_z = -p_z,$$

$$P = p + \mu \left(\frac{2}{3} - \zeta\right) \frac{1}{r} (ru)_r, \quad \varepsilon a < r < a,$$

axial and azimuthal velocity components in this case have profiles:

$$w = \frac{\varepsilon^{\gamma_+} w_+ - w_-}{\varepsilon^{\gamma_+} - \varepsilon^{\gamma_-}} \left(\frac{r}{a}\right)^{\gamma_-} + \frac{\varepsilon^{\gamma_-} w_+ - w_-}{\varepsilon^{\gamma_-} - \varepsilon^{\gamma_+}} \left(\frac{r}{a}\right)^{\gamma_+} + \frac{-p_z a^2}{\mu(4-\alpha)} \left(\frac{\varepsilon^{\gamma_+} - \varepsilon^2}{\varepsilon^{\gamma_+} - \varepsilon^{\gamma_-}} \left(\frac{r}{a}\right)^{\gamma_-} + \frac{\varepsilon^{\gamma_-} - \varepsilon^2}{\varepsilon^{\gamma_-} - \varepsilon^{\gamma_+}} \left(\frac{r}{a}\right)^{\gamma_+} - \left(\frac{r}{a}\right)^2\right),$$

$$\gamma_{\mp} = \frac{\alpha}{2} \mp \sqrt{\left(\frac{\alpha}{4} - 1\right)\alpha} \text{ at } \left(\frac{\alpha}{4} - 1\right)\alpha > 0,$$

Fig. 3.43 Raw brex exiting the extruder



and

$$v = \frac{\varepsilon^{\beta_+} v_+ - v_-}{\varepsilon^{\beta_+} - \varepsilon^{\beta_-}} \left(\frac{r}{a}\right)^{\beta_-} + \frac{\varepsilon^{\beta_-} v_+ - v_-}{\varepsilon^{\beta_-} - \varepsilon^{\beta_+}} \left(\frac{r}{a}\right)^{\beta_+},$$

$$\beta_{\mp} = \frac{\alpha}{4} \mp \left(\frac{\alpha}{2} + 1\right) = -\frac{\alpha}{4} - 1, \frac{3\alpha}{4} + 1.$$

The received analytical dependences allow one to qualitatively assess the flow of the formable mass in the extruder and can be used for further numerical simulation.

In zone 5, the brex is squeezed out of the holes in the die (Fig. 3.43), which completes the process of their formation.

3.5 Requirements to Metallurgical Properties of Briquettes

3.5.1 *Briquetting of Natural and Anthropogenic Materials in Blast Furnace (BF) Production*

The reasons why roller briquetting is not widely used in blast furnace production are associated with the need to ensure low moisture content of the components of the briquetted charge, which, in turn, limits the applicability of Portland cement and other hydrated binding materials as a binder. For the hardening of the cement stone in such a briquette, there would not be enough water. Organic binders are not known to ensure the integrity of briquettes at temperatures in the cohesion zone.

The search for ways to produce durable briquettes with the required hot strength level for blast furnace on the basis of roller briquetting has led to renewed interest in thermal briquetting. Companies Köppern and Sahut Conreur own technology for the production of briquettes from a heated mixture based on roller presses of a special design. Full-scale industrial tests carried out in 2011 in Japan at blast furnace No. 3 by Kobe Steel showed the possibility of achieving a positive effect from the use of roller briquettes made from a mixture of preheated coal and iron ore concentrate heated to 600 °C [122]. The manifestation of the binding properties of the plasticized coal during heating made it possible to achieve the required hot strength. However, the method of thermal briquetting was not widely used for the production of blast briquettes, since it did not provide a competitive advantage over sinter and pellets. In terms of thermal briquetting, the obvious advantage of cold briquetting, consisting in the absence of heat treatment and undesirable environmental impact, is lost.

Another development of the same company, in which the use of roller briquetting is possible, is based on the production of a new agglomerated product, called “ferro-coke,” obtained by coking the coal charge with the addition of iron ore or flue dust [123]. In contrast to thermal briquetting, the agglomeration of poor ore and coke breeze is carried out using a special binder based on naphthalene-type solvents used in coal mining. The obtained blast furnace briquettes are additionally carbonized at a temperature of 1000 °C for 6 h. Studies have shown the possibility of achieving high metallurgical properties of ferro-coke and formed the basis of the project to build a test plant for its production worth \$ 100 million, carried out by JFE Steel with Kobe Steel and Nippon Steel & Sumitomo Metal [124]. The pilot plant will produce 300 tons of ferro-coke daily. The main objective of the project is to test the effectiveness of using this new agglomerate product to reduce carbon dioxide emissions and the possibility of achieving the expected increase in the efficiency of blast furnaces by 10%. It is supposed to commercialize ferro-coke by 2022.

A concept based on a cold-bonded ferrocoke was proposed in [125]. To reduce coke consumption in blast furnace smelting, the authors recommend using so-called reactive coke agglomerate (RCA) on a cement binder. The essence of this concept is

to create a special RCA structure in which high homogeneity and orderliness of the mutual arrangement of iron ore and coke concentrate particles are achieved, ensuring their maximum proximity to each other, which leads to high reactivity and, as a result, to a decrease in coke consumption. Attempts to use roller and other presses for the production of such agglomerated products without their further heat treatment do not allow obtaining a mechanically strong briquette due to the high carbon content recommended by the developers of this technology—20% of the briquette mass. In this case, the proportion of cement binder required to provide the necessary strength may exceed values that justify the economic attractiveness of cold briquetting. Commercialization of this technology was carried out by the method of obtaining cold-bonded pellets using specially designed heat and moisture treatment, which significantly accelerated the curing of the pellets to achieve the required mechanical strength [126].

Thus, it is clear that the prospects for using roller briquetting for the production of thermo-briquetted blast furnace briquettes and ferro-coke are currently awaiting their determination.

In this regard, we will further consider the metallurgical properties of blast furnace briquettes obtained by the method of vibropressing and stiff extrusion. First of all, we will be interested in the mechanism of preserving the strength of briquettes when they are heated in a reducing atmosphere.

In Russia, the first vibropressing briquetting factory was commissioned at the JSC Tulachermet in 2003 [127]. The capacity of the line enabled a monthly production of up to 8000 tons of briquettes. Two types of briquettes were used as components of the BF charge: the so-called washing briquettes and iron and carbon briquettes. It is known that in some cases, technologists were faced with “cluttering” of the hearth of the blast furnace due to the deterioration of coke’s ability to filter when filling the voids between its particles with pieces of slowly moving smelting products. This can result in combustion of air tuyeres, decrease of hearth heating, and other phenomena, which reduce the melting performance. One of the most effective means of combating this phenomenon is “flushing” the hearth using liquid slag containing FeO or MnO. Typically, the special sinter made using mill scale serves as the “washing” material. Mill scale briquettes can also be used for such purposes.

The value for the design compressive strength of Tulachermet briquettes was supposed to be at least 6.0 MPa. After drying, its values were—3.83 MPa, and after heat-moisture treatment—6.9 MPa. In total during the course of the existence of the line, more than 52 thousand tons of briquettes were manufactured (about 50 thousand tons of briquettes containing iron and carbon, and 2700 tons of washing briquettes). During the unloading of the briquettes from the bunker, their bridging was noted [128]. The maximum shares of the briquettes in the charge of the blast furnaces were as follows: BF No. 1—32 kg/t of hot metal and BF No. 2—56 kg/t of hot metal. With the application of briquettes, flue dust blowout decreased by 4 kg/t. Factor analysis showed that with the application of iron- and carbon-containing briquettes the specific consumption of dry skip coke decreased by 14.4 kg/t of hot metal, which corresponded to the coke’s replacement in the

body of the briquettes with coke breeze by a ratio of 1 to 1. Pig iron production increased by 37 tons/day, which is associated with an improvement in the gas permeability of the charge column due to the improved granular composition of the charge. This helped to increase the blast volume and, as a result, to intensify melting. After several years of operation, the briquetting factory was closed as a result of changes in economic conditions affecting the availability of suitable carbonaceous materials for briquetting.

A series of campaigns on the use of vibropressed briquettes of varying compositions on a cement binder in the charge of blast furnace with a volume 1000 m³ was carried out in 2003–2004 by the Novolipetsk Steel Company (JSC NLMK) [129–131].

The results of experimental melts confirmed the effective application of iron- and carbon-containing briquettes as a new blast furnace charge component. Due to the presence of carbon, such briquettes are self-reducing and their utilization leads to a proportional reduction of coke consumption. The main results of the campaigns are as follows: Vibropressing can provide the required values for the mechanical strength of briquettes made of natural and anthropogenic oxide materials with a share of the cement binder of not less than 8–10% by weight of a briquette; the value of the compressive strength for most of the briquettes was not less than 30 kgf/cm² and ensured their integrity during overloads and transportation with a less than 5–7% fine generation (–10 mm).

In 2010 the Kosaya Gora Iron Works vibropressing briquetting factory (located in Russia) was commissioned for the production of 120,000 tons of briquettes from a mixture of iron ore concentrates and fines, and flue dust with a Portland cement binder (not less than 10% by weight of the briquette). The exposure time of the briquettes in a heat treatment chamber (for heat–moisture treatment) was 36 h. The density of briquettes ranged from 2.0 to 5.0 g/cm³. Their compressive strength was not less than 3.5 Mpa, and the moisture content was up to 9%. The share of briquettes in the ore part of the blast furnace load is 100 kg/t of hot metal. Bridging was noted during loading [76]. In total, the factory has produced over 300 thousand tons of briquettes. There is almost no information available in open domain concerning a systematic analysis of the results of the operation of this factory. The factory has practically been out of operation since October 2015.

In March 2012 in Finland at the Raahen Works Company, a vibropressing briquetting line for the production of briquettes for blast furnaces was commissioned after the closing of the sinter plant [77]. Briquetted charge consisted of: mixture of pellet fines (71,000 tons), coke dust (12,000 tons), premix of flue dust and steel scrap (59,000 tons), mill scale (59,000 tons), briquette fines (34,000 tons) and scrap (15,000 tons), slag cement (17,000 tons), and rapid cement (19,000 tons). Total amount of briquettes recycled via blast furnace process is 283,000 tons/year. Briquette size is 60 × 60 mm, and weight is 475 g. After the 48 h of strengthening, the cold strength of briquettes according to ISO 4696 was 74% (the share of pieces larger than 6.3 mm). Coke rate was decreased by 6% by feeding 120–130 kg of briquettes per 1 ton of hot metal into the charge of the BF due to the fact that the briquettes contained carbon. It is seen that vibropressing led to the formation of

significant quantities of briquette fines (34,000 tons/year). It was also impossible to agglomerate efficiently BOF sludge (60,000 tons/year; moisture content 33–39%) and BF sludge (30,000 tons/year; moisture content 20–25%) by vibropressing.

The results of full-scale testing and of the practical implementation of vibro-pressing briquetting technology confirm the possibility of achieving the required level in terms of the metallurgical properties of the agglomerated products. However, this technology creates some significant technological limitations, which are difficult to overcome, or leads to a significant increase in the cost of a briquette.

In April 2011, an industrial briquetting line was commissioned at the Suraj PL plant in Rourkela (India), producing brex using stiff vacuum extrusion technology for their use in a blast furnace. The management of the company decided to implement a project for the production of brex from a mixture of converter sludge, blast furnace dust, Portland cement, and bentonite. The main objective of the project was to increase the economic efficiency of the small blast furnace by replacing the purchased ore with cheap brex.

In the period from 2011 to 2018, several more briquetting plants were built, producing brex for blast furnace. The world's largest factory for the production of blast furnace brex was built in 2018, Lipetsk (Russia), at the site of NLMK. Its capacity is 700 thousand tons of brex per year.

Next, we will consider the metallurgical properties of blast furnace briquettes obtained by the methods of vibropressing and stiff extrusion. First of all, we will be interested in the mechanism of preserving the strength of briquettes when they are heated in a reducing atmosphere.

3.5.1.1 Metallurgical Properties of Vibropressed Blast Furnace Briquettes

The most widespread vibropressing for obtaining blast furnace briquettes was found in Sweden. The study of the metallurgical properties of such briquettes was first carried out at the Lulea University of Technology [132]. The metallurgical properties of briquettes of two different compositions (93.5% of pellet fines, 6.5% of Portland cement and 62.7% of pellet fines, 30.8% of sludge and dust, 6.5% of Portland cement) produced by the method of vibropressing were investigated. One peculiarity of these briquettes is a tendency to swell considerably during the reduction process using carbon monoxide at 950 °C, which is linked with a similar abnormal swelling of the indurated pellets [53–55]. The mechanism of the catastrophic swelling of iron ore pellets is associated with the growth of iron whiskers during wustite reduction, which is enhanced in the presence of CaO [133]. The degree of swelling decreased when adding hydrogen to the reducing gas. It was also noted that the tendency to swell in the presence of cement is reduced when its content in the body of a briquette exceeds 10% (mass). The largest degree of briquette swelling took place with a cement share in the mass of the briquette ranging from 4 to 6% [134]. It was noted that at high temperatures the converted phases of cement, olivine, and wustite react with the formation of (Ca, Mg,

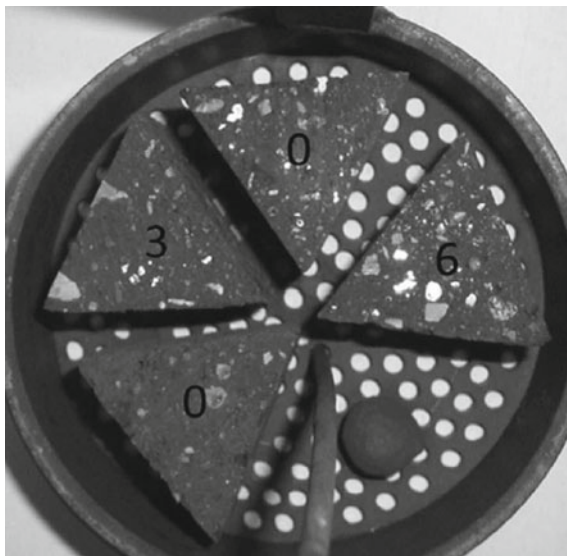
Fe_2SiO_4 (dicalcium silicate, forsterite, and fayalite). The properties of this phase are determined by the relationship between the value contents of pellet fines and cement. The formation of the silicate melt at a lower temperature is also possible (1150 °C). These briquettes were also tested in the experimental blast furnace. It is claimed that unlike testing of the briquettes in laboratory conditions, their reduction in the experimental blast furnace was not accompanied by catastrophic swelling. Reduced briquettes, after extraction from the experimental blast furnace, had a significant wustite core even with fairly profound lowering in the furnace. For the explanation, authors indicated the following possible reasons: a large volume of briquettes, creation of a slag system $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-FeO}$, and coating of the wustite grains in a molten slag.

The results obtained allowed to determine the effect of the particle size and phase composition of briquetted materials, and their moisture content, and the proportion of Portland cement binder on the metallurgical properties of briquettes, however, did not lead to an understanding of the mechanism for maintaining the strength of such briquettes when heated in a reducing atmosphere.

The authors of [135] approached the study of the metallurgical properties of briquettes produced industrially at the SSAB factory in Raahe came closest to identifying the mechanism of hot strength of vibropressed briquettes. To study the behavior of vibropressed briquettes when heated in a reducing atmosphere, a blast furnace simulator was used. Briquette components are mill scale (41.2%), scrap materials (23.4%), top dust (9.5%), aspiration dust from casting and dosing sections (4.8%), coke dust (6.4%) screening of pellets (2.8%), and other anthropogenic materials. Three different combinations were used as a binder: 10% Portland cement; 8% of Portland cement + 3% of crushed blast furnace slag; and 8% Portland cement + 6% crushed granulated slag. The briquettes were made on the industrial line of vibropressing; however, for testing in the simulator of the blast furnace, the briquette samples were cut into bars with a triangle-shaped section (Fig. 3.44).

However, in this case it is impossible to obtain authentic test results, since in this case the specific surface of the briquette fragment is higher than that of the original briquette, and therefore, the recovery rate is different. The following results were obtained: (1) Briquettes showed significantly faster recovery compared to pellets in the temperature range of 780–1100 °C, which can be explained by the presence of carbon in their composition and higher porosity, the growth of which, according to the authors, is due to the effects of phase hematite–magnetite transition; (2) swelling of briquettes was observed (25–50%) during the transition wustite–iron at 900–1000 °C; (3) the addition of crushed granulated slag contributed to the swelling of the briquettes; (4) the briquettes did not collapse, and the formation of dicalcium ferrite played a role in maintaining strength at high temperatures. In an earlier work on the mechanical strength of the industrial briquettes under consideration [136], it was argued that the replacement of part of Portland cement with slag Portland cement in combination with fly ash leads to an increase in the mechanical strength of the briquette.

Fig. 3.44 Location of fragments of briquettes and pellets in a basket for a blast furnace simulator [135]



The results of the above-mentioned blast furnaces campaign with vibropressed briquettes in the ore portion of the charge, conducted at NLMK in 2003, contributed to understanding the mechanism of preserving the strength of briquettes in a blast furnace.

At the first stage, to evaluate the efficiency of the technological scheme for processing iron–zinc-containing sludge, a batch (2500 tons) of briquettes (65% converter sludge, 20% coke breeze, and 15% Portland cement) was smelted. Briquette consumption ranged from 50 to 70 kg/t of hot metal in the first 5 days to 190 kg/t of hot metal in the last 24 h and averaged 121 kg/t of hot metal. The efficiency of using briquettes was evaluated by comparing the results of the furnace operation in the base period, which includes 15 days of operation of the furnace before the melting of briquettes and 7 days after their melting. When melting briquettes, the degree of coke substitution by fine-grained coke was 0.96 kg/kg.

At the second stage, a batch of 2475 tons of briquettes made of a mixture of iron ore concentrate, coke breeze, and Portland cement was smelted, with a gradual increase in the share of briquettes in the charge (122, 198, 303 kg/t of hot metal). The results of the heats confirmed that such briquettes are a complete self-reducing component of the blast furnace charge, the use of which ensures a reduction in coke consumption in the blast furnace smelting, proportional to their consumption. The share of such a component in the blast furnace charge is only marginally limited to a decrease in the furnace productivity due to a decrease in the iron content in the charge and can reach 50% or more.

At the third stage, a batch (2560 tons) of vibropressed briquettes from a mixture of blast furnace sludge (59%), mill scale (20%), coke breeze (10%), and cement (11%) was smelted in a blast furnace of 2000 m³. When unloading briquettes from

bunkers, their increased bridging was observed. The average consumption of briquettes for the period amounted to 62 kg/t of hot metal, with fluctuations in days from 36 kg/t of iron to 81 kg/t of hot metal. The efficiency of smelting of coke briquettes was evaluated by comparing the melting indices in the experimental and basic periods of the furnace operation. A slight decrease in the productivity of the blast furnace during the melting of briquettes is mainly caused by a decrease in the iron content in the charge, as well as the negative effect of increased basicity and viscosity of the slags formed from the oxides of the gangue of briquettes. There were also lower values of the carbon of coke substitution by coke breeze of briquettes compared to that obtained when melting briquettes from converter sludge (0.96 kg/kg).

The results of the investigation of the metallurgical properties of the laboratory briquettes made by vibropressing, as well as of briquettes used in full-scale testing, are described in [137]. In particular, the behavior of carbon-free briquettes made of magnetite concentrate (91.2%) and Portland cement (8.8%) and BOF sludge (91.9%) and Portland cement (9.1%) while undergoing heating in the reducing atmosphere has been studied. Since the cement binder maintains the strength of the briquette up to temperatures of 750–900 °C, the formation of new solid briquette microstructures was attributed to physical–chemical processes that occur in the body when heating the briquettes in a reducing atmosphere. Such processes are primarily a reduction of iron oxides in the solid-state reaction between wustite, oxides of cement stone, and gangue components of a briquette with the formation of calcium–iron–magnesium silicates.

In the briquettes made of magnetite concentrate and converter sludge, a zonal microstructure with a surface layer of metallic iron has been optically determined. This fact is due to the relatively high density of briquettes, their considerable size, and the lack of a solid reductant in their composition. In the briquettes made of iron ore magnetite concentrate, a magnetite to wustite reduction process is clearly diagnosed throughout the volume of the sample, and on the surface there is the layer of metallic iron with a thickness of 3–5 mm, forming a superficial shell (skeleton) of a briquette (Fig. 3.45, left). In the deeper layers (up to a distance of 20–25 mm from the surface of the briquettes), only small zones can be observed with particles of metallic iron on the edges of the wustite grains. In the central part of briquette, the metallic iron is missing and the entire iron-containing phase is represented only by wustite and ferrous olivine. Depending on temperature and duration of a briquette presence in a reducing atmosphere in different parts of the briquette, iron silicate phase was either in a plastic or a near-plastic state and was filling the space between grains of ore in the form of olivine phase (Fig. 3.45, right).

Due to the large content of SiO_2 in the concentrate (6.3%), the presence of impurities Al_2O_3 , MgO in the mineral phases of cement, as well as the extended surface of contact between the concentrate (particle size 70–120 μm) and cement stone particles, a large portion of the active wustite—a product of magnetite reduction—reacts with silica and forms a system Fe_2SiO_4 – Ca_2SiO_4 comprising an eutectic with a crystallization temperature of 1120 °C (phase diagram CaO – FeO – SiO_2 on Fig. 3.46). Iron silicate phase has a low reducibility, which together with

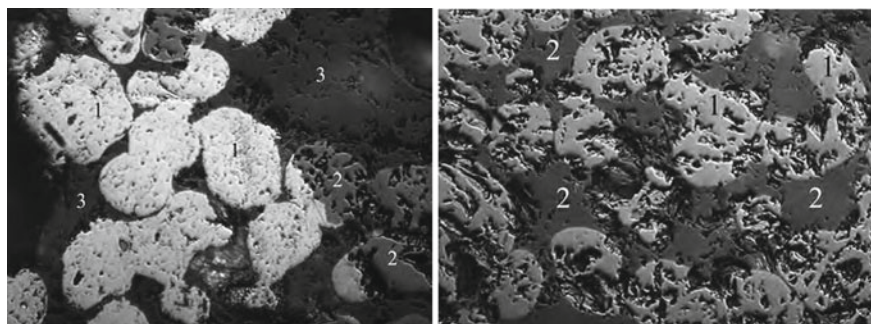


Fig. 3.45 Microstructure of a reduced briquette made of magnetite concentrate. Left: 1—metallic grains, 2—wustite, 3—olivine phase; right: 1—wustite, 2—olivine phase. Reflected light, magnification $\times 500$ [137]

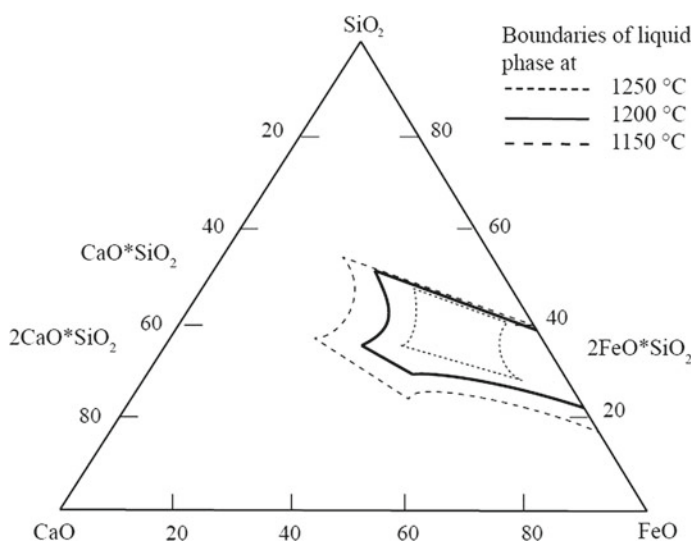


Fig. 3.46 Phase diagram of CaO-FeO-SiO₂ [http://www.crct.polymtl.ca/fact/phase_diagram.php?file=Ca-Fe-Si-O_CaO-FeO-SiO2-Fe_1300C_a\(Fe\)=1.jpg&dir=FToxid](http://www.crct.polymtl.ca/fact/phase_diagram.php?file=Ca-Fe-Si-O_CaO-FeO-SiO2-Fe_1300C_a(Fe)=1.jpg&dir=FToxid)

the diffusive difficulties and large size of a briquette explains the lack of metal iron in its central part. Conservation of the form of a briquette made of magnetite concentrate as it undergoes heating in a reducing atmosphere is provided by the formation of a surface metal iron frame with a thickness of 3–5 mm, which ensures the strength of a briquette at the stage of dehydration of calcium hydrosilicates in the cement stone. The destruction of the briquette when it is heated to 1150 °C is also hampered by the formation of a matrix of iron–calcium olivine in the entire volume of the body of the briquette [129–131].

It is known that the system CaO-FeO-SiO_2 has a eutectic (25% $\text{CaO} \cdot \text{SiO}_2$ and 75% $\text{FeO} \cdot \text{SiO}_2$) with a crystallization temperature of 1030 °C. There are also fields with a crystallization temperature close to 1150 °C.

Apparently, because of the limited time in the furnace at a temperature of 1150 °C and above, the iron silicate phase does not reach a liquidus temperature and remained in a plastic condition without violating the integrity of the briquette in the already established frame of metallic iron with a melting point above 1500 °C.

3.5.1.2 Metallurgical Properties and Optimization of Extrusion Briquette (Brex) Compositions for Blast Furnace Production (Experimental Work)

As a possible component of the blast furnace charge, two classes of brex were studied in [94]: sludge (based on a mixture of blast furnace and converter sludge) and ore-coke (a mixture of iron ore concentrate and coke breeze). For the manufacture of the first batch of laboratory brex, sludge and coke breeze were selected, which are generated in the blast furnace and oxygen converter shops of the Novolipetsk Metallurgical Combine OJSC and iron ore concentrate resulting from the enrichment of magnetite ferruginous quartzites at the Stoilensky GOK. The composition of brex is given in Table 3.8.

The brex pilot batches are made on a laboratory computerized extruder complex, simulating the processing of a briquetted mixture in feeders, pug mills, and extruders. Brex had a circular cross section with a diameter of 2.5 mm and a length in the range of 1.5–2.0-diameters. The moisture content in newly formed Brex No. 2 was 12.4%, and in Brex No. 4—11.9%. The vacuum in the working chamber of the extruder for the production of Brex No. 2 is 20.32 mm Hg, and Brex No. 4—45.72 mm Hg.

To estimate the crush strength of these brex, their cylindrical specimens (diameter 25 mm) 30 mm long were prepared. The load was applied along the vertical axis of the samples. The samples were tested before and after their heating in a reducing atmosphere (50% hydrogen + 50% nitrogen) to 1150 °C at a rate of 500 °C/h and subsequent cooling in a nitrogen atmosphere. Five samples of each type were tested.

Table 3.8 Components of sludge brex (No. 2) and iron ore concentrate and coke breeze brex (No. 4)

Brex component	Mass content, %	
	Brex No. 2	Brex No. 4
Portland cement	9.1	9.0
Coke breeze	—	13.5
Bentonite	—	0.9
Blast furnace sludge	54.5	—
BOF sludge	36.4	—
Iron ore concentrate	—	76.6

Table 3.9 Chemical composition of raw and metallized brex

Brex	Fe _t	Fe _{met}	η _{met}	FeO	CaO	MgO	Al ₂ O ₃	SiO ₂	C	Basicity	LOI
No. 2 (raw)	37.40	–		18.6	15.50	1.26	1.64	7.04	15.7	2.2	19.1
No. 2 (metallized)	64.5	51.6	0.8	16.8	–			–	9.66		
No. 4 (raw)	49.20			21.0	6.89	0.58	1.14	8.78	11.6	0.8	12.2
No. 4 (metallized)	82.6	67.1	0.82	18.9	–			–	7.80		

Table 3.10 Compressive strength of brex

Sample		Strength after heat treatment, kgf/cm ²	Strength before heat treatment, kgf/cm ²
No. 2	1	97.7	103.8
	2	124.7	89.4
	3	101.8	112.2
	4	105.0	124.7
	5	118.5	166.3
	Average value	109.5	119.3
No. 4	1	93.5	124.7
	2	95.6	103.8
	3	106.0	110.1
	4	87.3	103.9
	5	93.5	114.3
	Average value	95.2	111.4

All heat-treated samples retained their shape and size. The chemical composition of the raw and reduced brex is presented in Table 3.9. As can be seen from the test results (Table 3.10), after heating in a reducing atmosphere according to the specified mode, the strength of the samples of sludge brex decreased by 8.2%, while the strength of the ore and coke samples decreased by 14.5%.

The parameter characterizing the relationship of reducibility and strength during reduction is the so-called reduction disintegration index (RDI). This parameter describes the destruction during low temperature reduction. The mechanical stress resulting from the transformation of the crystal lattice of hematite leads to strong tensions in certain planes, resulting in the formation of cracks in the brittle matrix.

The results of tests for hot strength according to ISO 4696, carried out in [94], showed that RDI + 6.3 for ore and coke brex is 96.5%, which indicates high hot strength of brex. For sludge brex, the hot strength value is significantly lower (61.9%).

For comparison, the hot strength of sinter of a different basicity, obtained from iron ore concentrate (Table 3.11), was simultaneously evaluated according to the same standard.

The hot strength of sludge brex is comparable to the hot strength of sinter with a basicity of 1.2 and 1.4, but inferior to the hot strength of a sinter with a basicity of

Table 3.11 Indicators of hot strength of brex sinters of different compositions

Test material	RDI (+6.3), %
Brex No. 4 ^a (basicity 0, 75)	96.5
Brex No. 2 ^a (basicity 1, 93)	61.9
Sinter (basicity 1, 2)	64
Sinter (basicity 1, 4)	60
Sinter (basicity 1, 6)	77

^aBasicity = $(\text{CaO} + \text{MgO})/(\text{Al}_2\text{O}_3 + \text{SiO}_2)$

1.6. At the same time, the hot strength of the ore and coke brex significantly exceeds the corresponding indicators of all these sinters.

The study of the reduced samples allowed us to establish the mechanism for changing the structure of brex under conditions close to those of the upper horizons of the blast furnace and explain the reasons for the high RDI + 6.3 values. The mineralogical study of the structure of raw and reduced brex was carried out on polished thin sections in reflected light.

The structure of raw briquette No. 4 is represented by grains of magnetite, quartz, and coke breeze, packed in a binder of Portland cement and a small fraction of magnetite grains (Fig. 3.47). The main carrier of raw briquette strength is cement. The uniform distribution of the particles of materials in the entire volume of the cut slice from the periphery to the center was achieved by good mixing of the charge.

The microstructure of the reduced sample No. 4 (Fig. 3.48) is represented by a system of metallic iron grains and a partially crystallized iron–olivine phase sintered together, and inclusions of unreacted coke breeze. The strength carrier in the partially reduced brex No. 4 is not only the iron silicate phase, but also a framework of metallic iron formed from reduced grains of magnetite concentrate.

For comparison, in [94], the metallurgical properties of ore–coke brex based on hematite iron ore from the Belgorod iron ore district, obtained by the method of hydro-mining, were studied. The composition of ore and coke brex on the basis of hydro-ore is: hydro-ore—79%, coke breeze—15%, Portland cement—5.55%, bentonite—0.45%. The chemical composition of hydro-ore (%) is: Fe total—67.5; SiO₂—1.5; Al₂O₃—0.3; CaO—0.2; MgO—0.3; S—0.05; and P₂O₅—0.05. Basicity of brex is 0.56.

A mineralogical study has shown that the bulk of the ore minerals are represented by hematite (Fe₂O₃), less commonly by intergrowths of hematite with magnetite (Fe₃O₄). Iron ore concentrate silicates are most often observed in intergrowths with iron ore minerals. Figure 3.49 shows the microstructure of raw brex.

In order to assess the progress of the iron ore–coke brex reduction process, polished sections of brex samples were analyzed after being heated to temperatures of 900, 1100, and 1200 °C in a reducing atmosphere.

For brex heated to a temperature of 900 °C, the developed process of reducing iron oxides is typical (Fig. 3.50). There is a lot of wustite and magnetite in the central part of brex. Along the periphery, the recovery process is more developed (Fig. 3.51) and the formation of a skeleton is observed, by “merging” the metal grains (Fig. 3.52).

Fig. 3.47 Microstructure of the raw brex No. 4; reflective light; 100× magnification

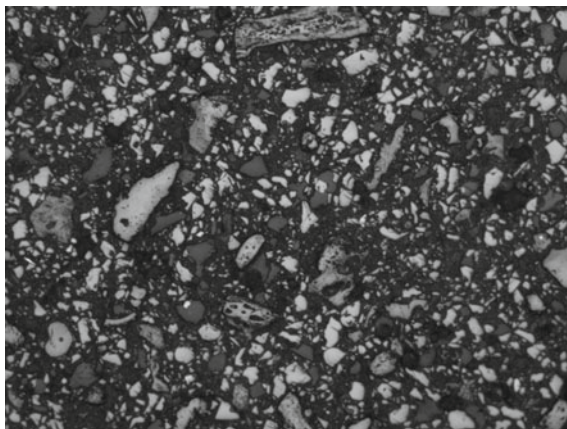


Fig. 3.48 Microstructure of the reduced brex No. 4; reflected light; 100× magnification

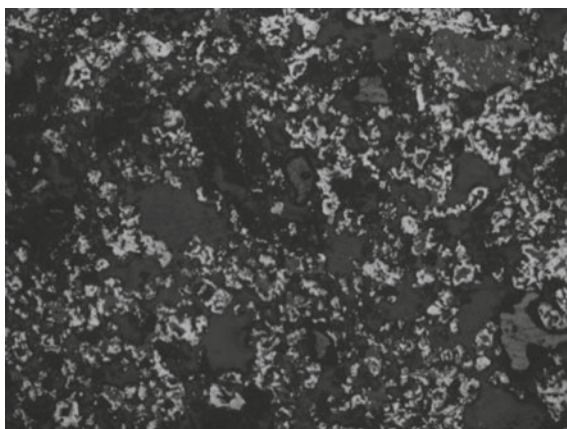


Fig. 3.49 Microstructure of the iron ore–coke brex; reflected light; 1—coke breeze; 2—grains of hematite iron ore (white) in cement bond (gray)

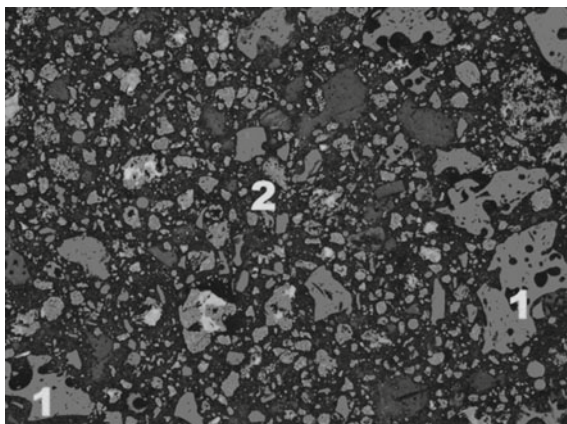


Fig. 3.50 Microstructure of the central part of the reduced brex heated to a temperature of 900 °C; reflected light; light gray areas—isolated areas of reduced wustite and magnetite; gray areas—silicate phases; 100× magnification

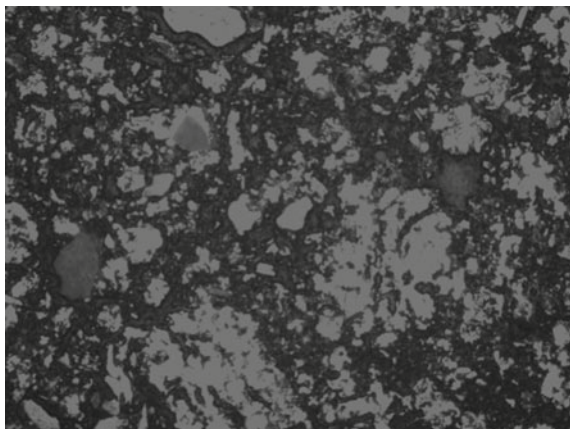


Fig. 3.51 Microstructure of the periphery of the reduced brex heated to a temperature of 900 °C; reflected light; white is a reduced metal; light gray is wustite; dark gray—silicate phases; 500× magnification

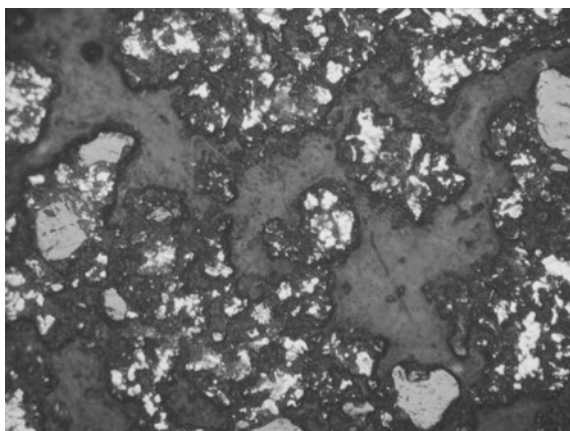
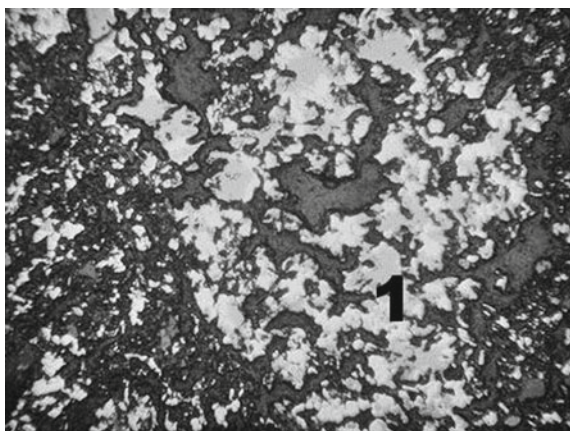


Fig. 3.52 Formation of a metal frame at the site of large hematite granules of hydro-ore (1) along the periphery of brex ($T = 900$ °C), reflected light, magnification $\times 200$



In the course of further heating, at temperatures close to 1000 °C, the reduction process is enhanced—the amount of the initial iron bound to hematite is minimized, and the iron-containing phases are represented by magnetite, wustite, and metallic iron.

Figure 3.53 shows the microstructure of the peripheral part of brex at a temperature of 1100 °C, where the formation of a metal frame is clearly visible.

A further increase in the reduction time of the brex and temperature up to 1200 °C leads to the intensive development of reduction processes. Most of the iron is in metallic form, and the rest is preferably wustite. The inclusions of unreacted coke breeze are less than at temperatures below 1200 °C, mainly in the center of brex. Also, unreacted ore quartz grains are locally observed. Figure 3.54 shows the microstructure of the center of brex at a temperature of 1200 °C.

Fig. 3.53 Microstructure of the periphery of the reduced brex at 1100 °C; reflected light; white areas—metal; gray—transformed mineral phases of the cement; 200× magnification

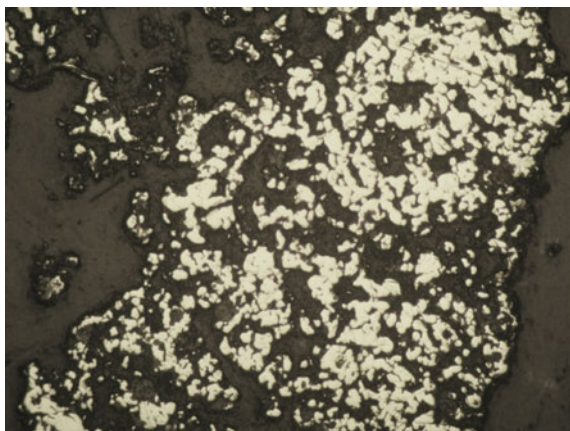
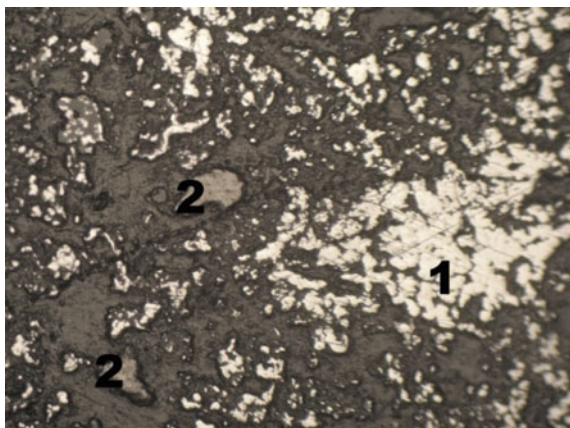


Fig. 3.54 Microstructure of the center of reduced brex (at 1200 °C); reflected light; 1—metal; 2—coke breeze; gray areas—transformed mineral phases of the cement; 200× magnification



Thus, with an increase in temperature and reduction time of brex, the main strength function is performed by a metal frame formed along the periphery and silicate phases. The strength carrier in brex No. 4 was a matrix of sintered metal grains and an iron silicate phase.

The raw briquette No. 2 consists of blast furnace and converter sludge, which are anthropogenic fine multi-component products (Fig. 3.55). Unlike briquette No. 4, in the cement bond of this briquette, the particles are more distant from each other.

The structure of reduced briquette No. 2 is represented by scattered fine grains of metallic iron (there is no metal frame made of sintered grains) and the silicate phase (Fig. 3.56).

Thus, the components of the mechanism of hot strength of brex can be: the formation of a skeleton of sintered metal grains (brex No. 4), the formation of a surface metal shell (brex from hydro-ores), and the formation of a liquid bond (silicate, iron silicate, brex No. 4 and No. 2).

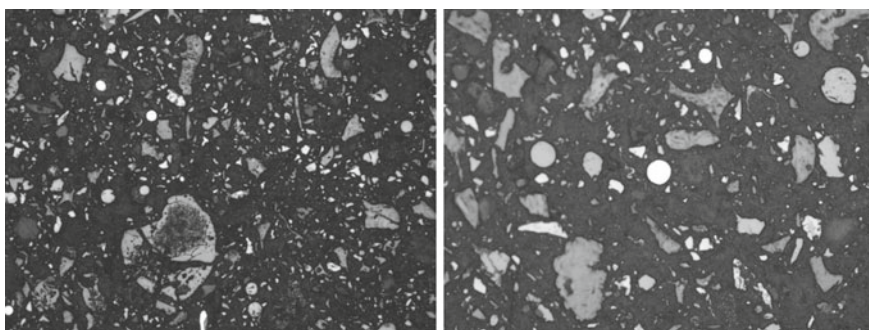
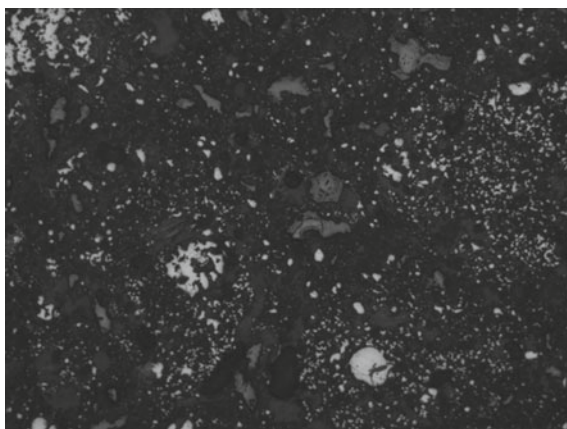


Fig. 3.55 Microstructure of raw sludge brex. Reflected light; 100× magnification (left); 200× magnification (right)

Fig. 3.56 Microstructure of the reduced sludge brex; 100× magnification



3.5.1.3 Metallurgical Properties of Industrial Brex Used as the Main Component of a Blast Furnace Charge

The metallurgical properties of brex produced on the above-mentioned industrial briquetting line, which was commissioned in April 2011 at a metallurgical plant owned by Suraj Products Ltd (Rourkela, India), were studied in [138]. The line produces brex for use in small-scale blast furnaces.

The layout of Suraj Products Ltd stiff extrusion line is shown in Fig. 3.57.

Due to the plasticity of brex, the transportation and storage operations are not accompanied by the formation of fine fractions. In two-shift operation, the briquetting department produces 200 tons of brex per day. In addition to conventional brex, as the main component of the blast furnace charge, washing brex from manganese ore fines are produced at the briquetting site. Brex are currently used as the main and only component of the charge on a small blast furnace with a volume of 50 m³. Prior to the construction of this line, the blast furnace operated with 100% rich hematite ore using limestone and dolomite as fluxes.

The main components of the brex are Linz-Donau (LD) process sludge, flue dust, iron ore fines, Portland cement, and bentonite (Table 3.12).

The main objective of the project was to increase the economic efficiency of blast furnace performance by replacing the purchase of iron ore with cheap brex made of a blast furnace dust and sludge from steelmaking.

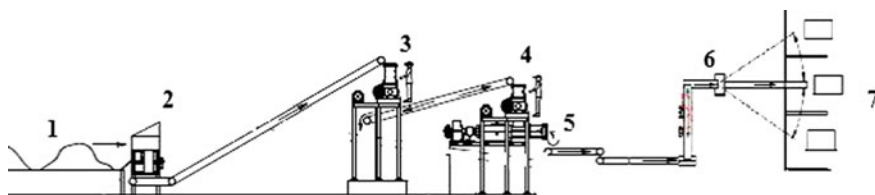


Fig. 3.57 Suraj Products Ltd. (India) stiff extrusion line layout: 1—raw material storage; 2—even feeder with a mixing area for the binder and plasticizer; 3—primary pug mill; 4—pug sealer; 5—extruder; 6—piler; 7—strengthening unit

Table 3.12 Chemical composition of the brex and their constituent components

Brex components shares, %	Fe ₂ O ₃	FeO	Fe _{tot}	LOI	SiO ₂	CaO	MgO	Al ₂ O ₃	TiO ₂	K ₂ O + Na ₂ O	C
Iron ore fines 18.9	88.53	—	62.0	4.37	2.71	0.3	—	3.51	0.22	0.2	—
Flue dust 28.3	53.0	—	37.1	—	6.3	4.9	0.2	5.1	—	—	30.5
LD sludge 47.2	17.9	65.4	63.4.0	—	1.3	8.6	4.9	0.3	—	—	1.5
Portland cement, 4.7	4.2	—	—	1.5	20.5	63.2	2.1	4.5	—	0.6	—
Bentonite 0.9	10.0	—	—	9.4	58.4	0.8	0.3	12.6	—	4.4	—
Brex 100	40.4	30.7	52.1	1.4	4.7	8.3	2.5	2.6	0.1	0.13	9.2

The reducibility and metallization of industrially manufactured brex when heated in a reducing atmosphere were investigated in comparison with the recoverability and metallization of iron ore fines.

For this, the following testing methodology was used [59]. The test chamber was a hollow corundum tube with an outer diameter of 85 mm and an inner diameter of 75 mm. The brex samples were placed in a graphite crucible placed inside the chamber and covered with coke breeze particles with 1–5 mm in width. The thickness of the coke breeze layer covering the entire crucible was 25 mm. After that, perforated inserts were used to block the crucible from both ends, which provided heat insulation. Water-cooled metal clips were installed on both sides of the corundum tube. The vacuum pump was connected to one of the clips together with an air supply system and a flow meter. Before heating, the internal volume of the corundum tube was evacuated to 0.5 mbar. Then, the heating process started ($10\text{ }^{\circ}\text{C}/\text{min}$) and after the temperature reached $800\text{ }^{\circ}\text{C}$, the air supply was switched on at a flow rate of $10\text{ L}/\text{min}$ until the end of the test. The brex samples were subjected to reducing roasting (in the CO atmosphere) in the $1000\text{--}1500\text{ }^{\circ}\text{C}$ temperature range at intervals of $100\text{ }^{\circ}\text{C}$. The test was performed at a fixed temperature for the duration of 2 h. The installation diagram and the sample positioning method are shown in Figs. 3.58 and 3.59.

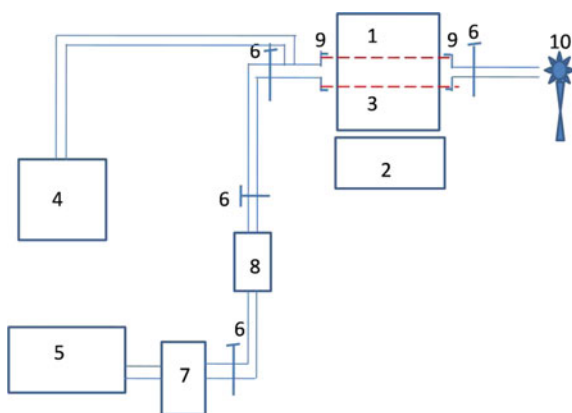
The chemical composition of the samples of ore and brex is given in Table 3.13.

The phase composition of the components of the iron is: iron ore—hematite, goethite, gibbsite, pyroxene, kaolin; top dust (Fig. 3.60)—magnetite, hematite, wustite, graphite, quartz, dicalcium ferrite; and converter sludge—magnetite, wustite, wollastonite, calcite.

The results of measuring the degree of reduction and metallization of ore samples and brex are given in Table 3.14.

Figures 3.61 and 3.62 show comparative curves of the degree of reducibility and metallization for samples of iron ore and brex depending on the heating temperature in a reducing atmosphere.

Fig. 3.58 Installation diagram to study brex behavior when heated in reducing atmosphere. 1—Oven, 2—controller, 3—hollow corundum tube with samples, 4—vacuum pump, 5—compressor, 6—isolation valve, 7—drying device, 8—flow meter, 9—gate valve, 10—burner



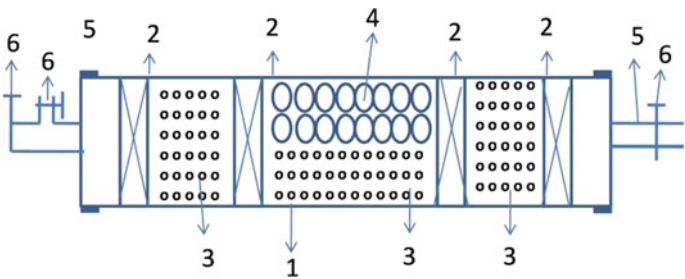


Fig. 3.59 Method of sample positioning in an experimental unit for studying bres behavior when heated in a reducing atmosphere. 1—Hollow corundum tube, 2—perforated unit, 3—coke breeze, 4—samples (ore or bres), 5—gate valve, 6—isolation valve

Table 3.13 Chemical composition of iron ore and bres, %

Element	Iron ore	Bres
CaO	0.2	12.28
SiO ₂	2.21	6.84
Al ₂ O ₃	3.11	2.65
Fe ₂ O ₃	88.53	66.09
MgO	—	1.34
TiO ₂	0.22	1.05

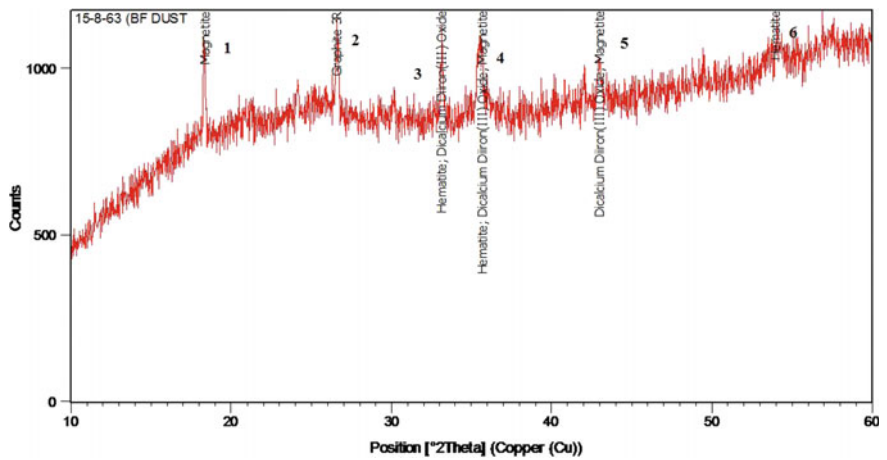


Fig. 3.60 Phase composition of flue dust (hematite, magnetite, dicalcium ferrite 2CaO–Fe₂O₃, graphite)

Table 3.14 Metallization and reducibility of iron ore and brex

T, °C	Fe _{мет} (ore/brex), %	Fe _{общее} (ore/brex), %	Metallization (ore/brex), %	Reducibility (ore/brex), %
1000	2.16/14.20	67.48/60.5	3.20/23.5	35/48
1100	12.69/20.96	69.52/61.7	18.25/33.97	52/62
1200	17.65/30.36	70.25/63.7	25.10/47.6	61/72
1300	30.33/44.74	73.3/65.6	41.30/68.2	65/80
1400	53.75/47.04	80.79/67.46	66.53/69.7	82/88
1500	84.25/79.22	90.4/80.87	93.20/97.95	93/99

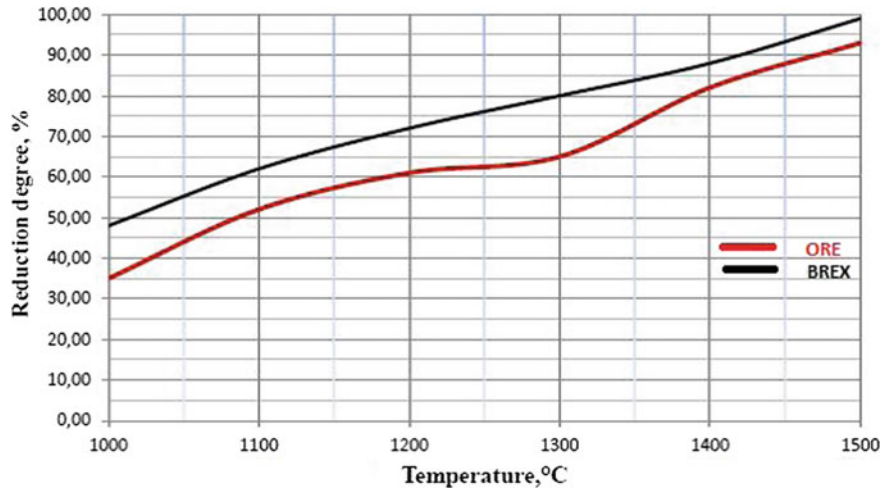


Fig. 3.61 Change in the degree of reduction of iron ore and brex when heated

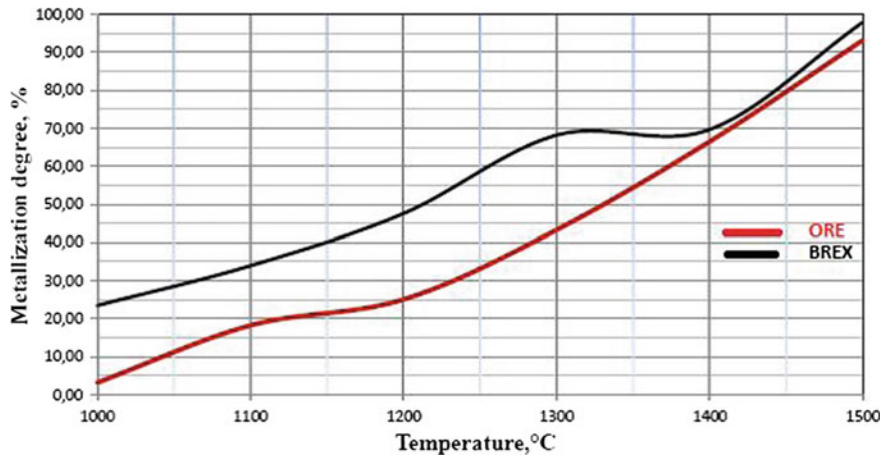


Fig. 3.62 Changes in the degree of metallization of iron ore and brex when heated

It can be seen that brex are reduced and metallized better than iron ore. Obviously, in the first place, this is due to the presence of carbon in the brex, introduced by blast furnace dust. Closer contact of iron oxide particles with carbon accelerates the reduction of brex compared to iron ore [139].

The dynamics of changes in the porosity of brex at different temperatures, which was established in [59], also contributes to improving the recoverability of brex. Values of porosity and density of brex and iron ore at different temperatures are given in Table 3.15 and in Fig. 3.63.

At 1000 °C, the density value of the brex has a local maximum (2.81 g/cm³). By 1200 °C, the transformation of hematite into magnetite is completed. The increase in porosity values in the temperature range of 1100–1200 °C is explained by the mechanical stresses in the body of brex, associated with the transition from the hexagonal lattice of hematite to the cubic lattice of magnetite. From 1200 °C, there is an increase in the density of brex (from 2.56 to 3 g/cm³ or more) and a decrease in the porosity of brex, which is associated with the formation of an iron silicate melt that fills the pore space and further with the development of the metal structure of brex.

Table 3.15 Porosity and density of brex and iron ore at different heating temperatures

Brex/iron ore	Porosity (%)	Density (g/cm ³)
Raw	25.8/18.4	2.60/4.11
500 °C	33.66/19.4	2.67/4.04
1000 °C	37.36/29.15	2.81/3.63
1100 °C	37.28/27.6	2.61/3.84
1200 °C	46.87/24.5	2.56/3.92
1300 °C	29.71	3.08
1400 °C	22.6	3.19

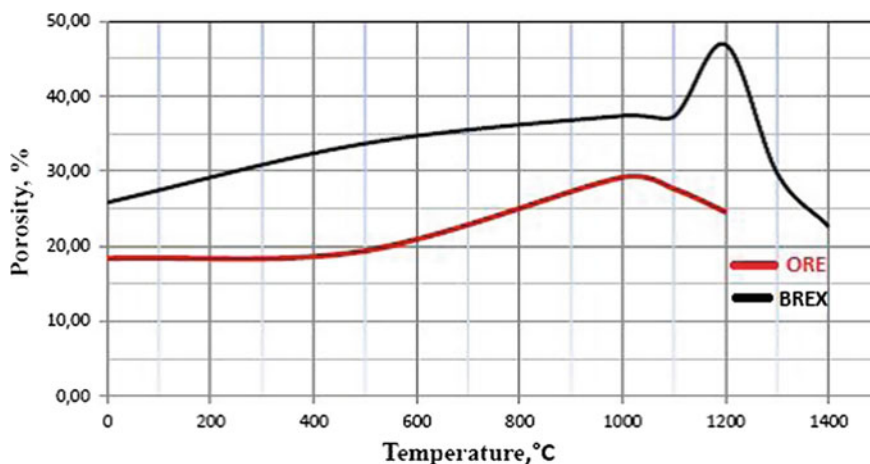


Fig. 3.63 Changes in porosity of brex and iron ore when heated to different temperatures

Figure 3.64 shows the microstructure of the sample after heating at 1000 °C.

The structure of brex contains hematite, magnetite, and wustite, and fragments of silicate phases and ore.

Monocalcium ferrite (CaFe_2O_4), melting incongruently at 1216 °C, and dicalcium ferrite are also observed in the structure of brex.

At a temperature of 1100 °C (Fig. 3.65), iron oxides are detected that interact with silicates.

At 1100 °C, when reduced to wustite, the ferrous iron becomes the melting component and the formation of the iron silicate melt is determined by the area of joint crystallization of olivine and dicalcium silicate (Fig. 3.46; Sect. 3.5.1.1).

The structure of the brex at 1200 °C is shown in Fig. 3.66.

At a temperature of 1300 °C (Fig. 3.67), the formation of dicalcium silicate, okermanite, and gehlenite is observed. The ore binding consists of metal and wustite grains.

Figure 3.68 shows images of the brex structure at 1400 °C. Metal mesh structure. Sintering of metal grains occurs.

Thus, the integrity of industrial brex heated in a reducing atmosphere after the loss of cement stone strength is achieved by the successive action of a number of mechanisms: the formation of the surface metal shell, the formation of the ore bond as a phase with the structure of ferrites and silicates, sintering the grains of the reduced metal.

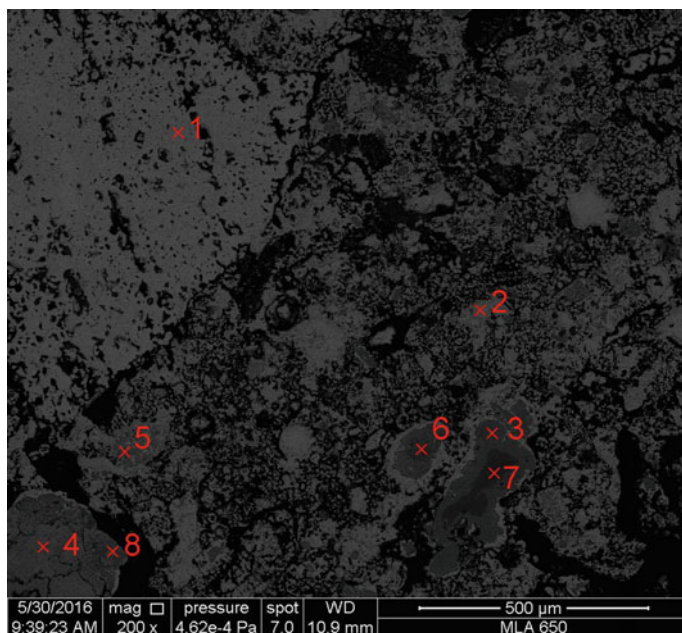


Fig. 3.64 Brex structure when heated to 1000 °C. 1—Hematite, 2—magnetite, 3—gehlenite, 4, 7, 8—solid solution $\text{CaOAl}_2\text{O}_3\text{--CaOFe}_2\text{O}_3$, 5—okermanit–helenite, 6—gehlenite

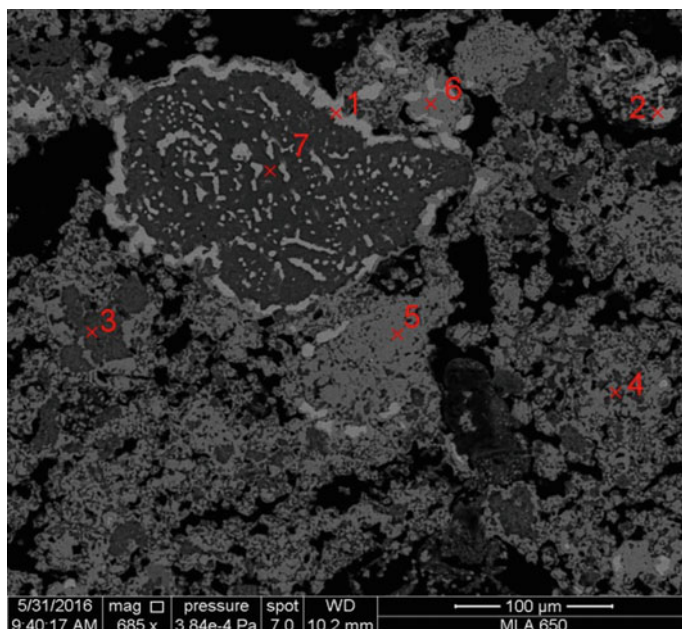


Fig. 3.65 Brex after heating at 1100 °C. 1, 2— α -iron, 3—olivine–dicalcium silicate, 4—wustite–melilite, 5, 6—wustite, 7—wustite–gehlenite

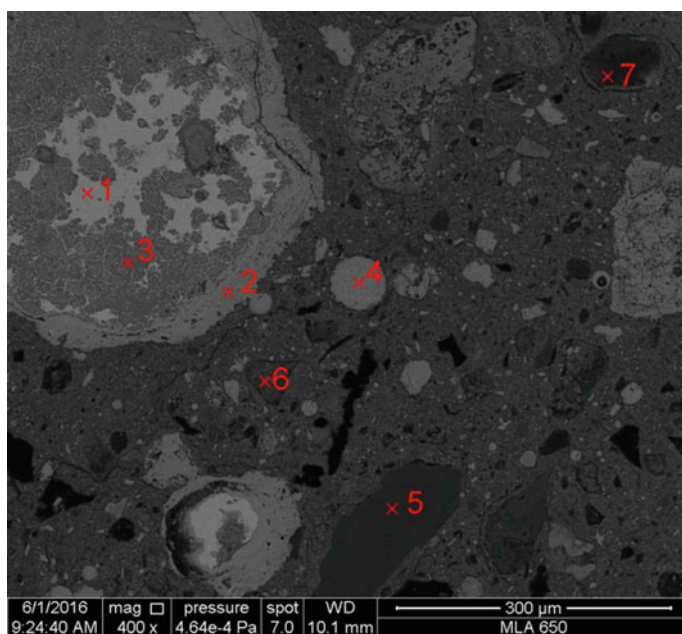


Fig. 3.66 Brex after heating at 1200 °C. 1— α -iron, 2—wustite and melilite, 3—dicalcium silicate, 4—magnetite, 5,6—spinel and dicalcium silicate

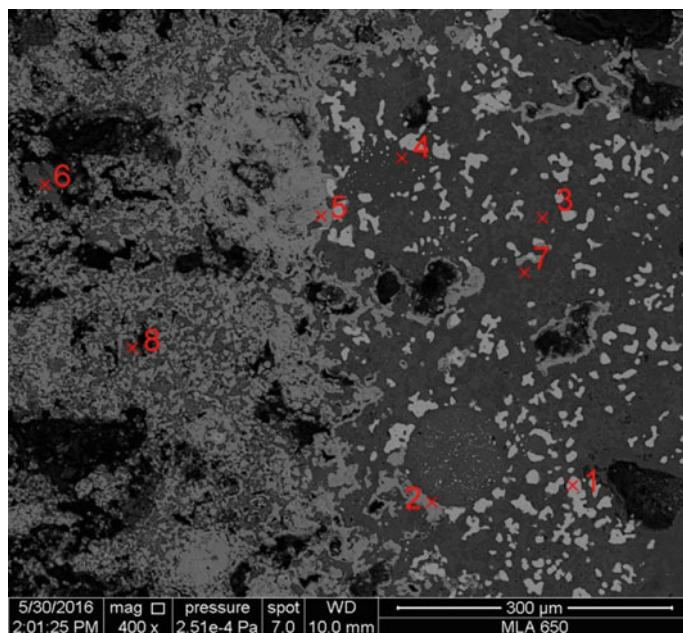


Fig. 3.67 Brex after heating at 1300 °C. 1— α -iron, 2—wustite, 3—dicalcium silicate, 4, 7—okermanite, 6, 8—gehlenite

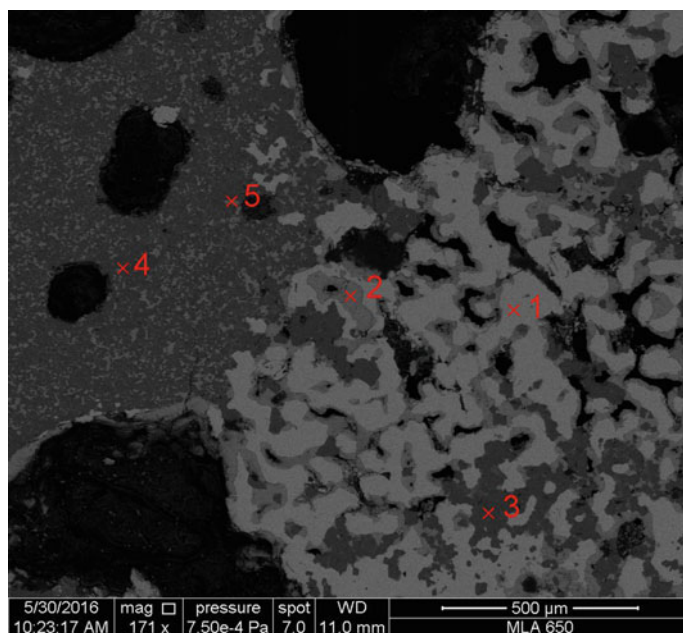


Fig. 3.68 Brex after heating at 1400 °C. 1— α -iron, 2, 5—wustite, 3, 4—silicates

3.5.1.4 Blast Furnace Operation with 100% Brex in Charge

The small-scale blast furnace (volume 45 m³) at Suraj Products Ltd is equipped with a skip hoist with a volume of 0.5 m³, a double-cone charging device, and hydraulic equipment for notch servicing, recuperative stoves and a two-stage dry gas cleaning system (dust collector + the 7 modules of the bag house filters) and sludge granulation equipment. The furnace has external watering and eight air tuyeres. The hot metal (foundry and pig iron) is immediately casted by the casting machine. The daily production of the blast furnace is 100–130 tons of pig iron.

The extrusion line of the blast furnace unit began operating in May 2011, using 10% of brex in the blast furnace charge. Gradually, the brex content of the charge increased to 80%. From the end of 2013, the blast furnace has been operating using 100% brex charge. Table 3.16 presents the main furnace operating parameters with brex in the charge at Suraj Products Ltd.

Table 3.16 Furnace operating parameters at Suraj Products Ltd.

Furnace operating parameters	100% ore	80% brex	100% brex
<i>Consumption, kg/t</i>			
Iron ore	1500	372	–
Brex	–	1425	1960
Limestone	150	–	–
Dolomite	144	–	29
Scrap	132	–	–
Quartzite	–	–	13
Mn ore brex	–	19	75
Coke ^a	680	530	490
Fe _{tot} in charge, %	57.6	50.4	45.5
Productivity, t/m ³ per day	1.9	1.62	2.0
Blast temperature, °C	925	900	1000
Blast pressure, kg/cm ²	0.5	0.34–0.38	0.38–0.42
[Si], %	1.0–1.8	1.0–1.5	0.8–1.1
[Mn], %	0.2	0.4–0.5	0.7–0.8
[C], %	3.8–4.0	3.75–3.90	3.80–3.95
[S], %	0.050–0.060	0.038–0.050	0.038–0.042
Cast-iron temperature, °C	1380–1440	1400–1450	1410–1450
(CaO), %	34.86	33.12	38.0–39.0
(SiO ₂), %	31.98	30.23	30.0–32.0
(Al ₂ O ₃), %	23.87	17.98	16.0–18.8
(MgO), %	9.46	9.48	8.0–9.5
(FeO), %	1.01	1.26	0.6–1.15
(MnO), %	0.35	0.75	1.3–1.0

^aThe size is 15–25 mm

When working on the charge with 80% brex and 20% iron ore coke consumption decreased by 150 kg/t of hot metal (22%) compared with operation on 100% iron ore. The reduction in coke consumption occurred both due to the carbon contained in the brex and due to the removal of limestone and dolomite from the charge. The productivity of the blast furnace that used 80% of brex in the charge decreased mainly due to a 7.2% decrease in iron content in this charge compared with the charge based on iron ore and raw fluxes. The transition to a mono-charge blast furnace operation resulted in a further decrease in coke consumption due to the additional carbon input. The increase in the blast temperature by 100 °C also contributed to the decrease in coke consumption. In addition, the use of manganese ore washing brex reduced the viscosity of slags and improved the processing of smelting products. As a result, the furnace productivity has increased due to the improvement of the structure of the charge column, the decrease in the viscosity of the primary slags, and the increase in the overall pressure drop. The reduction in specific heat loss also contributed to a reduction in coke consumption.

The development of new blast furnace smelting technology with the use of brex meant switching to a decreased burden level of blast furnace charge due to the difficulties in the operation of dry gas cleaning system. The gradual increase in the share of brex in the charge led to a significant increase in the humidity of the furnace top gas and a decrease in its temperature. As a result, bag filters began to become clogged with wet dust, and regeneration by their back pressure pulses did not achieve the effect. The reduction in the level of the burden practically did not affect the performance of the blast furnace due to the fact that the reduction of lower iron oxide (FeO) in the brex occurs predominantly in a direct way due to the carbon of coke contained in the brex, and the high reducing potential of the hearth gas and its temperature ensured the reduction of higher iron oxides to wustite.

Despite high specific heat losses due to the small volume of the blast furnace and low blast temperatures, the coke consumption during the operation of the blast furnace in the mono-charge of brex does not exceed 500 kg/t of pig iron. This is achieved due to the fact that the brex used in the above-mentioned blast furnace are self-reducing due to the presence of fine coke particles of flue dust in close contact with the dispersed particles of ore and steel-smelting sludge containing iron oxides, as well as due to the high basicity of the brex providing obtaining the necessary basicity of blast furnace slag without the use of limestone. To adjust the slag basicity and the content of magnesia in it, additives of quartzite and dolomite are used. As a result, coke consumption for pig iron smelting when operating at 100% brex was reduced by almost 200 kg/t of pig iron as compared with the operation at 100% rich iron ore using limestone and dolomite.

The results of more than 7 years of industrial operation of the stiff vacuum extrusion process line as part of the blast furnace shop showed that brex obtained from natural and anthropogenic dispersed raw materials have optimal and adjustable sizes, controlled chemical composition, and high metallurgical properties, and are a new type of agglomerated and fluxed component of the blast furnace charge. The work of a small blast furnace on a mono-charge from 100% of brex produced from a mixture of metallurgical wastes and iron ore fines demonstrates low coke

consumption (490–500 kg/t of pig iron) at a blast temperature of 1000 °C and an iron content in the flux mixture of 45.5%.

3.5.1.5 Assessment of Prospects for the Use of Carbon-Containing Briquettes from Iron Ore Concentrate

The effectiveness of brex in the charge of large blast furnaces was estimated by the method of mathematical modeling of blast furnace smelting using the DOMNA program developed in [140]. The blast furnace smelting in a furnace with a volume of 4297 m³, operating under the conditions of PJSC NLMK [141], is modeled. Taking into account the basicity of brex, the level of which is influenced by quantities of cement binder and bentonite (plasticizer), simulation of blast furnace smelting was carried out for a mixture consisting of three components—sinter, pellets, and brex. The share of pellets is determined by the capacity of the pelletizing plant (Stoilensky GOK, 6 million tons of pellets per year). The basicity of a brex made from iron ore concentrate and low caking coal is determined on the basis of the content of cement (6%) and bentonite (1%) in the composition of the brex, taken on the basis of the results of preliminary tests, and also taking into account the content of coal in the mixture. At the indicated contents of cement and bentonite, the basicity of brex (B2) is 0.50–0.55. The basicity of the sinter is determined on the basis of the accepted concept of replacing the agglomerate with brex and their basicity. When replacing 50% of the sinter in the blast furnace charge with brex, the basicity of the sinter should be between 2.8 and 3.2. It should be noted that with such basicity in the structure of the sinter the phases predominate, providing an increase in its strength compared to the sinter with basicity in the range of 1.5–1.7 characteristic of the sinter, produced in NLMK. The coal content in brex was determined by the method developed based on the results of studying the structural composition of brex after heating in a reducing atmosphere to 1400 °C, when, after reaching almost complete metallization, unreacted coke breeze particles remained in the brex structure due to its excessive content in the mixture for briquetting.

The consumption of carbon-containing material in the charge for briquetting is calculated based on the stoichiometric ratio of oxygen and iron in brex (O/Fe) by the time they arrive in the cohesion zone, where the temperature exceeds 1100 °C and reduction takes place only with the participation of solid carbon. It also takes into account the carbon content in coal or other carbon-containing material in fractions of a unit, the total iron content in the iron ore material, the accepted degree of iron oxidation in this material when the brex enter the cohesion zone, and the proportion of the cement and bentonite mixture in the briquetting charge [141].

To simulate the blast smelting, the calculated compositions of sinters with a basicity of 1.70 and 3.02 and the composition of brex from Stoilensky GOK concentrate were used, the proportion of carbon which was calculated by the method described in [141] (Table 3.17).

The simulation was carried out for the same composition of hot metal and its temperature ([Si] = 0.4%; [C] = 4.8%; and $T_{\text{pig iron}} = 1500$ °C) and for the same

Table 3.17 Chemical composition of raw materials, sinters, and brex, %

Materials	FeO	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	MgO	C	SO ₃
Portland cement	–	4.71	20.64	4.98	63.58	1.15	–	2.55
Bentonite	0.5	4.37	59.25	14.27	2.07	3.62	–	0.14
Caking coal	–	1.2	2.7	1.5	0.4	0.1	68.9	0.36
SGOK pellets	1.51	90.31	7.04	0.32	0.22	0.45	–	0.12
SGOK iron ore concentrate	29.2	62.3	6.62	0.18	0.26	0.1	–	0.05
Sinter (170)	11.81	66.0	6.70	0.72	11.37	2.51	–	0.05
Sinter (3.02)	10.0	60.8	6.30	0.7	19.0	3.0	–	0.06
Brex	24.83	53.28	7.67	0.71	4.09	0.19	5.5	0.22

reduction efficiency (the degree of approximation to the equilibrium composition of the gas in the wustite reduction zone). The results showed that due to the carbon contained in the brex, the coke consumption for hot metal production is reduced compared to the base case by 10%. When pulverized coal is injected with a flow rate of 160 kg/t of hot metal, coke consumption of 284 kg/t of hot metal is achieved, and when blowing natural gas with a consumption of 125 m³/t of hot metal, coke consumption of 354 kg/t of hot metal is achieved (Table 3.18).

Table 3.18 Results of the blast furnace smelting simulation when using a traditional charge and a new charge with one-third iron-carbon-containing brex

BF operation parameters	Basic variant	Variant 1	Variant 2
Sinter consumption B2 = 1.7, kg/t	1109	–	–
Sinter consumption B2 = 3.0, kg/t	–	557	575
SGOK pellet consumption, kg/t	546	557	541
Brex consumption, kg/t	–	557	575
SGOK iron ore consumption, kg/t	–	17	–
Fe content in charge, %	58.2	57.45	57.15
Coke rate, kg/t	391	354	284
Natural gas consumption, nm ³ /t	125	125	35
Pulverized coal consumption, kg/t	–	–	160
Blast rate, m ³ /min	7483	7568	7340
Blast temperature, °C	1240	1240	1240
O ₂ content in blast, %	30.5	30.5	30.5
Blast humidity, g/m ³	10	10	20
Top gas yield, m ³ /t	1545	1540	1470
Top gas pressure, kPa	240	240	240
CO, %	24.4	24.9	26.2
CO ₂ , %	23.2	22.6	23.9
H ₂ , %	9.7	9.9	8.2
Slag ratio, kg/t	318	314	323
Slag basicity, B2	1.01	1.01	1.02
Capacity, t/day	12.465	12.624	12.708
Capacity, t/m ² day	92.48	93.66	94.3
Reduction efficiency, %	94.2	94.2	94.2

3.5.2 Briquetting of Natural and Anthropogenic Raw Materials for Ferroalloy Production

Significant volumes of finely dispersed, effectively recyclable materials are created in the process of extraction and beneficiation of raw materials for ferroalloy production during their transportation to ferroalloy plants and ferroalloy smelting.

In particular, the mining and processing plants have accumulated large reserves of manganese ore fines with manganese content below the marketable value.

One of the most common anthropogenic raw materials is dust and sludge from gas cleaning of ferroalloy furnaces. The specific dust emissions of ferroalloy furnaces are 8–30 kg/t of ferroalloys. The content of manganese oxides in dust in the production of silicomanganese is 21–34.3%; in the production of ferromanganese—30–35%; and chromium oxides in dust in the production of ferrochrome—22–30% [96]. The use of finely dispersed raw materials without their agglomeration in submerged electric arc furnaces (SEAFs) disrupts the normal course of the process, leading to an increase in dust generation, a decrease in productivity and metal extraction rate, increased risks of accidents and number of hot downtime, and as a result deteriorates technical and economic indicators of the furnace generally.

The traditional method of agglomeration of such fine materials is sintering. Until 1973, ferroalloy plants did not have sinter plants [142]. The first sinter plant was commissioned at the Nikopol Ferroalloy Plant in 1973, and in 1979, the sinter plant at the Zestafoni Ferroalloy Plant was commissioned. The average productivity of sintering machines is 100 t/h (specific—1.2 t/m² per hour).

Another industrial method of agglomeration is pellet calcination at a temperature of 1150–1220 °C. With this calcination, the hardening of the pellet is provided by the resulting liquid phase. At the “Kashima” plant (Japan), for high-carbon ferromanganese smelting in SEAF with a capacity of 40 MVA, manganese concentrates are agglomerated in a 110 t/h capacity pelletizer and then calcined in a 75-m-long rotary kiln with a diameter of 3.5 m [143].

The experience of using briquettes in the charge of ferroalloy furnaces has confirmed the effectiveness of this kind of agglomeration technology. The first industrial experience of using briquettes based on manganese ore concentrates in the charge of the ore-smelting furnace was obtained in 1961, when 160 t of roll briquettes made of manganese ore concentrate (30.9% Mn; 4% Fe; 0.0577% P; 26.95% SiO₂; P/Mn = 0.0018; 0.33% S; 1.9% CaO; and 4.05% BaO) were used in a 2500 KVA furnace of the Zestafoni Ferroalloy Plant (Georgia) [144]. The results of the heats showed that this type of charge component is quite effective.

In 1966, full-scale industrial testing was carried out at the same plant for the smelting of ferrosilicon manganese in industrial ore-smelting furnaces using ore briquettes of manganese concentrate from the Chiatura deposit in the charge [145]. For industrial experiments, briquettes were made on a roller press with a capacity of 5 tons/h from ore with a particle size of 5–0 mm on a binder of sulfite-alcohol bard (SAB) with a density of 1.2 g/cm³. With an ore moisture content of 4% and an addition of 8% binder, the mixture was stirred for 15 min. Next, the mixture was

subjected to heat treatment. The fact is that the binding properties of the SAB are due to the occurrence of polymerization processes in it, leading to the formation of long chains of molecules in the body of the briquette. The polymerization reaction in the presence of manganese is most fully realized at temperatures of 160–180 °C. For iron ore briquettes, the polymerization temperature reaches 200 °C. Thus, the achievement of the required values of the strength of the briquettes required their drying at temperatures of 50–300 °C. Silicomanganese was smelted on a charge with ore briquettes in a three-phase open ferroalloy furnace with a capacity of 16.5 MVA. The furnace worked normally and stably, the gas permeability of the charge was good, and the flame was distributed evenly throughout the furnace. After 112 h of experimental melting, it was concluded that sufficiently strong briquettes can be obtained from manganese ore of this size suitable for use in the charge of ferroalloy furnaces. When working on ore briquettes, the furnace productivity increases, and the power consumption and the consumption of reducing agent are reduced.

In 1970, in the Dnepropetrovsk Metallurgical Institute, indicators of the smelting of marketable silicomanganese on a briquetted mixture of manganese oxide concentrates of grade I and II of the Nikopol deposit in the 1: 1 ratio and on sinter made from the same mixture were studied [146]. Before briquetting, the mixture of concentrates of a fraction of 10–0 mm was ground to a size of 3–0 mm. Briquettes were made on a semi-industrial roller press at a pressure of 500 kg/cm², and the binder was a mixture of bitumen, fuel oil, and SAB in an amount of 10% by weight of the charge. The charge was mixed in tanks with steam heated (to activate the polymerization of the SAB). Briquettes of two compositions were prepared and melted: with an excess of reducing agent (coal) in the amount of 50%, introduced to create a skeleton in the briquette and to increase its strength (mixture of concentrates—54.5%, river sand—9.1%, coal—27.3%, a mixture of bitumen and fuel oil—3.6%, SAB—5.5%), with a stoichiometric amount of reducing agent required for the reduction of silicon and manganese (a mixture of concentrates—60.6%, river sand—10.1%, coal—20.2%, a mixture of bitumen and fuel oil—3.6%, SAB—5.5%). Laboratory tests showed that the physical properties of raw briquettes were superior to those for roasted briquettes, so they refused to roast the briquettes. The values of mechanical strength and heat resistance were higher for raw briquettes. Commodity silicomanganese was decided to be smelted on raw briquettes. Semi-industrial smelting on briquettes of the above composition and on sinter was carried out in a three-phase open ore-smelting furnace with a capacity of 1.2 MVA at a voltage of 81.60–85.89 V and a current of 6000–6500 A with a continuous process with a closed top chamber.

Briquettes with an excess of reducing agent had a high electrical conductivity that, when melted, led to a significant increase in the load current and as a result to the rise of the electrodes and the opening of the top. To eliminate this phenomenon, 10% manganese concentrate was added to the briquette charge. Thus, 14 tons of briquettes with an excess of reducing agent, 1.2 tons of concentrate, and 200 kg of

dolomite were melted. Melting silicomanganese on briquettes containing a stoichiometric amount of reducing agent passed without any complications. The load was steady; except for briquettes, nothing was added to the furnace. Comparative data of heats at different loads (briquettes and sinter) showed that the melting of silicomanganese on briquettes should be more preferable than melting on the sinter.

The results of pilot heats formed the basis for the construction and commissioning in 1976 of a briquette factory at the site of the Zestafoni Ferroalloy Plant. Manganese ore briquettes (with the addition of gas cleaning dust and without it) were produced by roller presses of Sahut Conreur Company (France).

Briquetted charge was also used for smelting ferrosilicon. At the Zaporizhia plant of ferroalloys (Ukraine), briquettes were produced of sand, coking coal, and iron ore concentrate. The mixture was heated and stirred in a steam mixer and then pressed with a roller press. Raw briquettes were subjected to roasting at a temperature of 600–800 °C for 10–13 h to achieve a reduction degree of 70–80%. Smelting of ferrosilicon on the briquetted charge was carried out in a 3.5 MVA furnace. When working on briquettes, the furnace productivity increased, and the power consumption and reducing agent rates decreased [44]. The smelting of ferroalloys from briquetted charge became widespread in the USA, France, Japan, and Germany [45].

Melting technology of low-phosphorus carbon ferromanganese with 100% briquetted charge was described in [60]. In 1987, experimental tests of this technology were carried out under the conditions of the Nikopol Ferroalloy Plant in comparison with the traditional technology. A three-phase ore-smelting furnace with a capacity of 3600 KVA with coal lining was used as a melting unit. The essence of the technology was the smelting of carbon ferromanganese with the required low phosphorus content using the fluxless method on the charge, the ore part of which, in addition to graphite concentrate, contains a concentrate obtained by chemical enrichment of sludge. Low-phosphorus manganese slag obtained in the smelting of carbon ferromanganese by the fluxless method is used as a raw material in the smelting of low-phosphorus silicomanganese, refined ferromanganese, and metallic manganese. The results of the experimental heats with 100% briquettes showed that the briquetted charge provided an economically acceptable solution to the problem of smelting high-quality ferromanganese from highly phosphorus manganese ores.

In 1988, the first vibropress briquetting factory with a capacity of 110 thousand tons of briquettes for ferrochrome smelting was built at Vargön Alloys in Sweden [49]. Since 1991, this method of briquetting has been used in France by Eurometa SA for the agglomeration of the fines of the crushing of ferroalloys [50]. Ferroalloy fine briquettes were used in the foundry business.

The technology of smelting manganese ferroalloys using ore dust briquettes was developed at the Zestafoni Ferroalloy Plant [61]. The need for disposal of dust and sludge from furnace gas cleaning was due to the large volume of its formation

(50 thousand tons annually). Taking into account the metallurgical evaluation of waste, their dispersed state, and physicochemical properties, it was proposed to mix dry dust with previously dehydrated sludge and make briquettes from such a mixture with the addition of manganese ore concentrate. It has been established that to obtain mechanically strong briquettes (specific crushing force of 8–12 MPa), the optimum parameters of briquetting are: moisture content of the charge 4–6%, binder content (SAB) 6–8%, amount of fine component (dust and sludge) 30%, and minimum pressure of roller press 19.6 MPa. The comparative kinetics of the reduction of dust–sludge and ore briquettes and of manganese sinter was investigated. It was found that briquettes gave the greatest degrees of reduction at different temperatures. The utilization of manganese and silicon from wastes increased due to the presence of closely bound carbon and the inhibition of the formation of silicates, in contrast to the sinter. The results of high-carbon ferromanganese heats showed that the furnace productivity in the case of using briquettes increased from 73.33 to 75.67 tons/day, and the specific power consumption decreased by 90 kWh/ton. Coke consumption decreased by 34 kg/t.

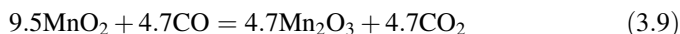
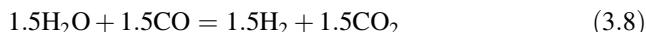
The first successfully implemented project with the use of SVE technology in the ferroalloy industry was the production of brex and their use in the charge for ferronickel smelting at BHP Billiton in Cerro Matoso (Montelibano, Colombia [147] in the framework of the RKEF (*rotary kiln—electric furnace*) process. The nickel content in this ore is usually small and ranges from 0.8 to 3.0%. During the RKEF process, laterite ores are sieved, ground, and added into a charge with a certain iron, nickel, SiO_2 , and MgO content. After that, the charge material is roasted and partially metallized with coal or coke fines. This semi-product and residual coke are then delivered to the electric furnace where ferronickel is smelted. In Cerro Matoso, the RKEF process entails the use of briquetted fines of nickel laterite ore.

SVE technology has not previously been used for the agglomeration of manganese and chromium ores. The first attempt to use it for such purposes took place in 2010. A full-scale pilot testing of this technology was conducted using brex as a charge component of industrial submerged EAF. The possibility of obtaining metallurgically valuable brex based on various combinations of manganese ore fines and dry gas cleaning dust formed during the production of silicomanganese was studied in [148].

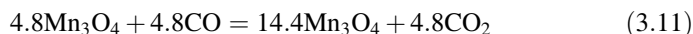
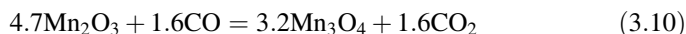
As in the case of blast furnace briquettes, the metallurgical properties of ferroalloy briquettes must ensure their integrity before entering the workspace of the reduction unit (cold strength) and in complex physical and chemical processes that occur at high temperatures under the reducing conditions of ore-smelting furnaces (hot strength).

Analysis of the combination of such processes allows us to distinguish four zones in the vertical section of the furnace, differing in the nature of the processes [149] occurring in them.

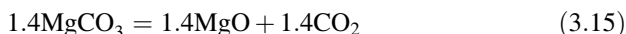
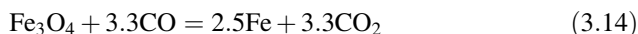
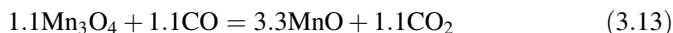
In the first zone (in the upper horizons of the top of the furnace), drying and calcination occur (25–438 °C):



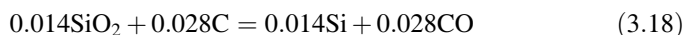
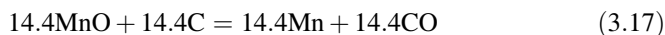
In the second zone, Mn_2O_3 is reduced by gas to Mn_3O_4 (438–773 °C).



In the third zone (773–1250 °C), direct reduction of Mn_3O_4 and carbon gasification reactions (Boudoir reaction) occur simultaneously:

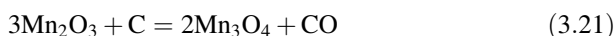


In the fourth zone (1250–1500 °C), MnO is melted in the slag and partially reduced to a liquid metal. In the same zone, SiO_2 is reduced and carbon is dissolved in the metal.



The metallurgical properties of ferroalloy briquette must ensure that the “melting rate” and “reduction rate” are equal. If the melting rate of ore materials is greater than the rate of formation of the metal and the final slag, then partially reduced slags are formed. Such slags penetrate into the lower horizons of the furnace, the reduction process turns into an unfavorable slag regime, the slag boils, and in general, the normal operation of the furnace is disturbed. Otherwise, there is a need to intensify melting by increasing the input of electric power into the unit. The equality of the rates of melting and metallization ensures the entry of metal and non-aggressive slag from the layer of charge materials into the furnace hearth.

The peculiarity of the processes of reducing oxides of iron and manganese in the ore-reducing electric furnace is associated with the passage of a portion of the electric current through charge materials. When using briquettes with a substantial content of carbonaceous reducing agent in its composition, the current begins to flow through the body of the briquettes, heating them, which significantly speeds up the reduction processes inside the briquette, and the direct passage of current through the briquette can lead to its destruction. The choice of the optimal content of reducing agent in the briquette should also take into account the possibility of reducing the cold strength of the briquette by adding a carbonaceous reducing agent. At the same time, the presence of a carbonaceous reducing agent sharply raises the temperature at which softening of briquettes begins and leads to an increase in the permissible critical current density [142]. In case of close contact of particles of manganese ore with carbon in briquettes, the reduction of higher oxides can occur with the participation of carbon:



3.5.2.1 Metallurgical Properties of Brex on the Basis of Manganese Ore Concentrate

Brex from primary oxidized manganese ore concentrate were tested for the purpose of this study. They were manufactured on the industrial SVE line in India. Portland cement (5% mass) was used as a binder; bentonite (1% mass) was used as a plasticizer. Table 3.19 shows the chemical composition of the primary oxidized manganese concentrate.

The share of particles larger than 0.071 mm is 22%; the manganese content of these particles is 35.4%. The share of particles smaller than 0.071 mm is 78%; the manganese content of these particles is 38.77%. Iron particles distributed in the samples of the concentrate in both size ranges evenly are 3.81–3.86%. The surface area of cement particles exceeds 4000 cm²/g. The chemical composition of cement is (%): CaO—62–64; MgO—2.5 (max.); SiO₂ 22–24; Al₂O₃—4.5; Fe₂O₃—4.5; SO₃—1.8; and alkali—0.6. The chemical composition of bentonite (%) is: SiO₂—58.4; Al₂O₃—12.6; CaO = 0.8; Fe₂O₃—10.6; and alkali—4.4.

Table 3.19 Chemical composition of primary oxidized manganese concentrate

Elements	Mn	Fe	SiO ₂	Al ₂ O ₃	CaO	MgO	P	S	Zn
Concentrate, %	38	3.84	10	1.36	17	0.76	0.07	0.10	0.084

Table 3.20 Physical and mechanical properties of brex after heating at different temperatures

Properties/T, °C	1000	1100	1200	1300
Porosity, %	43.48	39.10	32.22	15.02
Density, (kg/cm ³)	2.31	2.49	2.82	3.28
Compressive strength (kgf/cm ²)	34	43	47	61

Table 3.21 Main phases of brex from primary oxidized concentrate

Temperature, °C	Phases
20	Hausmannite (Mn ₃ O ₄); bixbyite ((Mn,Fe) ₂ O ₃); rhodonite (MnSiO ₃); and bixbyite C (FeMnO ₃)
1000	Jacobsite (MnFe ₂ O ₄) and Fe _{0.798} Mn _{0.202} O
1100	Fe _{0.798} Mn _{0.202} O
1200	Fe _{0.798} Mn _{0.202} O and Fe _{0.664} Mn _{0.336} O
1300	Fe _{2.08} Mn _{0.92} O ₄ and Fe _{0.798} Mn _{0.202} O
1400	Manganese

Physical and mechanical properties of the brex were measured after three-day strengthening in an open warehouse. The compressive strength was equal to 30 kgf/cm² and was measured on the Tonipact 3000 equipment (Germany) in accordance with the DIN 51067 standard. The open porosity was determined in accordance with DIN 51056 and amounted to 14.39%. Brex density averaged 2.59 g/cm³.

A specially designed unit, described in Sect. 3.5.1.3 (Figs. 3.58 and 3.59), was used to study the behavior of industrial brex samples from primary oxidized manganese concentrate during heating in a reducing atmosphere.

The physical and mechanical properties of brex after heating at different temperatures are given in Table 3.20.

The results of the phase analysis of the samples of initial brex and brex after heating for 2 h in a reducing atmosphere are presented in Table 3.21.

It is seen that in the presence of iron oxides an iron–manganese melt was formed, from which manganese was subsequently recovered.

3.5.2.2 Metallurgical Properties of Brex on the Basis of Manganese Ore Concentrate and Baghouse Dusts of Silicomanganese Production

Chiatura manganese ore concentrate (Republic of Georgia) and baghouse dust from silicomanganese production were used as raw material for brex production. The chemical composition of the manganese ore concentrate and silicomanganese production baghouse dust is given in Table 3.22. The main minerals of the concentrate are pyrolusite, psilomelane, and manganite. Pyrolusite from Chiatura manganese ore has a finely spherulitic (oolitic) and clastic brecciate structure.

Table 3.22 Chemical composition of manganese ore concentrate and baghouse dust

Material	Mn	MnO	Fe ₂ O ₃	FeO	Al ₂ O ₃	SiO ₂	CaO	MgO	P
Concentrate	35.0–45.0	–	1.2–2.2	–	2.0–3.5	14.0–25.0	2.0–3.5	0.86	0.20
Baghouse dust	–	29.74–31.41	–	0.30	0.01	30.0–34.0	1.67–2.42	1.50	–

Spherulite fragments do not exceed 0.25 mm in size. Pyrolusite is partially recrystallized up to hundredths of a millimeter during grain coarsening. The Chiatura oxide concentrate softening point is 1049 °C according to the data in [150]. Eighty-five percent of baghouse dust particles are smaller than 10 μm. Primary particles have a spherical shape due to phase transitions.

Two types of mixtures from the above materials were prepared for brex making: (1) a mixture of an equal mass (50:50) of concentrate and dust, and (2) a mixture of 70% concentrate and 30% dust. The granulometric composition of the second mixture is shown in Fig. 3.69.

Coke breeze was used as a reducing agent; it was provided by the owner of ferroalloy smelter. The coke breeze has the following composition ratio (%): carbon—68.72; volatiles—7.53; and ash—23.75; 88.46% of coke breeze particles are smaller than 0.635 mm in size. Its moisture content is 9.86%. Three brex mixtures with low binder content were tested in the study (Table 3.23).

Test samples of brex were produced using a computerized laboratory extruder that simulates the processing of a briquetted mixture in commercial even feeders, pug mills, and the extruder itself. The brex had a circular cross section of 2.5 mm in diameter and 1.5–2.0 mm in length. The average moisture content of freshly formed brex was 11%. The vacuum level in the working chamber of the extruder was maintained at 38–48 mm Hg.

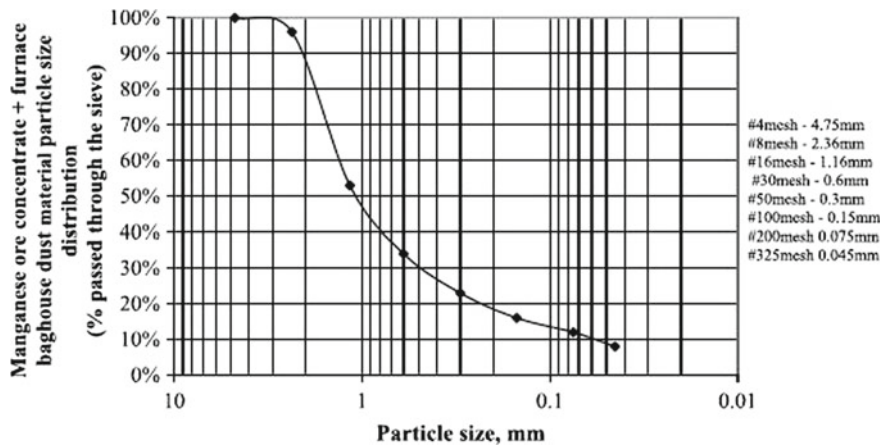


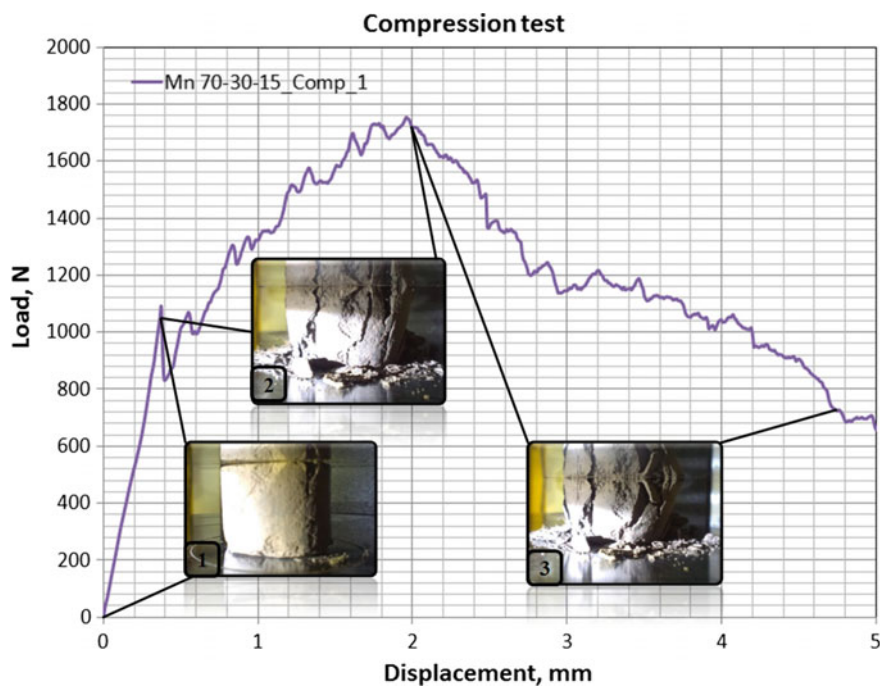
Fig. 3.69 Granulometric composition of mixture for brex production

Table 3.23 Composition of brex

Component	No. 1	No. 2	No. 3
Manganese ore concentrate	47.6	66.7	56.0
Coke breeze	—	—	15.0
Baghouse dust	47.6	28.6	24.0
Portland cement	4.8	4.7	5.0

Due to the cylindrical shape of brex, its cold strength was determined by measuring both compressive strength and tensile splitting strength, since these types of stress would be exerted on brex during actual transport and stacking. These properties were measured using an Instron 3345 system (USA). The compressive and tensile splitting strength tests were performed using six specially prepared brex samples with a diameter of 25 mm and a length of 20 mm which were subjected to compression and tensile splitting.

Figures 3.70 and 3.71 illustrate the behavior of brex and the mechanism of brex destruction during compressive and splitting strength tests. At the initial stage (1), the elastic loading of brex shows a linear dependence between the applied force and the displacement of the active pressing surface. The beginning of the second stage is characterized by a sharp decrease in the applied force due to the formation of surface fractures. At this stage, the “near-surface” layers of the brex are destroyed

**Fig. 3.70** Compression test of brex No. 3

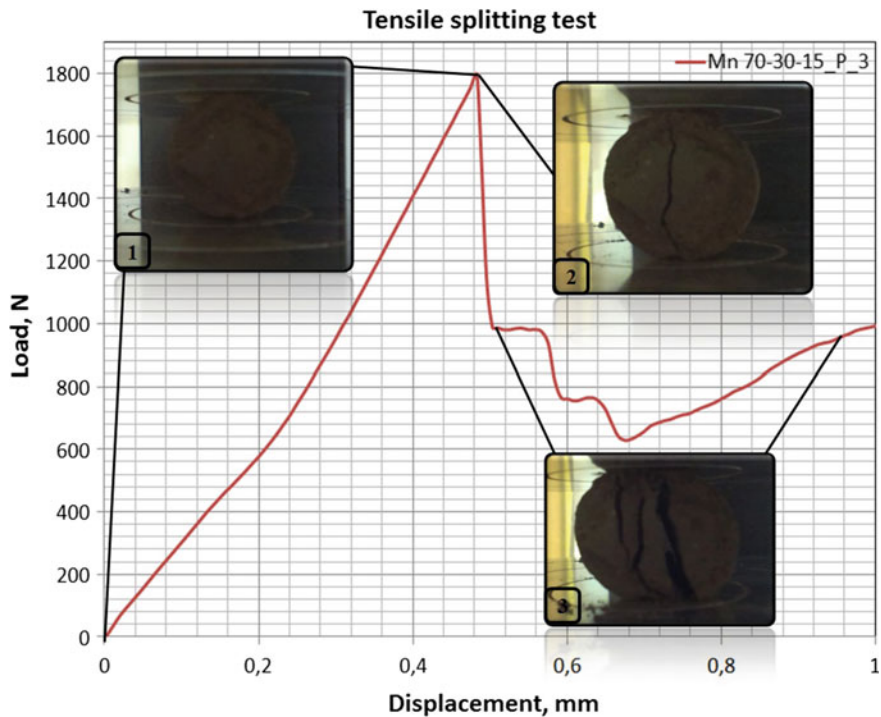


Fig. 3.71 Tensile splitting test of brex No. 3

Table 3.24 Mechanical strength of brex, kgf/cm²

Brex No.	Tensile splitting strength	Compressive strength
1	18.3	160.8
2	28.6	291.2
3	13.1	124.6

and peeled (15–20% of the radius). However, the “core” (central part) of the brex continues to endure the pressure, as evidenced by the core’s growth. A clear zonal structure of the brex can be observed in the radial direction. The near-surface layers of the brex have a relatively higher stiffness than its “core.” This statement is supported by the difference in slopes of the curves at Stage 1 and Stage 2.

In the third stage, once the applied force reaches its maximum, the “core” of brex is destroyed with a complete strength loss.

Table 3.24 illustrates the average compressive strength and splitting strength. Subsequently, compressive strength of samples of industrially manufactured brex No. 2 was tested by independent laboratory L. Robert Kimball & Associates, Inc (USA). The compressive strength of a sample with a diameter of 32.3 mm and a length of 57.7 mm was 206 kgf/cm². It is clear that the results obtained for

compressive strength significantly exceed the compressive strength of briquettes required for submerged EAF.

Brex porosity was examined by electron microscopy using an LEO 1450 VP microscope (Carl Zeiss, Germany) with a resolution of 3.5 nm in combination with X-ray computed tomography using a Phoenix V | tome | X S 240 tomograph (General Electric, USA). The computed tomography method was used to determine the sample porosity in the pore size range above 100 μm . The electron microscopy method was used to study the porosity fraction represented by pores with sizes less than 100 μm . Interpretation of these microscopic studies was carried out using the computer program STIMAN [151]. It was found that the porosity of the brex was 18.5% (5.6% is the porosity measured by computed tomography and 12.9% by electron microscopy). Subsequently, the porosity of industrially manufactured brex with the same content of major components (with 3% Portland cement) was measured at the above-mentioned independent laboratory and amounted to 18.7%.

Thermal studies using powder samples with a mass of 50–70 mg, carried out on an STA 449 C installation (Germany) in an argon atmosphere, in the temperature range of 20–1400 $^{\circ}\text{C}$ at a heating rate of 20 $^{\circ}$ /min, allowed to determine the nature of phase transformations in brex during their heating and showed that the thermal effects on the DSC curve for brex No. 1 and No. 2 are almost identical (Fig. 3.72).

The manganite ($\text{MnO}(\text{OH})$) dehydrates to form pyrolusite or β -kurnakit ($2\text{MnOOH} = \text{Mn}_2\text{O}_3 + \text{H}_2\text{O}$) in the temperature range 300–450 $^{\circ}\text{C}$. At temperatures above 400 $^{\circ}\text{C}$, psilomelane of manganese ore transforms to hollandite or hausmannite. Exothermic peaks with a maximum temperature of 795.8 $^{\circ}\text{C}$ in brex No. 1 and 801.0 $^{\circ}\text{C}$ in brex No. 2 are most likely associated with the dissociation of pyrolusite and the formation of β -kurnakit which is accompanied by oxygen release and mass loss. The same peak in brex No. 3 at a temperature of 742.8 $^{\circ}\text{C}$ is not followed by a loss of mass; it can be explained by the effects of recrystallization of amorphous phases. β -kurnakit decomposes in the temperature range 900–1050 $^{\circ}\text{C}$, and the formation of β -hausmannite takes place [152]. In the range 1080–1250 $^{\circ}\text{C}$, β -hausmannite is polymorphically converted to γ -hausmannite.

In brex No. 3, the endothermic peak in the 150–200 $^{\circ}\text{C}$ temperature range is accompanied by mass loss due to sorption moisture removal. In the 300–500 $^{\circ}\text{C}$ temperature range, there are no pronounced endothermic peaks, but there is a loss of mass associated with the reduction of MnO_2 to Mn_2O_3 . A phase transformation of manganite (MnOOH) into kurnakit occurs in the same temperature range. The endothermic effect with a maximum at 1031.7 $^{\circ}\text{C}$ is associated with the reduction of Mn_3O_4 to MnO due to mass loss; the effect at 1056.1 $^{\circ}\text{C}$ is determined by the ferric phase change.

The endothermic peak with a maximum at 1122.7 $^{\circ}\text{C}$ is determined by forming manganese carbide Mn_3C , where carbon recovers manganese from MnO . The coke breeze in brex provides for intensive iron and manganese reduction, marked by endothermic peaks at 1122.7 and 1213.2 $^{\circ}\text{C}$.

Figure 3.73 shows the microstructure of brex No. 2.

Portland cement is known to lose its binding properties at 750–900 $^{\circ}\text{C}$. Therefore, it is important to understand what provides for the hot strength of brex at

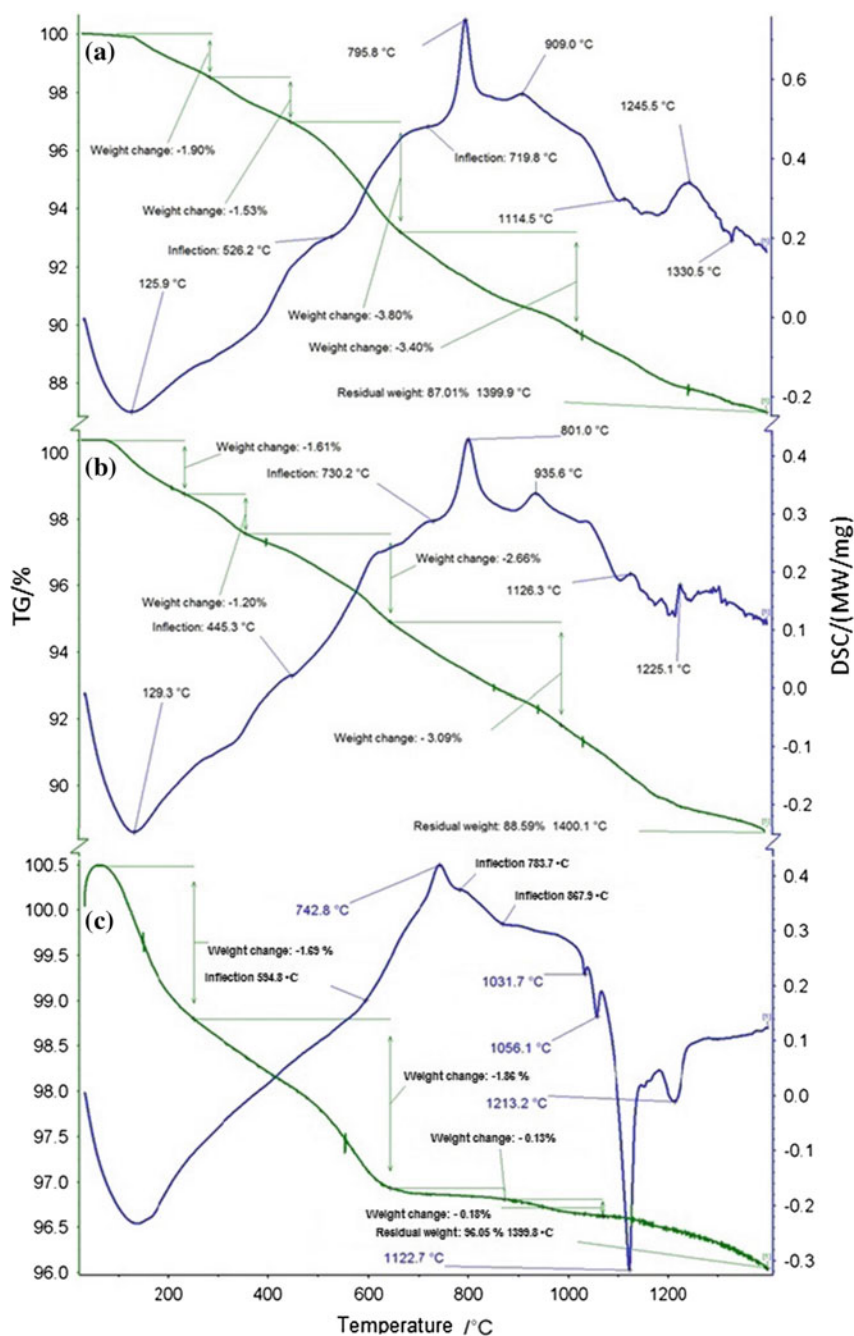


Fig. 3.72 Thermograms of the brex samples No. 1 (a), No. 2 (b), No. 3 (c) (left-hand vertical TG/%; right-hand vertical—DSC/(MWt/mg))

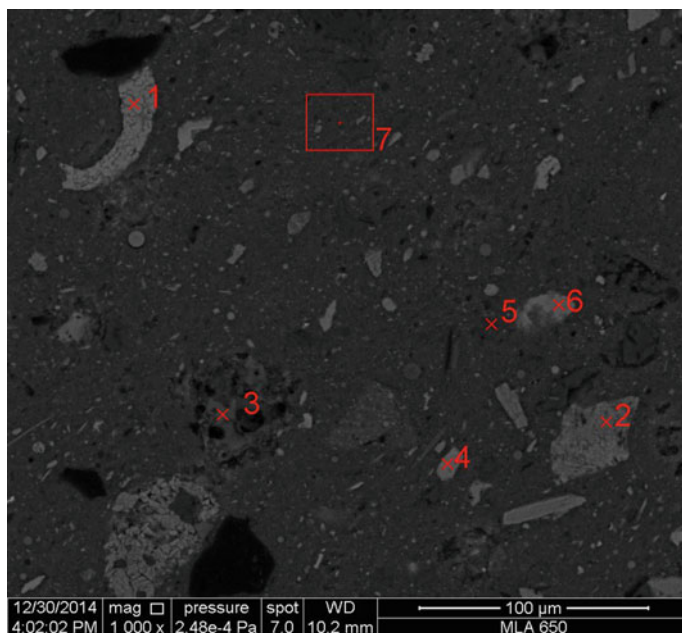


Fig. 3.73 Microstructure of brex No. 2 structure (1—pyrolusite, 2—gaussmanite, 3—diopside, 4—fayalite, 5—mullite, 6—pyrolusite, 7—solid solution of $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$)

temperatures higher than the above-mentioned temperature range. A previous study [153] explored the behavior of a pyrolusite sample of manganese concentrate from the Chiatura mine when heated in a reducing atmosphere (helium 40% and hydrogen 60%; heating at a rate of 20 °C/min). A cubic sample measuring $5 \times 5 \times 5$ mm was observed to gradually expand by a considerable amount up to 0.8 mm; the thermal expansion was accompanied by sample cracking. Cracks were first observed at 500 °C, with the number of cracks increasing with heating. The fractures formed during the tests are characterized by a certain orientation pattern. Radial and concentric cracks are found within the spherulites. Cracks in random directions are found in the interspherulite cementing mass. Despite this fracture pattern, the sample maintained integrity at 800 °C. After that, a slow and irreversible compression process began. In our opinion, a dense silicate phase (olivine or wollastonite) protected the sample from destruction. The formation of the phase in the indicated temperature range corresponds to the well-known phase diagrams of systems $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ and $\text{CaSiO}_3\text{--Mn}_2\text{SiO}_3$ (Figs. 3.74 and 3.75 [154]). Manganese silicates (tephroite— Mn_2SiO_4 and rhodonite— MnSiO_3) were discovered in the intervals between the oxide phase's grains of the Chiatura concentrate sample.

Up to 1250 °C, the strength of brex is provided by the dense structure of the mentioned silicate phases, and above this temperature two eutectics are formed in

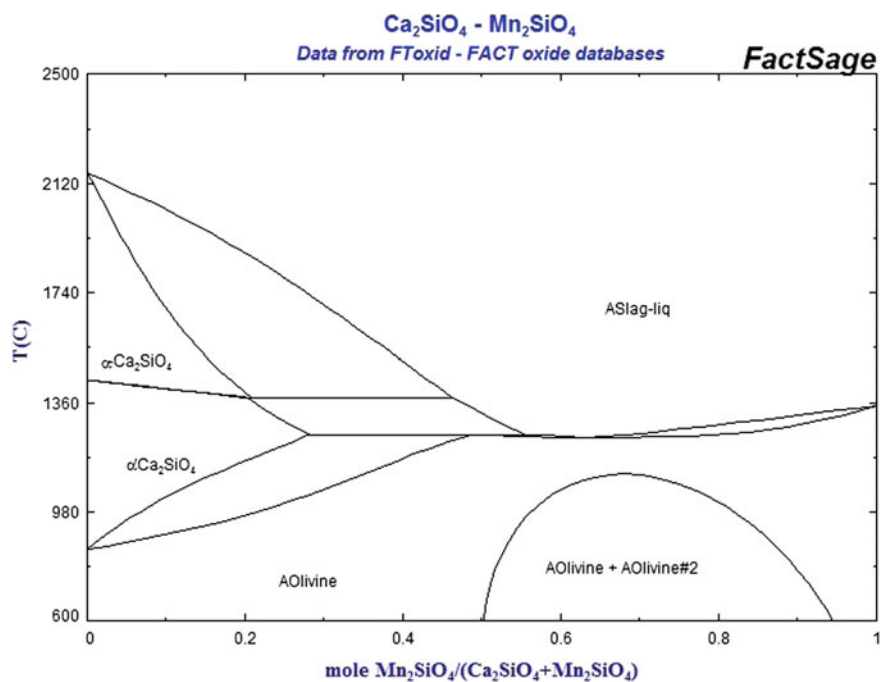


Fig. 3.74 Diagram of system $\text{Ca}_2\text{SiO}_4\text{--Mn}_2\text{SiO}_4$ [154]

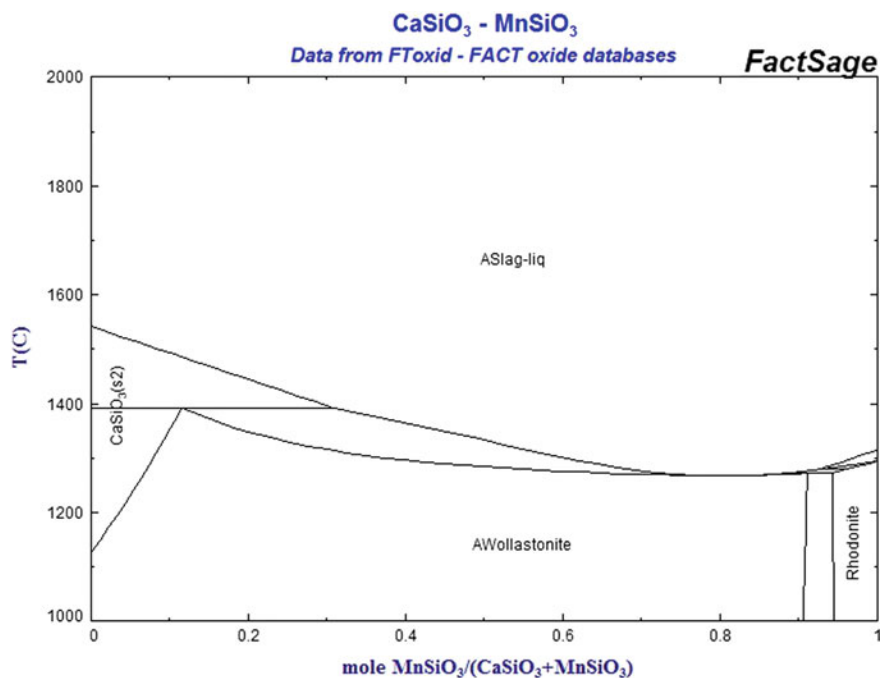


Fig. 3.75 Diagram of system $\text{CaSiO}_3\text{--MnSiO}_3$ [154]

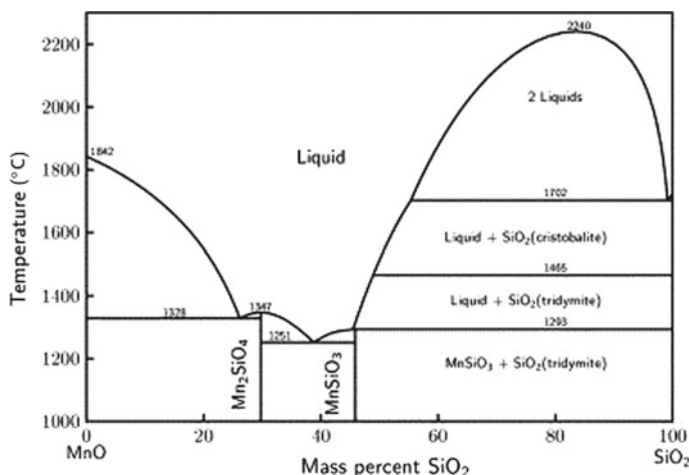


Fig. 3.76 Phase diagram of the MnO–SiO₂ system [155]

the MnO–SiO₂ system: tephroite + rhodonite + liquid (1251 °C) and tephroite + manganosite + liquid (1315 °C) which contribute to preserving the strength of the brex (Fig. 3.76, [155]), due to the appearance of a liquid binder.

An important property of brex for smelting ferroalloys in submerged EAF is the specific electric resistance. The measured specific electrical resistance of brex samples at a room temperature is given in Table 3.25.

The measuring system used in the study made it possible to investigate the dynamic pattern of brex resistance at a temperature up to 800 °C. As a result, the behavior of brex resistance was studied up to the first exothermic peak described in Fig. 3.91. It corresponds to a relatively deep brex immersion in the furnace to levels where lower manganese oxide is formed. Due to the low electric resistance of brex No. 3 (with 15% coke breeze in the mass of brex), which is lower than the resistance of lump manganese ore of the same deposit [156], this type of brex was excluded from further study.

Figure 3.77 shows the results of resistance measurements in brex No.1 and brex No. 2 when heated to 800 °C.

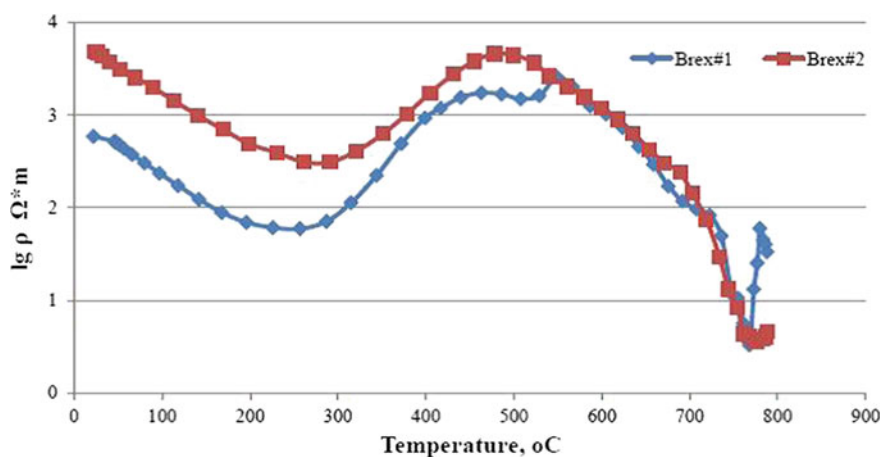
The increase in resistivity of brex in the 300–500 °C temperature range coincides with the above-mentioned endothermic effects of mass loss, which is associated with manganite dehydration and with kurnakit formation.

It is clear that the resistivity of brex No. 1 is lower than that of brex No. 2 because of the higher carbon content in brex No. 1 resulting from a higher baghouse dust content that adds carbon to brex No. 1.

Based on the above-mentioned conclusions regarding the physical and mechanical properties of brex, the behavior of brex during heating, and measurements of the specific electrical resistivity, brex No. 2 was selected as a component of the submerged EAF charge.

Table 3.25 Specific electric resistance of brex No. 1–No. 3 at room temperature

Brex No.	ρ , mohm mm	
1	26.3	25.5
2	32.3	28.9
3	9.42	12.4

**Fig. 3.77** Specific electric resistances of brex No. 1 and brex No. 2

3.5.2.3 Full-Scale Testing of Silicomanganese Smelting with Brex in the Charge of Submerged EAF

For the full-scale testing, an experimental batch of 2000 tons of brex of 1400 tons of Chiatura manganese oxide and 600 tons of aspiration dust from production of silicomanganese was manufactured using the Steele 75 extruder (Fig. 3.78). The components of the mixture were mixed in the ore yard by a front loader and fed to the extrusion line.

In the manufacture of this batch, it was decided to limit the proportion of binder (Portland cement) in the charge mixture of 3%, which was sufficient to ensure the strength of brex that withstood 20 overloads on the way from the briquetting factory to the ferroalloy plant: extruder—conveyors—dump truck—piles—front loader—truck—stack at the port of loading—front loader—bunker—grab—barge—grab at the port of discharge—bunker—conveyors—dump truck—stack in the ore yard of the ferroalloy plant wheel loader—hopper—oven. At the same time, the cumulative formation of fines (less than 6 mm) did not exceed 10%. Such a decrease in the mass content of the binder was made possible thanks to the well-known binding properties shown by dust aspiration from the production of manganese ferroalloys [148].

The pilot campaign was conducted in a stably operating industrial submerged EAF with a capacity of 27 MVA, with a productivity of 85 tons/day. The specific

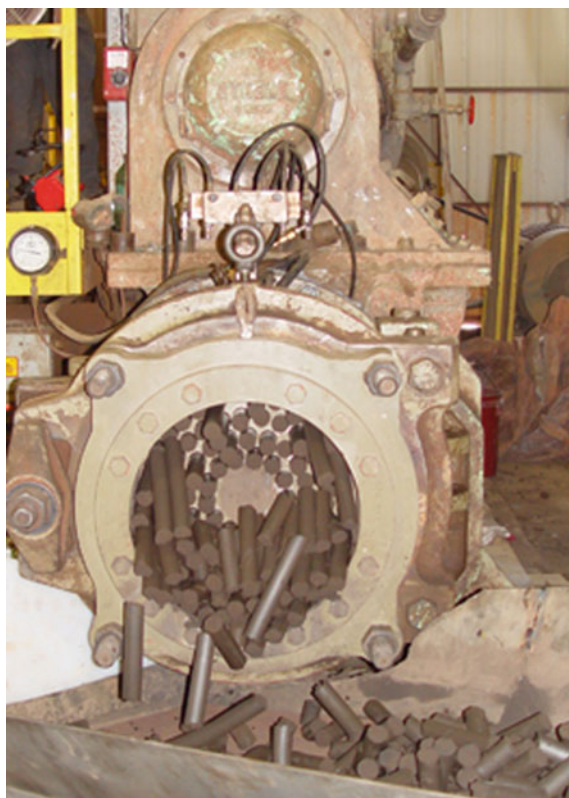


Fig. 3.78 Production of an experimental batch of brex No. 2

Table 3.26 Chemical composition of charge components

Material	Component composition						
	Mn	SiO ₂	CaO	MgO	Al ₂ O ₃	Fe	P
Ore 1	49.5	13.0	0.7	0.5	1.0	4.0	0.05
Ore 2	29.0	20.2	5.9	5.2	2.1	0.9	0.06
Brex	31.37	24.32	6.10	2.05	2.79	1.36	0.12
Scraps	23.3–38.6	N/A	N/A	N/A	N/A	N/A	N/A
Silicomanganese fine briquettes (vibropressed)	53	18	4	N/A	N/A	10.5	0.15

power consumption averaged 4200 kWh/t. The degree of recovery of manganese is 80%. The manganese content in waste slag is 12–14%.

The chemical composition of the manganese components of the mixture is given in Table 3.26.

Scraps are the internal wastes generated while deslagging the surface of metal in a ladle, cleaning buckets and furnace notch, sorting at slag dumps, and casting silicomanganese. Only the total manganese content in slags was determined; these values are given in Table 3.30. Briquettes made from silicomanganese fines are produced by the process of vibropressing (unconditioned fine fraction 0–6 mm). To impart the necessary strength to the briquettes made from these fines, Portland cement was used (10% mass).

A preliminary calculation of the composition of the charge was carried out to achieve stable manganese content in the ore part of the charge (Table 3.27).

For the accuracy of the comparison of the results of the furnace operation with and without brex, a monthlong period of furnace operation was observed. A weeklong period of the furnace operating without brex immediately preceding the beginning of the pilot period was taken as a reference.

It was decided to begin with 5% of the brex share in the ore part of the charge to get a first experience with the agglomerated burden. Over the course of three days of observation, no visible changes had been registered in the process of silico-manganese smelting; the furnace worked smoothly, with a constant and uniform current load during the period of brex use. The slight 0.3% decrease in manganese extraction during this period was due to furnace downtime associated with the tap-hole unit repair (1.5 h downtime). Then, for four consecutive days, the brex

Table 3.27 Composition of the charge (net tons)

Component of the charge	Reference and full-scale trial periods						
	Reference period	1	2	3	4	5	6
Mn Ore 1	0.526 (30%)	0.525 (30%)	0.525 (30%)	0.525 (30%)	0.525 (30%)	0.525 (30%)	0.525 (30%)
Mn Ore 2	1.205 (70%)	1.120 (65%)	1.030 (60%)	0.855 (50%)	0.705 (41%)	0.600 (35%)	0.525 (30%)
Brex	—	0.087 (5%)	0.175 (10%)	0.350 (20%)	0.500 (29%)	0.605 (35%)	0.690 (40%)
Estimated weight of charge	1.730	1.732	1.730	1.730	1.730	1.730	1.740
<i>Incoming manganese with</i>							
Ore 1	0.262 (43%)	0.262 (42.6%)	0.262 (42.6%)	0.262 (42.4%)	0.262 (42.2%)	0.262 (42.1%)	0.262 (41.8%)
Ore 2	0.350 (57%)	0.325 (53%)	0.299 (48.6%)	0.224 (40.1%)	0.205 (32.8%)	0.174 (27.9%)	0.152 (24.2%)
Brex	—	0.027 (4.4%)	0.054 (8.8%)	0.109 (17.5%)	0.160 (25%)	0.188 (30%)	0.214 (34%)
Manganese charge weight	0.612	0.614	0.614	0.619	0.622	0.624	0.628
Average manganese content, %	35.4	35.5	35.6	35.8	36.0	36.1	36.1

share in the charge was maintained at 10%. Improvement in the furnace top functioning was visually apparent. Gas flames throughout the furnace's top area confirmed an improvement in gas permeability of the column of the charge and the uniformity of the temperature distribution over the surface of the furnace top. Deeply submerged electrodes functioned without producing surface blowholes in the electrode circle and in the surrounding area. No sintering in the electrode circle was observed. During the next three days, brex share in the charge was increased up to 20%. The furnace operated smoothly, the electrodes were deeply submerged, the current load had no visible abnormalities or jolts, and the gas permeability of the charge was good for the entire area of the furnace top. Throughout the next week, the brex share of the charge was increased to 29%. The furnace worked well. An increase in the rate of the charge descent in the electrode circle, especially during the tapping, indicates an increase in the melting rate of the charge in the active zone of the furnace. The furnace top functioned smoothly without surface blowholes with a constant load current, smooth, without bumps and drops. Melt out was good, and metal and slag were sufficiently warmed up. However, in the end of this period, there was a furnace downtime for 4 h due to reasons not related to the brex presence in the charge (electrical problem in the transformer).

The beginning of the next phase of the pilot period, when the brex share rose to 35% substituting the ore 2, was associated with a problem caused by a disruption in the tap-hole electrode bypass, resulting in its shortening and the deterioration of the melt output. The bulk of the slag remained in the furnace. This resulted in an increased coke rate and scrap withdrawal from the charge along with briquettes of silicomanganese fines. During this period, a deterioration in the technical and economic performance of the furnace had been registered, namely an increase in specific energy consumption and specific consumption of manganese ore raw materials, as well as a reduced extraction of manganese. To restore its normal functioning, the furnace heating rate was increased so as to warm up the slag and ensure its normal tapping.

In the final phase (week) of the pilot operation period, the furnace worked with the brex share in the charge up to 40%. The furnace operation was characterized by a good current load, and top gas release was smooth, with no surface blowholes and furnace charge downsides, and with a normal tapping.

As the share of brex in the ore part of the charge increased, the share of ore 2 was proportionally reduced, which is an equivalent substitute for the amount of manganese introduced, since the average manganese content in brex was 31% and in ore—29% (Tables 3.28 and 3.29).

Substitution of the essential part of manganese ore in the charge with brex based on ore fines and aspiration dust led to an improvement in the technical and economic indicators of the process as a whole. The pilot industrial campaign itself went without any visible changes in the technological process: The furnace worked smoothly, with a constant current load, the melt was produced according to the schedule, there were no significant changes in the chemical composition of the metal and slag, and the gas permeability of the furnace throat improved.

Table 3.28 Furnace parameters during the reference and the full-scale trial period

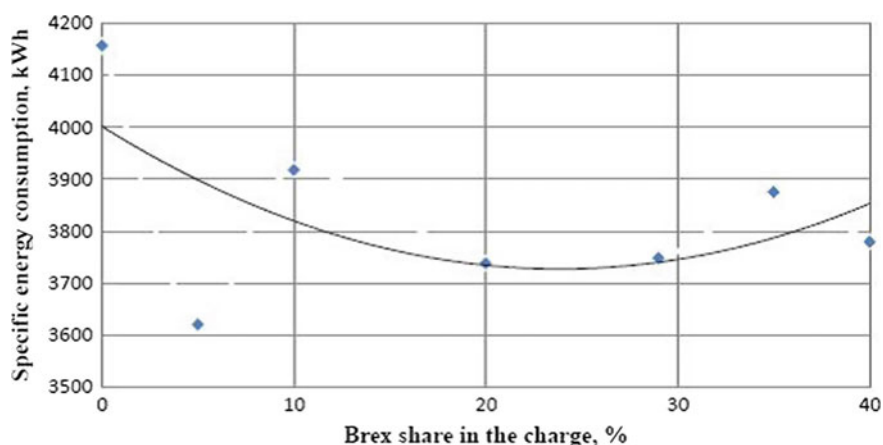
Parameter		Reference and full-scale trial periods						
		Reference period	1	2	3	4	5	6
Actual metal production over a period of time, t	Ton	816.323	298.4	277.1	196.6	570.6	397.2	757.2
	b.t (basic ton)	839.670	300.7	285.8	199.5	584.75	393.2	767.8
Actual furnace performance, %		98.9	97.6	97.4	99.7	96.2	98.6	93.6
Power consumption, MW		3339.27	1078.2	1085.4	734.7	2120.8	1536.3	2821.48
Specific power consumption, kW * h/b.t		3977	3586	3798	3682	3627	3908	3675
Ore 2	t(29% Mn)/b.t	1.106	0.933	0.892	0.714	0.635	0.626	0.492
	t(48% Mn)/b.t	0.668	0.563	0.539	0.431	0.383	0.378	0.297
Ore 1	t(49.5% Mn)/b.t	0.565	0.505	0.482	0.509	0.480	0.524	0.484
	t(48% Mn)/b.t	0.582	0.520	0.497	0.525	0.495	0.540	0.499
Brex	t (31.37% Mn)/b.t	0	0.077	0.164	0.273	0.387	0.571	0.605
	t(48% Mn)/b.t	0	0.050	0.107	0.178	0.252	0.373	0.395
The total consumption of raw manganese ore	t/b.t	1.671	1.515	1.538	1.496	1.502	1.721	1.581
	t(48% Mn)/b.t	1.250	1.133	1.143	1.134	1.130	1.291	1.191
Coke, t/b.t		0.446	0.339	0.420	0.405	0.395	0.415	0.413
Quartzite, t/b.t		0.419	0.499	0.524	0.465	0.529	0.456	0.475
Silicomanganese fine briquettes t/b.t		0.158	0.082	0.103	0.092	0.120	0.110	0.094
Scrap (Mn content in scrap, %), t/b.t		0.358 (23.3)	0.601 (29.9)	0.462 (33.0)	0.477 (35.3)	0.461 (32.0)	0.455 (25.8)	0.373 (38.6)
Electrode mass, t/b.t		0.034	0.032	0.030	0.035	0.028	0.033	0.028
Manganese extraction from the ore component, %		80.1	79.8	80.7	80.7	83.6	79.1	79.9

The specific energy consumption during the experimental period has significantly decreased. In the base period, the power consumption per 1 ton of alloy was 4091 kWh. When 40% of manganese-containing brex were fed into the ore part of the charge, the specific energy consumption decreased to 3727 kWh per 1 ton of alloy (Fig. 3.79).

The next positive factor of the campaign was an increase in extraction of manganese from the ore component of the charge. If in the comparative period of

Table 3.29 Main component composition during the reference and pilot operation period

Phase	Main component composition								
	In metal				In furnace charge				
	Mn	Si	Fe	P	MnO	MgO	SiO ₂	CaO	Al ₂ O ₃
Base	66.64	17.71	14.06	0.127	10.50	7.38	44.28	21.43	15.29
1	66.33	16.30	14.25	0.128	12.70	7.14	45.33	20.31	13.46
2	66.90	17.69	14.18	0.098	12.89	6.52	44.78	18.67	13.80
3	66.77	16.45	14.21	0.12	11.30	6.77	44.57	19.86	15.07
4	68.02	16.02	14.01	0.14	11.79	6.39	45.11	19.42	15.13
5	65.98	15.22	14.30	0.16	15.08	5.73	46.20	26.11	15.71
6	66.08	17.07	14.25	0.18	10.8	5.17	45.30	19.83	15.35

**Fig. 3.79** Dependence of specific energy consumption on the share of brex in the furnace charge

the furnace operation without brex, manganese extraction from the ore part of the charge averaged 80%, while using 30% of the brex in the ore part of the charge, manganese extraction reached 83.5% (Fig. 3.80).

The deterioration of the manganese extraction parameters in the period preceding the final one was not related to the presence of brex in the charge and was due to the stoppage of the furnace and problems with the electrode. The reduction in coke consumption is illustrated in Fig. 3.81.

The obtained results formed the basis for the design and construction of several briquetting factories based on stiff vacuum extrusion in different countries around the world. In particular, a briquette factory with a capacity of 260 thousand tons of briquettes per year was put into operation at the Chelyabinsk Electrometallurgical Plant in Russia. Briquettes are made from a mixture of manganese ore and

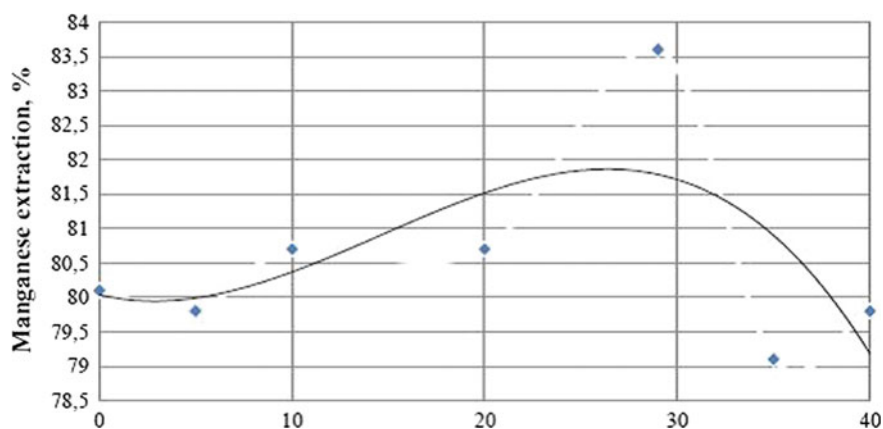


Fig. 3.80 Manganese extraction as a function of the brex share in the furnace charge

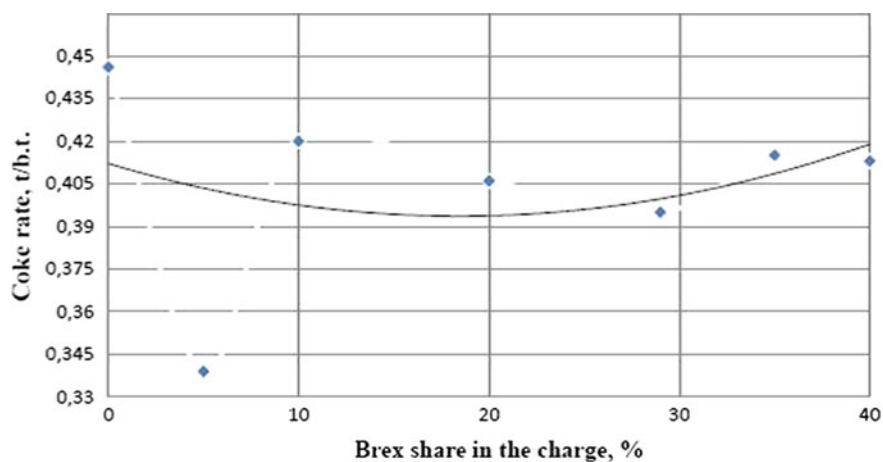


Fig. 3.81 Dependence of coke consumption on the share of brex in the furnace charge

baghouse dusts (Fig. 3.82). The ratio of these components in the briquette charge depends on the type of imported ore fines. At 30% of the dust content in the mass of the briquette, only 1.5% of the cement by mass of the briquette is required. The share of cement increases to 3% at 15% of the content in the dust in the briquette.

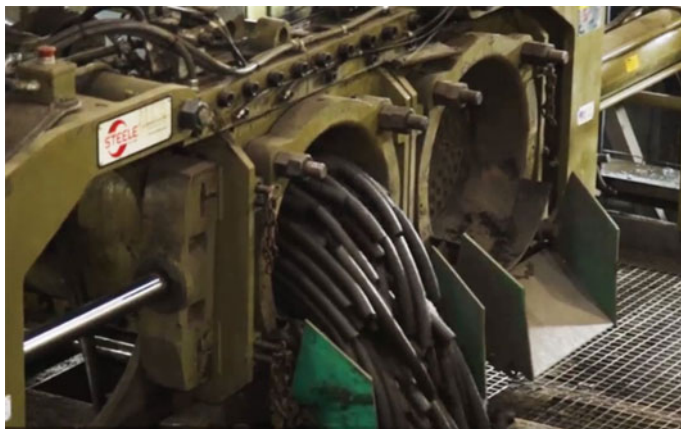


Fig. 3.82 Production of brex in Chelyabinsk (Russia)

3.5.2.4 Metallurgical Properties of Briquettes on the Basis of Chromium-Containing Materials

The possibility of obtaining inexpensive and efficient agglomerated charge materials for smelting ferrochrome without prior calcination has always attracted ferroalloy technologists. However, cold briquetting of chromium ore fines and concentrates is not widespread and is still significantly inferior to sinter and pellet production. Practical experience of using roller presses and vibropressing confirmed the possibility of achieving satisfactory metallurgical properties of briquettes obtained by such methods. Suffice it to mention the experience of the Serov Ferroalloy Plant [45], which confirmed the feasibility of replacing lumpy chromium ore with briquettes due to productivity growth (by 4%) without deterioration of the slag mode with a calm and even furnace running. The specific energy consumption (kWh/t) decreased by 1%. The decrease in chromium extraction when working on briquettes (by 2.3%) is due to the additional consumption of ore to increase the ore layer.

Also known are the successful results of the full-scale industrial testing of Globe Metallurgical Inc. [26] using briquettes made of Turkish chromite ore. A mixture of lime and molasses was used as a binder (5% by weight). The share of briquettes in the ore part of the charge reached 100%. Since 1988 in Sweden, as noted earlier, the plant for the production of briquettes by vibropressing has been successfully operating at Vargön Alloys.

However, roller briquetting is accompanied by the formation of a significant amount of waste. Achieving hot strength requires the use of significant quantities of expensive binder. Vibropressing technology also involves the heat treatment of raw briquettes and inevitably leads to the “dilution” of the charge component thus obtained due to the need to use a substantial amount of binder. A significant amount of cement binder inevitably also leads to an increase in the sulfur content in the

alloy. This, in particular, caused the closure of the vibropress briquetting factory at the Serov Ferroalloy Plant.

The SVE method opens up new opportunities for the widespread commercialization of cold briquetting chromium ore materials due to its higher performance, sufficiently high strength of raw briquettes and significantly lower binder content required to achieve the required level of metallurgical properties, and the lack of thermal processing of raw briquettes.

In [157], the metallurgical properties of two types of briquettes made of chrome-containing materials—ore and ore-coal (including ore-coke) briquettes—were studied.

The choice of cement as a binder was also based on the results of studies of hot strength of laboratory briquettes made of chromium ore concentrate, described in [158]. The hot strength of briquettes was determined by the method of linear heating of the sample under load (2 kg) at a rate of 17 °C/min under reducing conditions. The choice of the load value corresponds to the pressure of a briquette column with a height of 2 m. Reducing conditions are provided by conducting an experiment in a stagnant furnace atmosphere of gaseous reaction products (CO) and placing the test sample of the briquette between two graphite plates, which simulates the contact of the briquette with pieces of coke in an electric furnace.

An experimental setup for determining the hot strength of briquettes based on fine-grained chromium ore when heated in a reducing atmosphere in the temperature range 20–1800 °C is shown in Fig. 3.83. Before the start of the experiment, the briquette was installed in the isothermal zone of the furnace between graphite plates. The top plate was prevented by the load and the alundum displacement indicator with a total mass of 2 kg. The furnace was closed, pumped out, and filled with argon. In the course of linear heating at a rate of 17 °C/min, set by the furnace programmer, the gas from the furnace was vented, maintaining the pressure in the furnace equal to the atmospheric pressure. Changes in the sizes of the briquette were fixed according to the movement of the alundum pointer. To improve the accuracy of the readings, an Intel digital microscope was used, which made it possible to conduct linear movements on the computer screen with an accuracy of 0.01 mm. If the absolute value of the displacement is 1 mm (typical for the first heating period of the briquette, when the usual thermal expansion of the briquette prevails), then the relative measurement accuracy is 1% (rel.), which is sufficient for technical measurements. After the experiment, a metallographic section was prepared from the “crushed” briquette and a metallographic analysis of the phase components formed in the briquette was performed.

Comparison of softening curves (dilatometric curve) and the results of metallographic analysis of briquettes after melting makes it possible to qualitatively compare the melting and reduction rates for a given briquette composition and thus simulate their behavior in the ore-smelting furnace. The use of the method of linear heating under load can be illustrated by the example of briquette No. 1 from Kazakhstan concentrate of chromium ore with cement as a binder (6% by mass) in comparison with briquette No. 2 with the addition of coke breeze (8% by weight)

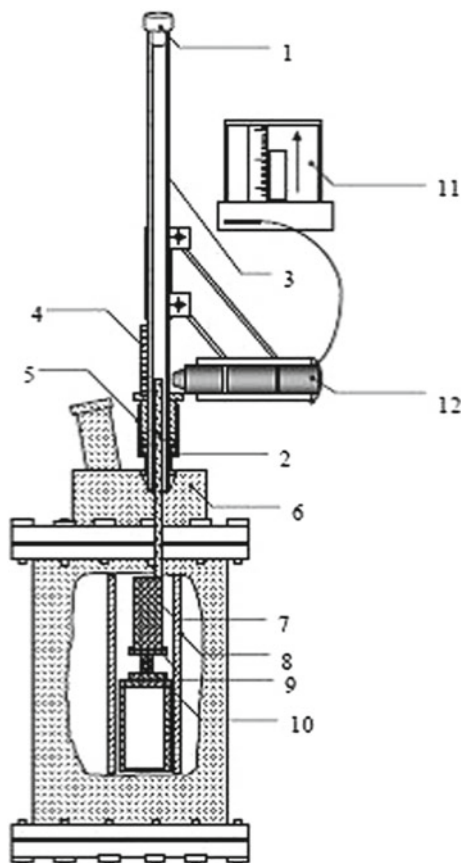


Fig. 3.83 Installation diagram for determining the hot strength of briquettes in reducing conditions with a temperature change from 293 to 2073 K. 1—Rubber stopper; 2—alundum index pointer; 3—transparent quartz tube; 4—ruler; 5—vacuum tight sleeve; 6—cover; 7—load weighing 2 kg; 8—graphite heater; 9—pressure graphite plates; 10—tested briquette; 11—the computer; and 12—digital microscope

and with the synthetically modified liquid glass substance (Penolite) as a binder (6% of the mass) and with the briquette No. 3, which differs from the briquette No. 2 by the absence of coke in its composition.

Photographs of briquettes and polished sections from such briquettes are presented in Figs. 3.84, 3.85 and 3.86. Figure 3.87 shows the softening curve of briquettes when heated under load.

Briquette No. 1 has a high final softening temperature—1620 °C, which allows intensive processes of formation of ferrochrome to develop at the places of contact of the ore briquette with carbon pressure plates. The bulk of the briquette at the end of the experiment turns into a pasty solid–liquid state. In general, it can be assumed

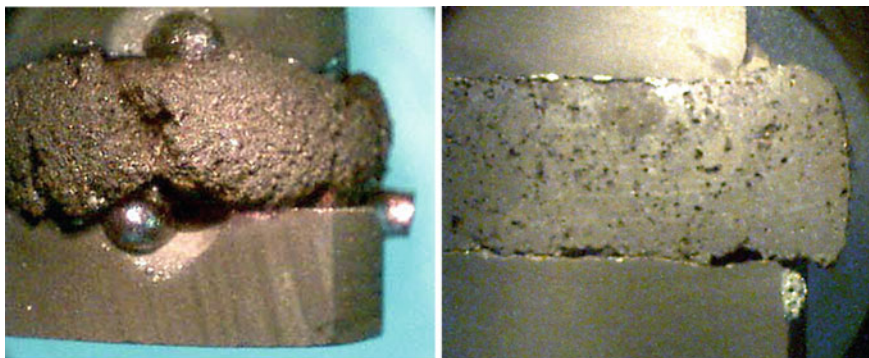


Fig. 3.84 Appearance and thin sections of briquette No. 1 with a cement binder after determining the hot strength (on the left is a briquette; on the right is a thin section, magnification 10). The composition of the briquette—Kazakhstan chrome ore and cement grade M500 in the amount of 6% by weight of the ore, drying at room temperature for 24 h. The experimental conditions are linear heating of the sample at a rate of 17 °C/min to a temperature of 1680 °C under a load of 2 kg in a reducing atmosphere



Fig. 3.85 Appearance and thin sections of ore-coke briquette No. 2 with a Penolite binder after determining the hot strength (on the left is a briquette; on the right is a thin section, magnification 10). The composition of the briquette—Kazakhstan chrome ore, coke breeze—8% by weight of ore, and Penolite in the amount of 6% by weight of the ore, drying at room temperature for 24 h. The experimental conditions are linear heating of the sample at a rate of 17 °C/min to a temperature of 1780 °C under a load of 2 kg in a reducing atmosphere

that for this case the melting rate corresponds to the rate of reduction of the components of the briquette by carbon.

Interestingly, the smallest drops of metal are distinguishable in the body of briquette No. 1, although in this case this process does not receive development. The most likely reason for this is the transfer of the reducing agent from carbon pieces to ore grains in the form of gaseous carbon-containing molecules of the type CH_x along cracks and pores of the briquette. Such a mechanism for the

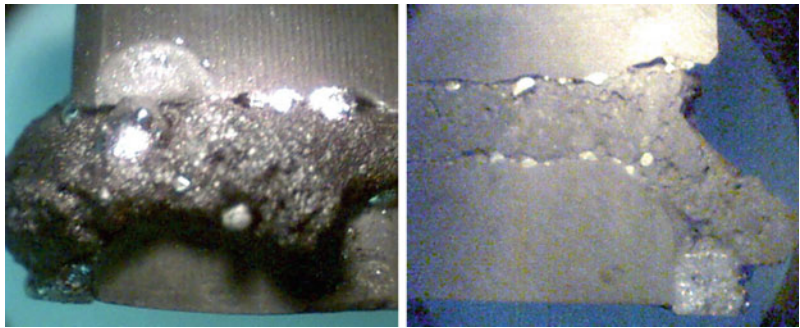


Fig. 3.86 Appearance and thin sections of briquette No. 3 with a Penolite as a binder after determining the hot strength (on the left—briquette and on the right—thin section, magnification 10). The composition of the briquette is Kazakhstan chrome ore and Penolite in the amount of 6% by weight of the ore, drying at room temperature for 24 h. Experimental conditions—linear heating of the sample at a rate of 17 °C/min to a temperature of 1780 °C under a load of 2 kg in a reducing atmosphere

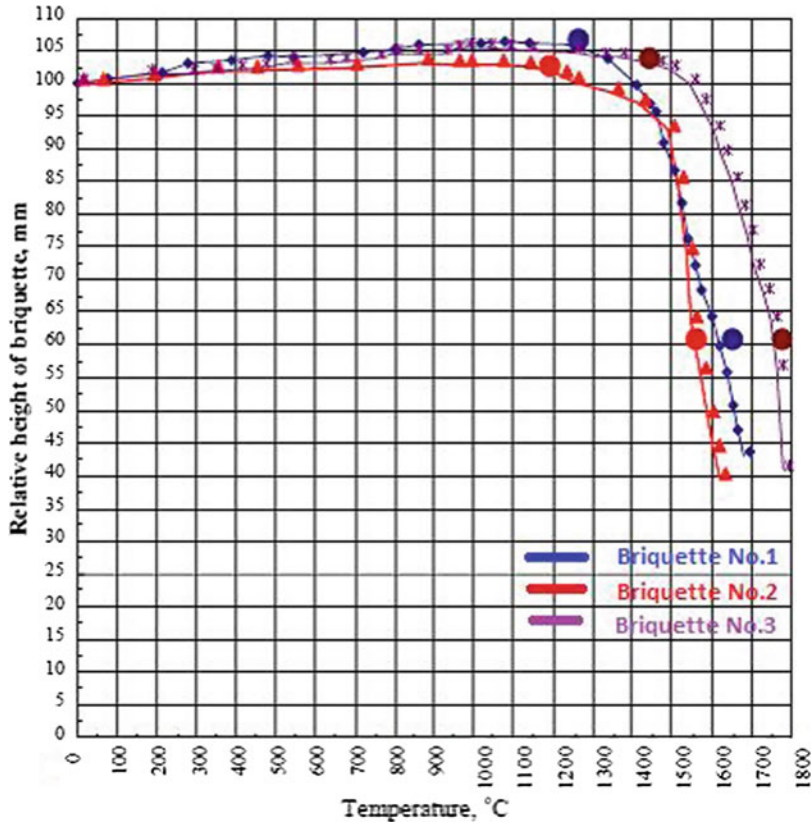


Fig. 3.87 Softening curves for briquettes No. 1–3

carbothermic reduction of chromites was proposed in [159] to explain the results of a study on the reduction of Ural chromium ores by carbon. Creating conditions in the ore-smelting furnace for the formation of gaseous carbon-containing compounds with increased reducing ability can be a significant reserve for the intensification of reduction processes.

Adding 8% of coke to the composition of the briquette No. 2 leads to a decrease in the softening end temperature to the level of 1550 °C, i.e., less than for cement-bonded briquettes (1620 °C). However, the reason for the decrease in this temperature here is not the melting of the ore material, but the intensive formation of liquid metal inside the briquette. The appearance of metallic liquid in the body of the briquette leads to its weakening and crushing, although the remainder of the ore material of the briquette is predominantly in the solid state. In this case, the melting rate lags behind the rate of reduction of the components of the briquette by carbon, which allows increasing the heating rate of such a charge without disrupting the process conditions.

Briquette No. 3 shows a record of high softening end temperature of 1765 °C. At such a high temperature, there is an intensive reduction of chromic ore with carbon at the interface of briquette–graphite; there is a vigorous outflow of droplets of ferrochrome from the briquette. The remaining substance of the briquette (“slag residue”) is squeezed out under load from the pressure plates, but retains the solid–liquid state. Here, also, the melting rate corresponds to the reduction rate of the components of the briquette with carbon, but the reduction process until the softening of the briquette goes much further in terms of the amount of ferrochrome produced. This is natural, because this binder (Penolite) allows “overheating” of the briquette by more than 100 °C than the cement binder, with the corresponding larger development of reduction processes.

Figure 3.84 shows appearance and thin sections of briquette No. 1 with a cement binder after determining the hot strength (on the left is a briquette; on the right is a thin section, magnification 10). The composition of the briquette is Kazakhstan chrome ore and cement grade M500 in the amount of 6% by weight of the ore, drying at room temperature for 24 h. The experimental conditions are linear heating of the sample at a rate of 17 °C/min to a temperature of 1680 °C under a load of 2 kg in a reducing atmosphere.

The addition of a carbonaceous reducing agent leads to an intensification of the reduction processes, which opens up possibilities for increasing the productivity of the electric furnace. But at the same time, the choice of the optimal content of carbon-containing reducing agent should be based on the analysis of the totality of the consequences of its introduction into the composition of the briquette, including the reduction of mechanical strength and the growth of electrical conductivity.

In [160], based on the results of the study of hot strength of laboratory briquettes No. 1–3, the metallurgical properties of extrusion briquette (brex) were studied on the basis of screenings and concentrates of Kazakh chrome ore with the addition of coal.

At the first stage, the metallurgical properties of the ore–coal briquettes of the following composition were investigated: briquette No. 4—concentrate of

chromium ore (71.4%), coal (23.8%), and cement (4.8%); and briquette No. 5—concentrate of chromium ore (76.2%), coal (19%), and cement (4.8%).

The following average values of mechanical strength in tensile and compression tests for these briquettes were obtained: briquette No. 1—28.8 kgf/cm² and 80.56 kgf/cm², and briquette No. 2—47.8 and 84.6 kgf/cm², respectively. The appearance of the briquette No. 2 after splitting and compression tests is shown in Fig. 3.88.

It can be seen that when splitting a briquette sample brex up into larger fragments than during compression and in both cases the amount of fines generated is insignificant, which confirms the expediency of using cement as a binder.

To determine the heat resistance of briquettes, a cylindrical sample (diameter 26.4 mm) weighing 33.6 g was placed in a melt heated to a temperature of 1500 °C, which was further heated to 1650 °C after lowering the briquette into it. A sample of briquette was removed from the melt after 10 min. The mass loss of the sample of briquette No. 4 was 31.25%, and its diameter decreased to 21.5 mm (Fig. 3.89).

The dependence of the conductivity of briquette No. 4 on the temperature is shown in Fig. 3.90. It is seen that closer to 800 °C begins almost exponential growth of electrical conductivity, which can lead to the above-mentioned negative consequences in the operation of the furnace. The conductivity of such a briquette at 788 °C is almost 6 times higher than that of a briquette based on manganese ore fines and aspiration dust (briquette No. 2 from Sect. 3.4.2.2) and 6 orders of magnitude higher than the conductivity of lumpy chromium ore [161].



Fig. 3.88 Briquette No. 5 after splitting (left) and compressing (right)

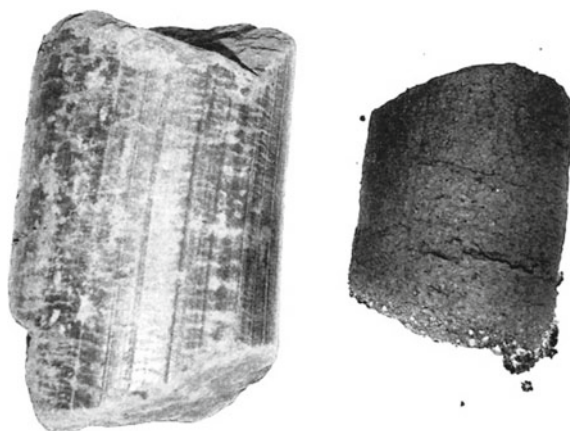


Fig. 3.89 Sample briquette No. 4 before (left) and after holding for 10 min at 1650 °C

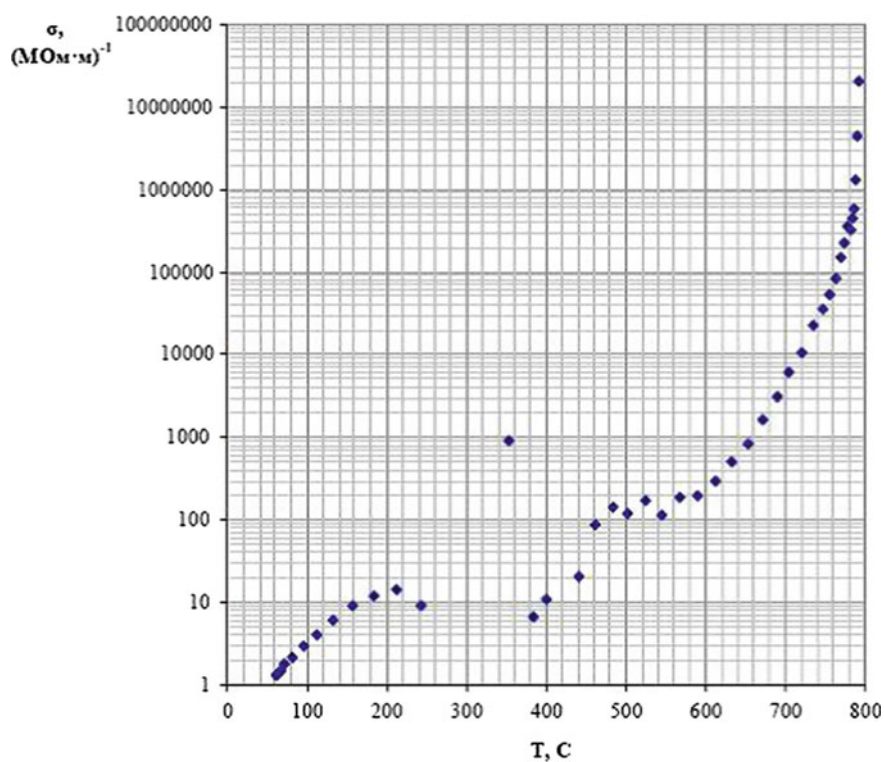


Fig. 3.90 Electrical resistivity of briquette No. 4 when heated



Fig. 3.91 Test results for dropping brex with bentonite

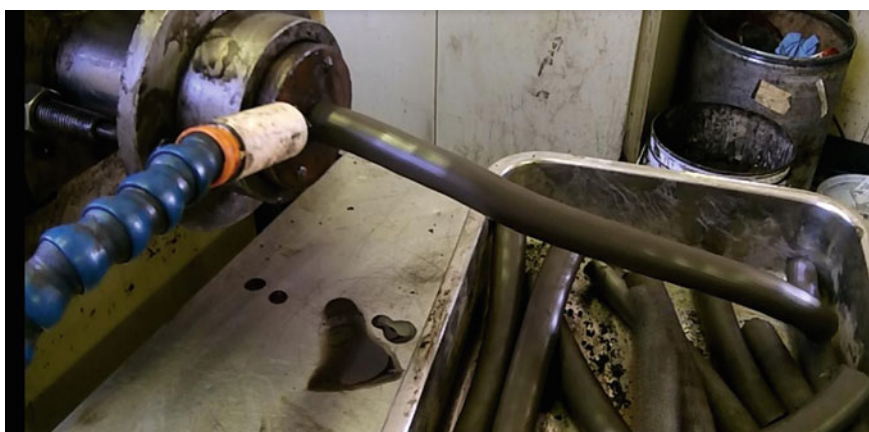


Fig. 3.92 Making brex on a laboratory extruder

The properties of chromium ore brex on a bentonite binder were also studied. The main component of brex is the gas cleaning dust of carbon ferrochrome production (97% of the mass of brex). Bentonite has been used as a plasticizer and binder, providing high impact strength. The fraction of the fine fraction (particles less than 5 mm in size) formed after four drops of brex samples onto a concrete floor from a height of 2 m did not exceed 1% (Fig. 3.91).

The strength of the raw brex is also shown in Fig. 3.92, which shows the moment when the raw brex on the bentonite binder is squeezed out of the die of the laboratory extruder. Raw brex was so strong that it easily moved the cuvette with previously made samples.

Fig. 3.93 Industrial production of chromium-based brex at Aktobe Ferroalloy Plant



The results obtained formed the basis for designing an industrial line for the production of brex in Kazakhstan (TNK Kazchrome, Aktobe), which was commissioned in 2017 (Fig. 3.93). Currently, brex are successfully used as a component of the charge of ore-smelting furnaces for smelting ferrochrome [162].

3.5.3 Briquetting in Direct Reduced Iron (DRI) Production

One more application of briquetting in our time has become the agglomeration of dispersed oxide and metallized materials of the processes of direct iron production (DRI).

In 2002, POSCO launched a briquette factory for the production of 500 thousand tons of briquettes per year from small coal as a substitute for expensive coking coal in the FINEX process [67].

In 2011, a briquette factory was built in Brazil as part of an industrial demonstration plant operating according to the Tecnoired process [68]. Briquettes are used in the batch furnace of the low furnace kiln process as an alternative to unburned

pellets. In 2015, the plant successfully reached a design capacity of 75 thousand tons of pig iron per year.

In 2016, Qatar Steel put into operation a roller factory equipped with a South Korean-made press (Jeil) for the agglomeration of metallized dusts and sludge formed in the process of direct production of iron in the Midrex reactor. By 2018, the factory produced 200 thousand tons of briquettes, which were successfully melted in the company's electric furnaces.

Primetals completed a set of studies that confirmed the viability of using roller briquettes as components of the Midrex process charge and in 2015 announced plans to build a briquette factory in Corpus Christi (Texas, USA) as part of a direct reduction reactor construction project (Midrex). The factory, commissioned in 2016, produces 160 thousand tons of dust briquettes, sludge, and pellet screenings per year.

Emirates Steel has announced the construction of a factory for the production of briquettes for the agglomeration of metallized and oxide materials generated in the Midrex process. Briquetting services will be provided by Phoenix Services [63].

The technological scheme of mini-factories producing rolled products using oxidized pellets as feedstock includes the production of metallized pellets in direct iron production reactors and/or the production of hot briquetted iron (HBI), steel smelting in electric furnaces, and its continuous casting and rolling production. At such enterprises, importing annually large amounts of iron ore pellets for producing HBI, tens of thousands of tons of fine iron-containing waste are produced annually during unloading, storage and subsequent loading of pellets into metallization reactors, unloading of metallized pellets, and their briquetting. Preliminary estimates show that the involvement of such materials in the secondary circulation in the form of briquettes would make it possible to smelt additional steel and free up significant areas occupied by stored waste.

In [163, 164], the possibility of using stiff vacuum extrusion to obtain agglomerate products suitable for use as charge components of Midrex process industrial reactor was studied. Brex were placed inside the deformable steel packages, permeable to reducing gas, which at the end of the process could be removed from the reactor, which allowed visually determining the state of the reduced brex and studying their chemical composition and properties. This method of introducing brex into the reactor charge allowed simulating adequately their behavior in real conditions, including the mechanical pressure of the surrounding traditional charge and the effect of the reducing gas. The appearance of the steel package is shown in Fig. 3.94.

For the tests, a prepared mixture was used consisting of pellets fines (52.6%), metallized sludge (26.4%), mill scale (15.8%), and 5.2% of the electric arc furnace dust (EAF dust). The granulometric composition of the initial mixture and after its regrinding on a laboratory roller crusher is shown in Fig. 3.95.

The granulometric analysis of the pellet fines and mill scale showed that: Pellet fines—8% of particles are larger than 6.30 mm, 60% have sizes in the range from 0.15 to 6.30 mm, and 32% are smaller than 0.15 mm; mill scale—1% of particles



Fig. 3.94 Steel baskets for charging brex together with pellets into a Midrex reactor

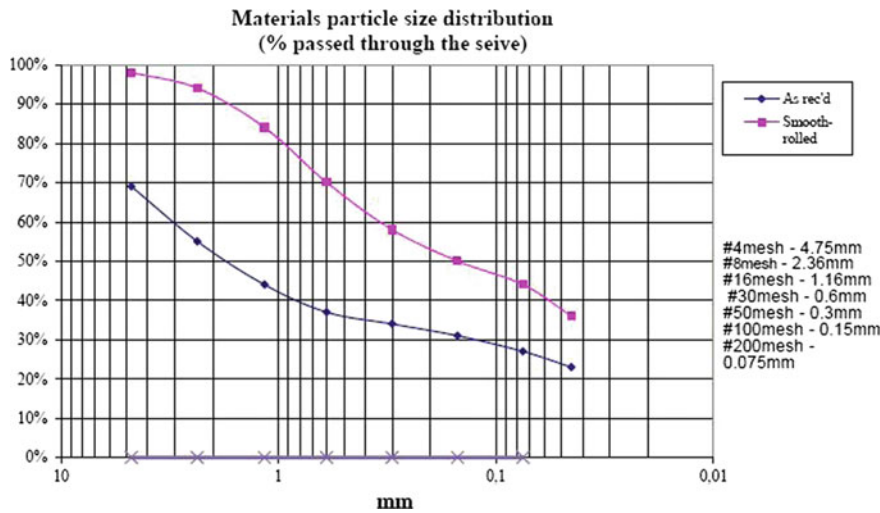


Fig. 3.95 Granulometric composition of the mixture of materials for briquetting: (1) initial mixture and (2) after additional pulverization (the maxima on the curves correspond to the mixture’s content of particles smaller than 5 mm)

are larger than 10.0 mm, 98% have sizes in the range of 0.15–10.0 mm, and 1% are smaller than 0.15 mm. The chemical compositions of the components of the mixture are given in Table 3.30.

Table 3.30 Chemical composition of the components of the mixture for brex production

Chemical compounds	Pellet fines	Mill scale	Sludge	EAF dust
Fe _{tot}	65.00	70.0	66.2	29.68
SiO ₂	2.50	1.00	2.14	4.25
CaO	1.30	0.15	4.38	19.74
MgO	0.75	0.10	0.69	24.27
Al ₂ O ₃	0.95	0.25	0.83	1.32
MnO	0.10	1.20	0.16	0.96
S	0.015	0.015	0.01	0.13
Na ₂ O + K ₂	0.034	–	0.33	1.42

Three batches of brex were produced, differing only in the type of binder used (Tables 3.31 and 3.32), which affected the physico-mechanical properties of brex (Table 3.33). The magnesia binder was made on the basis of magnesium sulfate heptahydrate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$).

One of the most important properties of brex, which determine its reducibility to a significant degree, is porosity. The study of the structure of the porosity of the samples was carried out using the software “STIMAN” [151]. To study the microstructure of the samples and the morphology, a fresh cleaved surface of the sample was used. For morphological studies of the microstructure, the secondary electron regime was used, which allows to obtain high-quality halftone images in a wide range of magnifications. The “STIMAN” technique allows obtaining correct images with sharper boundaries between pores and particles. The Phoenix V | tome | XS 240 industrial X-ray micro-tomography system, equipped with two X-ray tubes: micro-focus with a maximum accelerating voltage of 240 kV/power of 320 W and nanofocus with a maximum accelerating voltage of 180 kV/power of 15 W, was used to analyze the distribution of pores in the range of large and superlarge (from 1 to 100 μ and more). Primary data processing and the creation of a volumetric model of the sample based on X-ray images (projections) were performed using the software datos | x reconstruction, and the visualization and analysis of data on the

Table 3.31 Charge components for brex production

Charge components	Batch number		
	02-01	02-02	02-03
Pellet fines	50.0	50.0	50.0
Sludge	25.0	25.0	25.0
Mill scale	15.0	15.0	15.0
EAF dust	5.0	4.75	5.0
Slaked lime	5.0		
Portland cement		5.0	
Magnesium binder			5.0
Bentonite		0.25	

Table 3.32 Chemical composition of brex

Elements and oxides	Batch number		
	02-01	02-02	02-03
Fe _{tot}	62.47	61.3	62.61
C	1.49	1.40	1.05
CaO	9.24	8.41	4.30
MgO	3.61	3.07	6.24
SiO ₂	2.45	4.91	2.76
Al ₂ O ₃	1.29	1.81	0.99
TiO ₂	0.104	0.12	0.119
V ₂ O ₅	0.076	0.073	0.079
MnO	0.343	0.36	0.349
P ₂ O ₅	0.074	0.087	0.062
S	0.075	0.0816	0.502
Na ₂ O + K ₂ O	0.193	0.926	0.831
Cl	0.035	0.028	0.019
ZnO	0.362	0.4	0.346

Table 3.33 Physico-mechanical properties of brex

Elements and oxides	Batch number		
	02-01	02-02	02-03
Fe _{tot}	62.47	61.3	62.61
C	1.49	1.40	1.05
CaO	9.24	8.41	4.30
MgO	3.61	3.07	6.24
SiO ₂	2.45	4.91	2.76
Al ₂ O ₃	1.29	1.81	0.99
TiO ₂	0.104	0.12	0.119
V ₂ O ₅	0.076	0.073	0.079
MnO	0.343	0.36	0.349
P ₂ O ₅	0.074	0.087	0.062
S	0.075	0.0816	0.502
Na ₂ O + K ₂ O	0.193	0.926	0.831
Cl	0.035	0.028	0.019
ZnO	0.362	0.4	0.346

elements of the volume image using the software VGStudio MAX 2.1 and Avizo Fire 7.1. The survey was carried out at an accelerating voltage of 100 kV and a current of 200 mA. Shooting resolution was 5.5 μ .

The difference in the porosity values for these samples in the specified range of pore sizes (1–100 μm) exceeds 50%. In sample 02-01, open porosity prevails (pores are interconnected), and in sample 02-03, mostly closed porosity prevails. In other words, the permeability of samples of brex varies greatly. Such a difference in the porosity structure of brex also manifested itself at the very stage of their manufacture. Sample 02-03 was the only one whose manufacture was not accompanied by partial dehydration of the extruded mixture.

To study the behavior and reducibility in the Midrex industrial reactor, brex placed in deformable gas-permeable steel bags were loaded into the reactor along with pellets. At the end of the process, the packages were removed from the reactor, which made it possible to visually determine the state of the reduced brex (Fig. 3.96) and study their chemical composition and properties.

Brex on magnesia binder showed the greatest integrity, and the highest degree of fine generation is inherent to brex on cement binder. Lime binder brex were destroyed to a much lesser extent.

The mechanical strength of the reduced brex was determined in tensile splitting tests: brex 02-01—0.4 N/mm² and 1.2 N/mm² for brex 02-03. It can be seen that the strength of brex on the magnesia binder practically did not change as compared with its initial value (Table 3.38). Thus, the weakest brex in the “cold” state showed high hot strength. Accordingly, the degree of metallization of these brex turned out to be the highest among all tested samples. The decrease in the degree of



Fig. 3.96 Raw (top left) and reduced brex after extraction from steel packages

Table 3.34 Chemical composition and metallization of reduced brex

Elements and oxides	Batch number		
	02-01	02-02	02-03
Fe _{tot}	74.86	69.02	86.86
Fe _{met}	49.11	18.66	84
Metallization, %	65.6	26.96	96.71
C	1.75	0.89	1.02
CaO	9.11	6.71	5.07
MgO	2.93	2.24	7.81
SiO ₂	3.41	4.35	4.04
Al ₂ O ₃	1.57	1.45	2.13
TiO ₂	0.11	0.12	0.12
V ₂ O ₅	0.072	0.075	0.07
MnO	0.34	0.43	0.39
P ₂ O ₅	0.076	0.074	0.0134
S	0.0256	0.093	0.26
Na ₂ O + K ₂ O	0.48	0.51	0.74
Cl	0.018	0.013	–
ZnO	0.18	0.3	0.045

metallization of brex on the lime and cement binder is associated with a violation of the gas permeability of the packets due to the blockage of the holes with small fractions of collapsed brex. The chemical composition of the reduced brex and the degree of their metallization are presented in Table 3.34.

The structure of the reduced samples of brex was studied by light microscopy using Nikon equipment (ECLIPSE LV100-POL polarization microscope equipped with DS-5M-L1 digital photomicrography system) and MLA 650 instrumental automatic complex (FEI Company).

For tests, samples of brex on a magnesium binder and preserved integrity samples of brex on a cement and lime binder were used [164].

Low basicity zoned pellets ($\text{CaO/SiO}_2 = 0.3\text{--}0.5$) in the brex composition are represented by fragments of different mineral compositions: nuclei in the form of magnetite residues and shells consisting of hematite splices with calcium ferrites. Scale has a magnetite composition—a solid solution $(\text{Fe, Mn}) \text{O} \cdot \text{Fe}_2\text{O}_3$. A special role in the composition of brex is played by the EAF dust, which contains the main melt-forming components of the charge: CaO, MgO, SiO₂, MnO, and Na₂O.

The iron-containing minerals of the pellets and mill scale were partially reduced to the metal in the reduced and preserved integrity samples of the brex on the cement binder. Metallization of such brex after extraction from the reactor turned out to be equal to 94.21%. In the absence of an external mechanical effect, the surface of the brex on the cement binder cracked, which led to their softening. It is known that briquettes from pellet fines on a cement bond with a cement content in the range of 4–8% of the mass of the briquette, as well as the pellets themselves,

exhibit abnormal swelling upon reduction [53–55]. Note that earlier tests were performed with supplying brex on a cement binder in rigid baskets that prevented their mechanical destruction [165]. The appearance of rigid baskets and brex on the cement binder after removal from the reactor is shown in Fig. 3.97.

In the major body of the cement-bonded brex extracted from the steel mesh packages, there are the areas with the phases that are close in terms of their



Fig. 3.97 Rigid steel baskets for charging brex into the Midrex reactor (left) and the appearance of brex on the cement binder after removal from the reactor

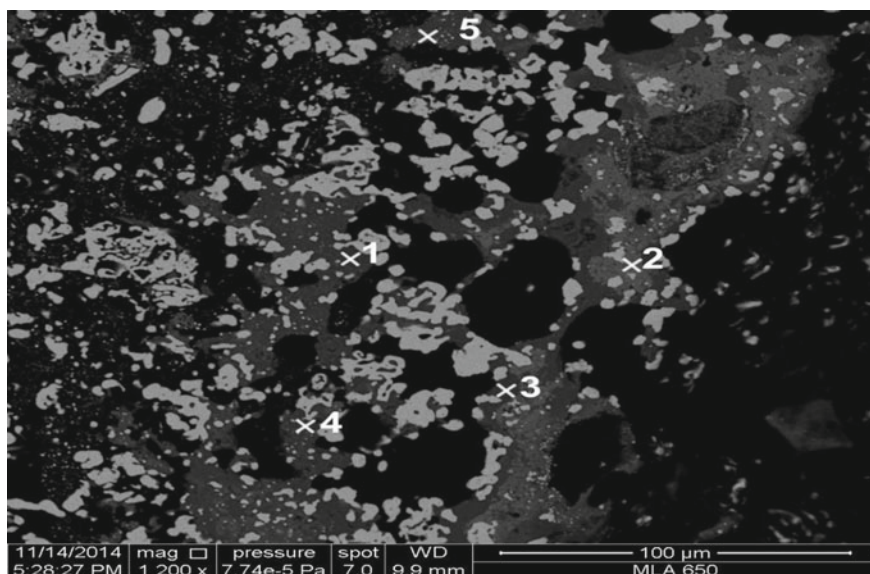


Fig. 3.98 SEM image of the reduced cement-bonded brex. 1, 3, 4—Binary metasilicates; 2—silica containing calcium ferrite; and 5—dicalcium ferrite

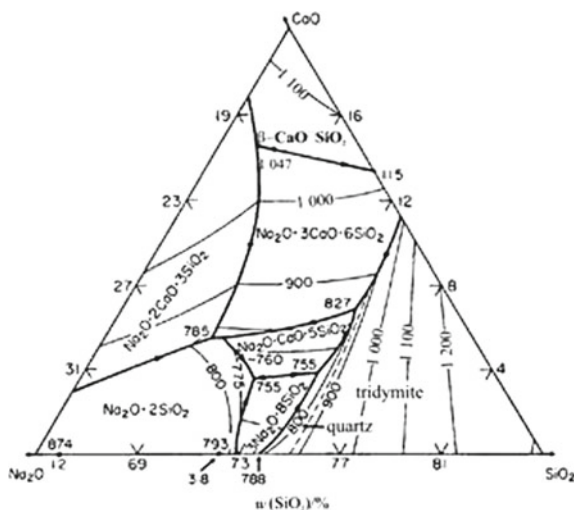


Fig. 3.99 Diagram of the system $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ [166]

composition to the binary metasilicates $2\text{Na}_2\text{O} \cdot \text{CaO} \cdot 3\text{SiO}_2 (\text{N}_2\text{CS}_3)$ and $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2 (\text{NC}_2\text{S}_3)$ without any presence of iron (Fig. 3.98).

N_2CS_3 melts incongruently [166] (melting starts at 1141 °C with the creation of 78.5% of the melt and 21.5% of NC_2S_3 , and ends at 1203 °C). NC_2S_3 melts congruently with an extensive field of primary crystallization. In the temperature range of the Midrex process, only two eutectics correspond to the diagram in Fig. 3.99: 755 °C— $\text{N}_3\text{S}_8 + \text{NCS}_5 + \text{S}$ (N_2O —22%; CaO —3.8%; and SiO_2 —74.2%) and 827 °C— $\text{N}_2\text{CS}_3 + \text{NC}_2\text{S}_3 + \text{NS}_2$ (N_2O —36.6%; CaO —1.8%; and SiO_2 —60.7%). In the phases detected by X-ray microprobe analysis, the CaO content exceeds 10%, which indicates the absence of melt formation in the indicated areas. The detected phases at temperatures in the range of 870–950 °C can be in a plastic state with an insignificant content of the liquid phase, as illustrated in Fig. 3.100.

In the cement-bonded brex, the alkali silicate phase is predominantly associated with the smallest, dusty fractions of the charge containing alkalis. The silicate bonding is not fully developed in the sample's body. Optical study of the samples of the reduced brex shows the pieces of dicalcium silicate (Ca_2SiO_4) crystals—a high-temperature phase that forms part of the cement.

Lime-bonded brex have a higher degree of metallization and a deeper interaction between charge components. According to the test results in rigid steel baskets, the degree of their metallization was 96.65%. For samples of brex extracted from deformable steel packages, the inconstancy of the composition of the iron silicate phase in different parts of the body of brex is typical. Most often, combinations of the silicate phase with metallic iron are observed. The primary iron silicate phase is

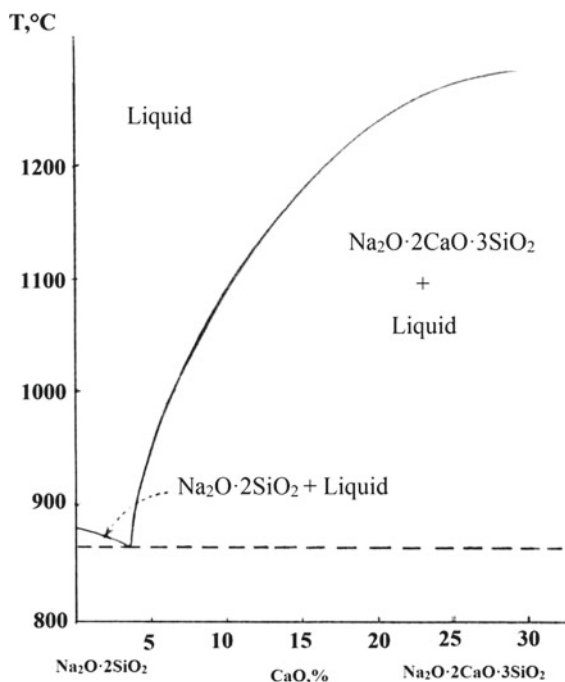


Fig. 3.100 Diagram of system $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ – $\text{Na}_2\text{O} \cdot 2\text{CaO} \cdot 3\text{SiO}_2$ [166]

in its composition close to the composition of the olivine phases and is characterized by an increased basicity ($\text{CaO}/\text{SiO}_2 = 0.8\text{--}0.9$).

Under the conditions of reduction existing in the Midrex reactor, a system of metallic whiskers forms on the contact of fragments of pellets with melt in the body of bres (Fig. 3.101).

In some cases, mineral formations with a high content of calcium oxide (in different areas up to 40 mass%) occur in lime-bonded bres, and the content of silicon oxide is 25–26 mass%. No other oxides are found in the composition of the amorphous iron–calcium phases with high calcium content. The composition of such phases is close to the melilite phase ($\text{Ca}_2\text{Fe}_3 + \text{Si}_2\text{O}_7$).

The predomination of the fine fraction within the bres is of particular interest. It consists of a combination of metal with calcium ferrites. Apparently, in pellet fines, consisting of the combination of hematite with calcium ferrite, the hematite phase was the first to reduce and such reduction took place without breaking contact with the ferrite.

Bres with magnesium sulfate binder exhibited the highest degree of metallization.

For the first time in [164], it was found that during the metallization process, the microstructure of the initial bres is not preserved. Bres is close to the state of a two-phase system: a metal and a silicate phase. However, the composition of the

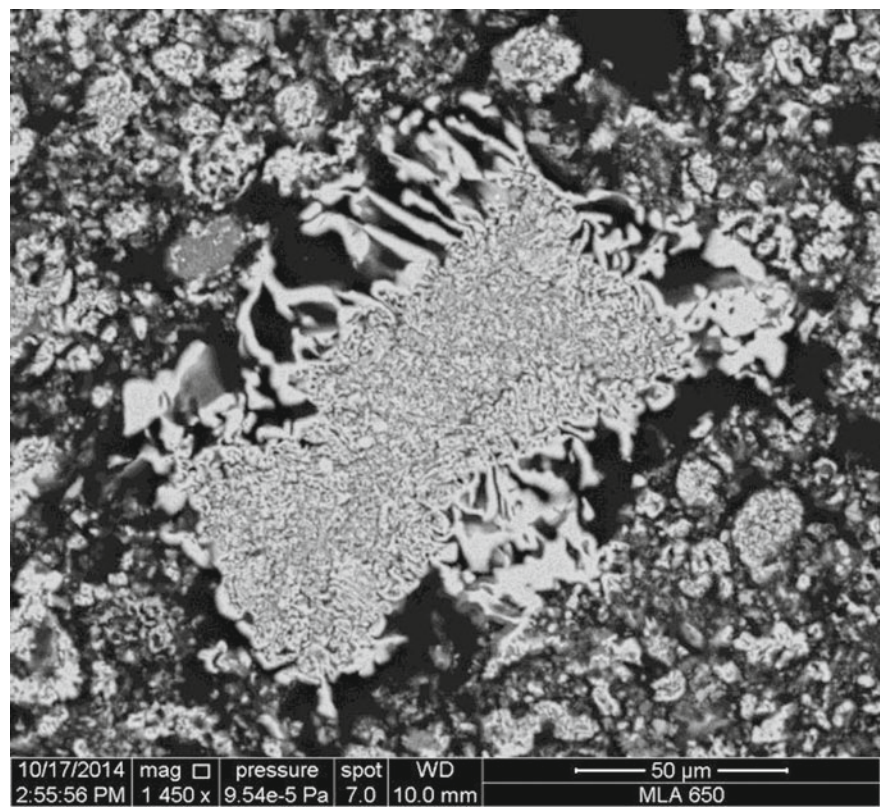


Fig. 3.101 Generation of the metallic “whiskers” at the contacts of the pellet fines and melts

silicate part remains variable in close volumes of the reacted fines. According to X-ray spectral microprobe analysis, two mineral species predominate among the studied phases, close to olivine and melilite compositions (Fig. 3.102), but each of them differs in the content of oxides of iron, magnesium, and manganese.

Thus, it is clear that the mechanism of the strengthening of brex samples in each case has its own specific characteristics. For cement-bonded brex, a lack of hot strength during heating in the reducing atmosphere is associated with their swelling and with the limited formation of silicate bonding. The strength of lime-bonded brex during the reduction process is provided by formation in the solid phase of the iron–calcium silicates, similar in composition to the olivine phase with a low melting temperature. Brex with the magnesium sulfate-based binder has the highest degree of generation of the two-phase metal–silicate system at the end of the metallization process.

During the process of reduction of the brex placed in deformable steel packages, their porosity changed in a different way. The results of the morphological studies are given in Table 3.35.

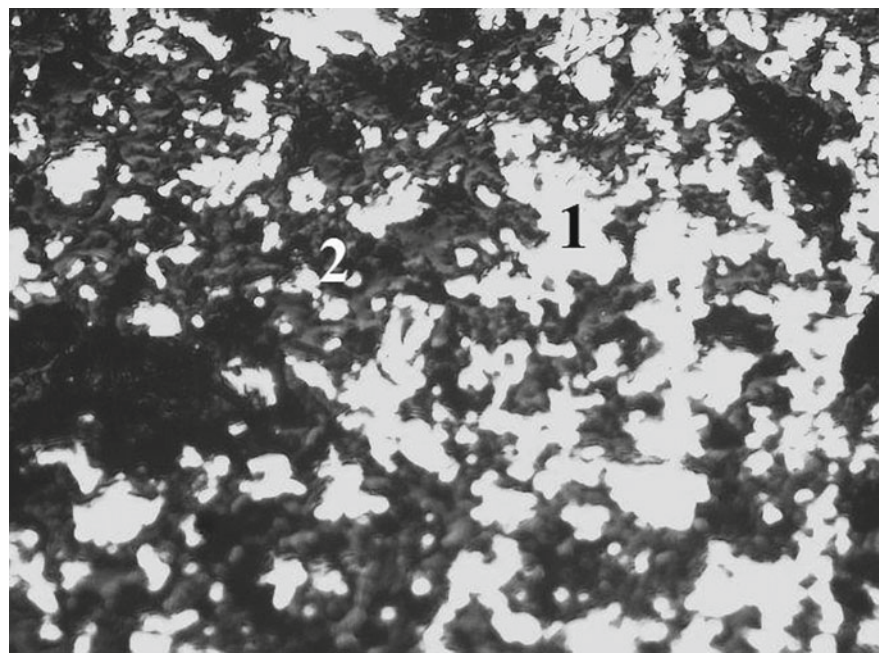


Fig. 3.102 Optical microscopy of the reduced lime-bonded brex (1—iron, 2—melilite; magnification 200)

Table 3.35 Morphological parameters of the original and reduced brex^a

Brex	Porosity SEM/ SEM + CT	Share of pores of different dimension categories in the total porosity (P_{tot} , %. Diameter in microns					Maximum diameter, μm
	P_{tot} , %	D1	D2	D3	D4	D5	Dmax
		<0.1	0.1–1.0	1.0–10	10–100	>100	
Brex No. 1	31.6	0.6	8.6	25.6	65.2	0.0	57.6
	37.3	0.5	7.2	21.4	66.8	4.1	407.2
Brex No. 1 (reduced)	32.9	0.2	9.0	38.4	52.4	0.0	70.94
	38.3	0.1	7.7	32.4	49.8	10.0	504.49
Brex No. 2	31.2	0.6	8.0	30.1	61.3	0.0	45.78
	35.7	0.5	7.0	26.2	61.3	5.0	299.96
Brex No. 2 (reduced)	37.9	0.2	9.3	31.1	59.1	0.3	100.51
	40.4	0.2	8.9	29.5	55.2	6.2	583.77
Brex No. 3	31.8	0.6	5.8	28.4	65.2	0.0	62.92
	32.9	0.5	5.5	27.2	65.3	1.5	191.89
Brex No. 3 (reduced)	32.8	0.2	3.2	35.7	60.9	0.0	71.75
	39.3	0.2	2.6	28.9	58.0	10.3	736.41

^a P_{tot} —total porosity calculated by the analysis of SEM image; $D1$ – $D5$ —different dimension categories of pores; D_{max} —maximum pore diameter; CT—computer tomography

During the process of metallization, the total porosity of brex with a magnesium sulfate binder increased by 19.5%, cement-bonded brex by 13.15%, and brex with lime as a binder only by 2.6%. The porosity increased due to large and mega-pores (larger than 100 μm): For brex with magnesium sulfate binder, they increased by 6.9 times, and for lime-bonded brex they increased by 2.43 times. In cement-bonded brex, the growth of share of large share was 1.24 times. The maximum diameter of pores in brex with a magnesium sulfate binder has increased by almost three times and in brex with a lime—by 1.23 times.

It can be assumed that the driving mechanism for the development of porosity in the brex was the crystal lattice-type changes during the hematite–magnetite phase transformation (at temperatures when the effect of binding materials is maintained), which results in an increase in the volume of the brex. This increase in volume is accompanied by mechanical stresses, which may lead to the partial destruction of brex, which leads to an increase in the proportion of large and mega-pores and to the formation of internal cracks. The stronger the brex is mechanically, the less it is prone to such partial destruction.

It should be recognized as successful the results of tests only for brex on a magnesium binder. The limitation of using brex on a magnesium binder during such recycling is an increased content of sulfur in the binder, which will partly pass into the top gas. In the absence of flue gas desulfurization, sulfur with gas will flow into the reformer, poisoning the catalyst. It is this parameter that will determine the allowable content of such brex in the charge of the metallization furnace.

The test results make it possible to consider the use of stiff vacuum extrusion for the implementation of the recycling of these wastes by briquetting them and metallizing the brex together with pellets. Tests in the Midrex industrial reactor of brex obtained using a magnesium binder from dispersed waste generated during production of metallized pellets and steelmaking have shown the possibility of achieving a high degree of metallization of the brex while preserving their integrity. The degree of metallization of brex on the magnesium binder (96.71%) is comparable to the degree of metallization of the main product of reactors for the direct production of iron—metallized pellets.

Tests in the Midrex industrial reactor of brex obtained using a magnesium binder from dispersed waste from the production of metallized pellets and steelmaking have shown that it is possible to achieve a high degree of metallization of the brex while preserving their integrity. The degree of metallization of brex on a magnesium binder (96.71%) is comparable to the degree of metallization of the main product of Midrex reactors for the direct production of iron—metallized pellets. The test results make it possible to consider the use of stiff vacuum extrusion for the implementation of the recycling of these wastes by briquetting them and metallizing the brex together with pellets. Brex on the magnesium binder, as a component of the mixture of reactors for direct production of iron, was granted a patent of the Russian Federation No. 2579706 [167].

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Chapter 4

Best Available Technologies for Agglomeration of the Raw Materials for Blast Furnaces



The best available technologies (BAT) concept was first time used in 1992 by OSPAR Convention for the protection of the marine environment of the North-East Atlantic for all types of industrial installations.

The best available technology must meet a set of criteria:

- the lowest level of negative impact on the environment per unit of time or volume of products (goods), work performed, services rendered;
- economic efficiency of its implementation and operation;
- application of resource-and energy-saving methods;
- period of its implementation;
- industrial implementation of this technology on two and more objects having a negative impact on the environment.

With regard to the processes of production of agglomerated iron-containing materials, the list of the BAT and their technological indicators is presented in the information technology directories of the best available technologies [1, 2].

4.1 Production of Sinter as a BAT

Sinter production, carried out by burning solid fuel in the airflow filtered through a layer of the iron ore charge, remains the primary method of agglomeration of iron ore materials to date. As a result of physical and chemical processes in the sintering layer, emissions of pollutants are formed:

- dust emissions are caused by the mechanical removal of the fines from the sintering layer or formed in the process of destruction of materials (sinter when coming of the sintering belt; cooling, crushing, and screening of the sinter cake after sintering);

- carbon monoxide (CO) emissions which, due to the combustion characteristics of the distributed solid fuel in the sintering layer (due to incomplete combustion), are technologically justified;
- emissions of sulfur dioxide (SO₂), depending on the sulfur content in coke fines, which is used as fuel, as well as the composition of iron ore charge;
- emissions of nitrogen oxides (NO_x) from combustion in ignition hoods; partially solid fuel combustion, and also due to the emission of “thermal” nitrogen oxides due to the nitrogen content in coke breeze and iron ore materials.

The sintering process involves a significant impact on the environment. It is enough to say [3] that in the structure of pollutant emissions of the integrated metallurgical plant for all the most significant emission components (dust, carbon monoxide, sulfur dioxide, nitrogen oxides), sinter production holds the leading positions (Table 4.1).

A priority source of emissions during sinter production, as can be seen from Table 4.1, is the processes of combustion. To ensure the goals of minimizing the impact on the environment and reducing the consumption of resources, the following technical solutions which can be attributed to the best available in the sinter production are applied [1]:

- reduction of fuel consumption due to rational charge preparation (optimization of granulometric composition of charge components, the component composition of the charge, the size of coke fines, etc.);
- increase in the height of the sintered layer (in most cases requires some amount of reconstruction of the sintering machine);

Table 4.1 Air emissions from major iron and steel industries^a

Production	Share of production in total emissions of components, %			
	Dust	CO	SO ₂	NO _x
Sinter	31.1	77.8	61.0	26.0
Steel making	19.7	5.4	0.02	6.5
Refractory (lime burning)	18.4	0.4	0.4	5.4
Blast furnace	17.3	3.5	0.3	3.0
Thermal power station—steam and air blower station	7.4	n/d	36.7	36.6
Coke making	2.0	7.8	1.0	9.1
Rolling production	1.2	n/d	0.2	10.5
Repair	1.0	4.9	0.02	1.5
Other	1.9	0.2	0.36	1.4
Total	100	100	100	100

The figures in bold show the contribution of sinter plants to emissions

^aFor specific enterprises can be characterized by different values while maintaining the structure of emissions

- improvement of the combustion conditions of coke fines in the layer by increasing the gas permeability of the charge [optimization of the pelletizing process, the introduction of lime, the use of modulators of combustion (water mist)];
- recirculation of waste gas heat (depending on the process requirements, different volumes of recirculation are possible, but under the conditions of moisture content, it cannot exceed 35%; in any case; the processing of agglomeration gases requires an obligatory additional supply of air (oxygen); organization of the flow of agglomeration gases is associated with an additional power consumption).

The above measures, improving the classical sintering technology, essentially provide no more than 20% reduction in emissions; the most radical technical solution (recycling of agglomeration gases) at the maximum possible amount of recycling reduces emissions to 50% (and thus obtain a specific emission at the level not higher than 10 kg/t of agglomerate).

4.2 Production of Pellets as a BAT

Pellets production refers to pyrometallurgical technologies, since the strengthening of agglomerated granules (raw pellets) requires high-temperature (1250–1350 °C) firing.

The emissions generated by the pellets production are due solely to the combustion of natural gas to ensure the heat requirements of firing and the chemical transformation of the components of the charge (oxidation of sulfur compounds):

- emissions of NO_x from the combustion process in heated sections of an induration machine hearth;
- emissions of SO_2 , determined by the sulfur content in iron ore material (concentrate);
- dust emissions due to mechanical removal of dispersed particles of raw pellets, indurated pellets during unloading from the induration machine, their sieving, loading.

Due to stoichiometric combustion of natural gas, there is no chemical under-burning, so carbon monoxide is practically not formed.

Measures to reduce emissions of nitrogen oxides are associated with the use of burners of special design with the low formation of nitrogen oxides, or technology of selective catalytic reduction of nitrogen oxides (efficiency up to 60%).

4.3 Stiff Extrusion Briquetting as a BAT

Pyrometallurgical technologies of agglomeration are associated with the formation of essential emissions, which logically leads to the conclusion that for the radical reduction of environmental impact in the technologies of preparation of metallurgical raw materials for smelting, combustion-free processes are promising.

The technology of production of cold-bonded pellets is studied in detail in Chap. 2 (Sect. 2.4).

To obtain the proper strength, cold-bonded pellets contain a binding substance (the most applicable is Portland cement) and therefore require heat and moisture treatment followed by strengthening for 7–28 days or drying with heating (the optimum temperature is 200–250 °C).

The technology of briquetting by the method of stiff vacuum extrusion is devoid of such disadvantages. The technology does not require heat treatment of raw extrusion briquettes (brex), and it allows to obtain a durable material (hot strength of the briquette from magnetite concentrate and coke fines in terms of $RDI_{+6.3}$ exceeds $RDI_{+6.3}$ of sinter with a basicity of 1.2–1.6) of isometric shape and metallurgical dimensions, suitable for loading into a blast furnace (as well as for use in other metallurgical units).

As in the case of cold-bonded pellets, a binder is required to be introduced into the batch for the production of brex, the consumption of which is reduced in comparison with the production of non-ignition pellets, and in some cases (for individual charge) the addition of a plasticizer is required in the batch for the production of brex.

Technological scheme of the brex production has been described in Chap. 3 (Sect. 3.5.1.3; Fig. 3.73).

The main sources of environmental impact in the production of brex are the following:

- warehouse of raw materials (unloading operations of charge materials, storage and feed into the technological process);
- department of dosing, mixing, extrusion;
- brex unloading, stacking, and handling of stacks (the attrition of the fine fraction, shipment to consumers);
- aspiration system of brex making unit.

The main component of emissions into the atmospheric air in the production of brex is inorganic dust. According to the assessment, the specific emission of inorganic dust in the production of brex does not exceed 0.05 kg/t.

The technology of briquetting by the method of stiff vacuum extrusion is very effective not only as a method of utilization of anthropogenic materials, but primarily as an environmentally safe alternative to the agglomeration process [1].

4.4 Comparative Analysis of Technologies for Agglomeration of the Raw Materials for Blast Furnace

Comparison of various agglomeration technologies according to the criteria of the best available technologies [1, 2] is presented in Table 4.2.

From Table 4.2, in comparison with the production of sinter and pellets, brex have a minimal performance impact on the environment and energy consumption and requires significantly smaller investment, which qualifies the technology of briquetting by stiff vacuum extrusion as the best available technology.

Agglomerating iron-bearing materials by the stiff vacuum extrusion is a highly efficient technology which is capable to compete with sinter production. Brex fully complies with the requirements imposed by the conditions of the blast furnace.

Table 4.2 Characterization of various agglomeration technologies according to the criteria of the best available technologies (BAT)

#	BAT criterion	Agglomerated iron-containing material		
		Sinter	Pellet	Brex
1	The minimum level of impact on the environment, kg/t			
	– Dust	≤ 1.2	≤ 0.6	0.05 ^a
	– Nitrogen oxide	≤ 0.55	≤ 0.535	0
	– Sulfur dioxide	≤ 4.0	≤ 0.5	0
	– Carbon oxide	≤ 14.0	~ 0	0
	Total emissions, kg/t	≤ 20	≤ 2	≤ 0.05
2	Resources consumption			
	– Solid fuel, kg/t ^b	23.6–48.9	0	0
	– Gaseous fuel, m ³ /t	2.45–6.3	9.5–15.0	0
	– Electricity, kWh/t	23.0–48.7	29.0–48.5	15.0–33.0
3	Investments, USD/t ^c	~ 5000	~ 5500	~ 2000
4	Implementation period, years ^d	3	3	2

Notes

^aEstimation (based on following sources: ore warehouse, loadings, dosing, and mixing of charge components, the unloading of the finished brex, stacking and stack handling, aspiration system of shop floor space)

^bRefers to the provision of heat treatment

^cAdopted the averaged specific indicator for the implementation on a “turnkey” basis

^dThe conditional duration of the investment cycle for productivity of 1 million tons of the product is taken; for the production technology of brex, the duration is reduced due to significantly lower metal consumption level (the volume of construction works)

In terms of environmental impact and resource consumption, this method can be qualified as the best available technology.

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