

# EXTRACTIVE METALLURGY OF ACTIVATED MINERALS

P. BALÁŽ

Process Metallurgy 10

## **EXTRACTIVE METALLURGY OF ACTIVATED MINERALS**

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Process Metallurgy 10

# EXTRACTIVE METALLURGY OF ACTIVATED MINERALS

by

**P. BALÁŽ**

Institute of Geotechnics, Slovak Academy of Science, Slovakia



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## **DEDICATION**

Dedicated to my wife Ela and sons Peter, Pavol and Matej.

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## INTRODUCTION

Mechanical activation of solid substances is one of the component of the modern scientific discipline of mechanochemistry. At present, mechanochemistry appears to be a science with a sound theoretical foundation which exhibits a wide range of potential application. Amongst the commercially operating processes: modification of the properties of building materials, a new method of fertilizer production, activity enhancement and regeneration of catalysts, new methods of producing slow-dispensing medical drugs, control of reactions in chemical technology and preparation of advanced materials.

Mechanical activation is of exceptional importance in mineral dressing and extractive metallurgy and this area forms the topic of this book and is the result of more than twenty years of research and graduate teaching in the field.

The first chapter deals with the history of mechanochemistry, its theories and models and describes the development of ideas in the field of mechanical activation of solids. The equipment used for mechanical activation and their working regimes are also described.

The second chapter is devoted to selected modern identification methods (infrared spectroscopy, photoelectron spectroscopy, electron paramagnetic resonance, Mössbauer spectroscopy and X-ray diffraction) which are commonly used for the investigation of mechanically activated solids. The principles, practical application and limitations of these techniques are presented with examples drawn from the study of minerals.

All the currently available knowledge relating to physico-chemical properties of mechanically activated minerals, i.e. particle disintegration, new surface formation, aggregation and crystal structure disordering are summarized in the third chapter. The changes in these physico-chemical properties are frequently observed to occur concomitantly, e.g. there are relationship between new surface area formation and disordering of crystal structure and between disordering and changes in the hyperfine structure of mechanically activated minerals.

Polymorphous transformations in minerals induced by intensive grinding are the topic of the fourth chapter.

Chapter five, six and seven are concerned with the central problem of the solid state chemistry, i.e. the relationship between structure and reactivity of solids. This is examined for thermal decomposition (chapter five), chemical leaching (chapter six) and bacterial leaching (chapter seven) and verifies the stimulation and control of the elementary processes of extractive metallurgy by means of mechanical activation of reacting components. The careful choice of grinding conditions enables us to study the structural sensitivity of solid-gas or solid-liquid reactions. The most important results from these chapters are:

- enhancement of reductive decomposition and solid state exchange reactions, especially from the view-point of wasteless and ecologically harmless processes in extractive metallurgy,
- new knowledge concerning chemical leaching of minerals containing gold and silver, especially from the view point of intensification of extraction of these metals and
- the possibility of enhancing the rate of bacterial leaching of sulfides by activating the minerals.

The closing chapter is concerned with technological aspects of the mechanical activation of minerals. The effect of mechanical activation by intensive grinding is examined for flotation, oxidative leaching of non-ferrous metals, gold and silver extraction, sorption of metals from industrial liquors, etc. Some results deserve particular attention due to the achievement of separation not previously achieved e.g. selective extraction of copper and zinc from CuPbZn concentrates and the application of mechanochemical leaching of CuSb concentrates which is heading for industrial exploitation in a new hydrometallurgical plant in Slovakia. Other processes where mechanical activation plays a role, such as ACTIVOX<sup>TM</sup>, METPROTECH, IRIGETMET and SUNSHINE, are described in this chapter as well.

This monograph is designed for researchers and operators in the areas of extraction metallurgy, mineral processing, mineralogy, solid state chemistry and material science as well as for university students of this orientation. It is hoped that this book will encourage newcomers to the mechanochemistry to do useful research and discover novel applications in this field.

## **Chapter 1 MECHANOCHEMISTRY AND MECHANICAL ACTIVATION OF SOLIDS**

- 1.1. History of mechanochemistry**
- 1.2. Theories of mechanochemistry**
- 1.3. Mechanical activation**
- 1.4. Equipments for mechanical activation**
- 1.5. References**

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## 1.1. History of mechanochemistry

The first systematic papers concerned with the effect of grinding on properties of substances were published in the last century by Carey Lea [1.1-1.3]. He investigated the halides of gold, silver, platinum and mercury and observed that they decomposed to halogen and metal because of trituration (fine grinding) in a mortar. According to the author, the decomposition cannot be attributed to temperature because these substances exhibit sufficient thermal stability. In these publications, it was for the first time pointed out that not only heat, light and electric energy but also mechanical energy is able to initiate chemical reactions.

Flavickij [1.4-1.5] and later Parker [1.6-1.7] investigated the chemical reactions initiated by trituration in more detail. The method of trituration was applied later to qualitative analysis of natural mixtures in geology [1.8].

Tamman [1.9] investigated the effect of mechanical energy on metals. According to this author a part of this energy (5-15 %) remains accumulated in material thereby raising its thermodynamic potential. Owing to this fact a considerable increase in the rate of material dissolution occurs. In the forties, Clark and Rowan found that the grinding of solid substances could produce equal effect like high pressure or shear strain [1.10]. Bowden and Tabor [1.11] allege that temperatures over 700°C can be observed at the contact of solid substances exposed to friction. These high temperatures, however, last only  $10^{-4}$ - $10^{-3}$  s. According to this hot-spot model, these localized temperatures significantly promote the mechanically induced reactions.

In fifties, Peters investigated the influence of mechanical energy on a great number of reactions, such as synthesis and decomposition of carbonates, redox reactions, reactions connected with colour change, etc. [1.12-1.13]. The author points out the thermodynamic point of view concerning realization of reactions. Heinicke alleges in his monograph [1.14] that many reactions for which the equilibrium thermodynamics does not afford favourable conditions can be realized by the effect of mechanical energy. In some cases, the application of nonequilibrium thermodynamics seems to be serviceable.

A typical reaction is the oxidation of gold by carbon dioxide



This reaction (1.1) is improbable from the point of equilibrium thermodynamics: at 25°C the change of Gibbs free energy is  $\Delta G = + 312 \text{ kJmol}^{-1}$ . However, in paper [1.15] it was determined that under conditions of mechanical treatment the reaction proceeds.

The term mechanochemistry was introduced by Ostwald [1.16-1.17] who was engaged in the systematization of chemical sciences from the energetic point of view. He understood mechanochemistry in a wider sense when compared with the present view, regarding it as a part of physical chemistry like thermochemistry, electrochemistry or photochemistry. Subsequently, the boundaries of mechanochemistry were contracted. For instance, Hüttig [1.18] assumes that mechanochemistry includes only the release of lattice bonds without any formation of new substances (i.e. he supports the physical approach) while Peters [1.13] puts in this category transformations due to mechanical stress of material which are accompanied by chemical reaction. At present the definition of Heinicke is widely accepted: „*Mechanochemistry is a branch of chemistry which is concerned with chemical and physical-chemical transformations of substances in all states of aggregation produced by the effect of*

mechanical energy“ [1.14]. The definition put forward by Butjagin is: „*Mechanochemistry is a science on acceleration and initiation of reactions in gases, liquids and solids by the effect of plastic energy*“ [1.19]. In German literature we also meet with the term tribochemistry. But in this case the effects of friction, lubrication and abrasion accompanying the grinding of substances in solid state are given particular attention.

## 1.2.Theories of mechanochemistry

In the sixties, Thiessen proposed the first model in mechanochemistry – *the magma-plasma model* [1.20]. According to this model a great quantity of energy is set free at the contact spot of colliding particles. This energy is responsible for formation of a special plasmatic state which is characterized by emission of fairly excited fragments of solid substance, electrons and photons over a short time scale (Fig. 1.1). The surface of contact particles is rather disordered and local temperatures can reach more than 10000 Celsius. Thiessen distinguishes the reactions which occur in the plasma from the reactions taking place at the surface of particles during the significantly excited state, or immediately after its expiration. These considerations led to an important conclusion which is valid for mechanically activated reactions - these reactions do not obey a single mechanism.

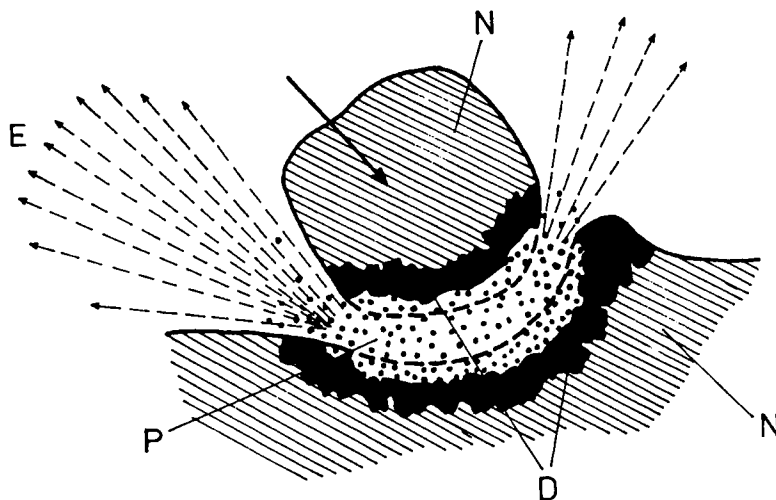


Fig. 1.1 Magma-plasma model for the impact stress of flying grain, E – exoemission, N – normal structure, P – plasma, D – disordered structure [1.20].

The German school elaborated the concept of „hierarchy“ of energetic states which appeared to be very important for analysis of the processes induced by the effect of mechanical energy [1.20-1.24]. In this concept, a large number of excitation processes occur due to mechanical activation and are characterized by different relaxation times (Table 1.1).

Table 1.1 Relaxation times of excitation processes in mechanically activated solids [1.24]

| Excitation process                                                            | Relaxation time                         |
|-------------------------------------------------------------------------------|-----------------------------------------|
| Impact process                                                                | $> 10^{-6}$ s                           |
| Triboplasma                                                                   | $< 10^{-7}$ s                           |
| Gaseous discharge                                                             | $\sim 10^{-7}$ s                        |
| “Hot spots”                                                                   | $10^{-3} - 10^{-4}$ s                   |
| Electrostatic charging                                                        | $10^2 - 10^5$ s                         |
| Emission of exoelectrons                                                      | $10^{-6} - 10^5$ s                      |
| Triboluminescence                                                             | $10^{-7} - 10^3$ s                      |
| Lattice defects<br>(e.g. $V_k$ centres in LiF with different<br>temperatures) | $10^{-7} - 10^6$ s                      |
| Dislocation motion                                                            | $10^5 \text{ cms}^{-1}$                 |
| Lattice vibrations                                                            | $10^{-9} - 10^{-10}$ s                  |
| Fracture formation                                                            | $10 - 10^3 \text{ cms}^{-1}$            |
| Fresh surface                                                                 | at $1.3 \cdot 10^{-4}$ Pa: $1 - 10^2$ s |
| Life time of excited metastable states                                        | at $10^5$ Pa: $< 10^{-6}$ s             |
|                                                                               | $10^{-3}$ s                             |
|                                                                               | $10^{-2}$ s                             |

Thiessen [1.24] shown the value of classifying tribochemical reactions according to the excitation processes initiating the individual reactions and to subdivide these excitation processes in their temporal courses. This way one will arrive at a hierarchic model, in which the most highly excited states having the shortest excitation times stand at the beginning and the numerous other states with smaller excitation incorporate themselves according to their temporal occurrence in the dissipation phase into the model.

During one of the first conferences on mechanochemistry in Berlin 1983 Thiessen demonstrated the different stages of an impact stress by a *spherical model* (Fig. 1.2).

By this simplifying model it could be shown that the impact stress is combined with the appearance of different species. This state is limited to very small spaces and very short times and qualified as triboplasma [1.24]. The concept of triboplasma was later developed from thermodynamic and kinetic point of view.

The short life of triboplasma causes no Maxwell-Boltzmann distribution so that an equilibrium temperature cannot be given and the chemical process taking place in this excitation phase cannot be described by the laws of thermodynamics. The conversions in triboplasmas are of a stochastic nature. The highest stage of energy excitation changes dynamically into the next stage, characterized by the relaxation of the plasma states and termed “edge-plasma” and “post-plasma”. A step diagram of the energy dissipation was composed for the total process in the form of a “hierarchy” of the energy states (Fig. 1.3). A number of physical processes (see Table 1.1) take place in this step, such as the recombination of plasma products, the propagation of dislocations, fracture processes, the propagation of photons and the emission of electrons and photons which have important functions for the initiations of chemical reactions [1.14].

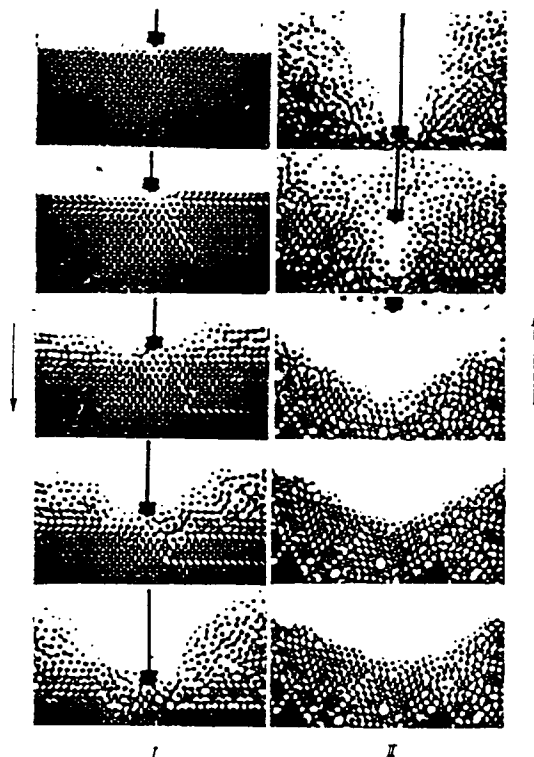


Fig. 1.2 Different stages of the impact stress schematically shown by the *spherical model* (↓ - penetration into the lattice of the solid, ↑ - decay phase up to the condition of frozen lattice distortion) [1.24].

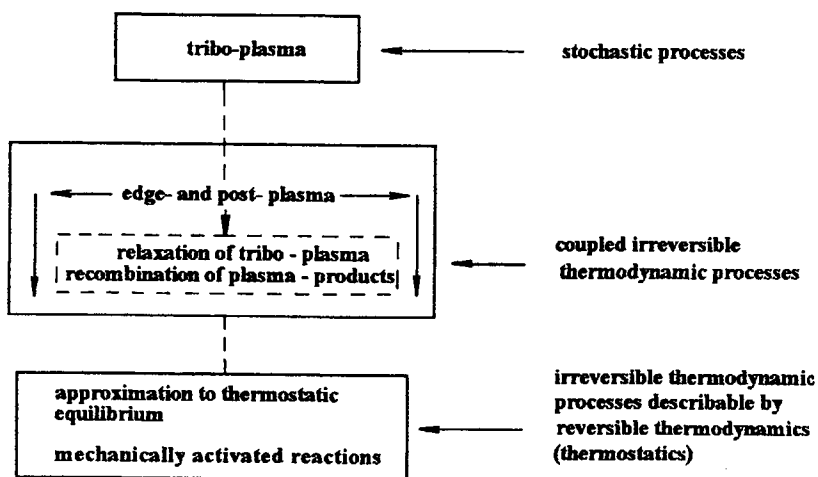


Fig. 1.3 Step diagram of the energy dissipation on solids stressed by impact [1.22].

The general kinetics of a mechanochemical reaction during the steady – state effect of mechanical energy on a reacting system may be shown by Fig. 1.4.

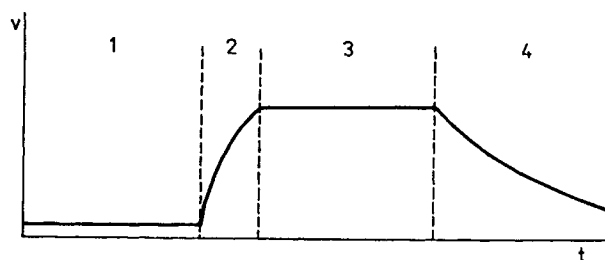


Fig. 1.4 General diagram of a mechanochemical reaction course,  $v$  – reaction velocity,  $t$  – reaction time, 1 – reaction on untreated solid, 2 – rising reaction, 3 – steady-state reaction stage, 4 – decaying reaction [1.14].

From Heinicke [1.14], the reaction occurs before the beginning of the mechanical treatment (phase 1) is determined by the thermal excitation and is therefore a function of the reaction temperature. However, at room temperature most solid reactions proceed immeasurably slowly. The application of mechanical energy generally results in a significant increase of the solid reaction velocity (phase 2). After having passed through the rising phase a constant reaction velocity appears under external constant conditions (phase 3). After the interruption of the treatment, the decay phase comes into the existence (phase 4).

It was shown later that the mechanochemical reaction course described by Fig. 1.4 had a general character. However, the course of reaction is not only determined by the type of reaction but also by the kind and the intensity of applied mechanical energy, since these factors also determine the formation of the defects mainly responsible for the solid state reactions.

The authors of *dislocation theory* allege that the mechanical action on solid substances gives rise to dislocations which come to the surface and subsequently become areas with increased chemical activity [1.25]. The motion of dislocations in solid substance is accompanied by the formation of phonons due to interactions between dislocations and other dislocations, defects, admixtures or interfaces.

*The phonon theory* emphasizes the distribution, mutual effect and origination of phonons in the course of disordering of solid substances by grinding [1.26].

Butjagin developed *the theory of short-lived active centres* [1.27]. It consists of the idea that new surface arising during mechanical activation are unable to stabilize in the  $10^{-9}$ - $10^{-11}$  seconds of thermal excitation. During the  $10^{-4}$ - $10^{-7}$  seconds required for stabilization, chemical bonds are liable to rearrangement, the electric surface relief is formed and further relaxation processes proceed. The decay of short-lived centres is related to the relaxation of excess energy. In vacuo, this relaxation is due to rearrangement of chemical bonds, whereas the interactions of short-lived centres with the molecules of surrounding medium are responsible for relaxation in chemically active medium. This is a case of exothermic process which can be accompanied e.g. by luminiscence or other phenomena involving radiation of energy.

Hüttig elaborated *the thermodynamic theory of active state* of solid substances [1.18]. He defined the activated solid substance as a thermodynamically and structurally unstable arrangement at temperatures exceeding the melting point. He characterized the activated state of solid substance by “residual” Gibbs energy  $\Delta G$

$$\Delta G = G_T^* - G_T \quad (1.2)$$

Where  $G_T^*$ ,  $G_T$  and  $T$  are the free enthalpy of activated solid substance, free enthalpy of this substance in non-activated state and temperature, respectively.

According to Zelikman [1.28] the quantity  $\Delta G$  consists of two terms

$$\Delta G = \Delta G_1^* + \Delta G_2^* \quad (1.3)$$

where  $\Delta G_1^*$  is the residual surface energy and  $\Delta G_2^*$  is the energy of lattice defect formation.

It holds for surface energy  $\Delta G_1$

$$\Delta G_1 = \sigma \Delta S \quad (1.4)$$

where  $\sigma$  is specific surface energy and  $\Delta S$  is change in overall surface of a solid. According to Schrader [1.29] for intensive grinding and activation the surface energy  $\Delta G_1$  is approximately equal to 10 % of overall Gibbs energy  $\Delta G$  for ionic crystals.

According to the Gibbs-Helmholtz equation it holds

$$\Delta G = \Delta H - T\Delta S \quad (1.5)$$

where  $\Delta H$  is enthalpy and  $\Delta S$  is entropy. If entropy  $\Delta S$  is small (crystal structure is preserved and its disordering is slight), the term  $T\Delta S$  is small and the Gibbs energy  $\Delta G$  is predominantly determined by change of enthalpy  $\Delta H$ . For highly disordered solids the entropy  $S$  becomes significant and the term  $T\Delta S$  cannot be omitted. In this case the value of  $\Delta G$  can be calculated from experimental values of the equilibrium constants of chemical reaction according to the equation

$$\Delta G = - R T \ln \frac{K_p^*}{K_p} \quad (1.6)$$

where  $K_p^*$  and  $K_p$  are equilibrium constant of activated substance and equilibrium constant of this substance in non-activated state, respectively.

Boldyrev analyzed in his *kinetic model* the specific features of mechanochemical effects from the view-point of limiting stages of the process [1.30]. The decomposition process of solid substance can be evaluated according to activation, deactivation and proper chemical reaction. We can discern two boundary cases: the decay is limited either by the processes of excitation and bond splitting (e.g. thermal decomposition) or by following stages (e.g. transformation of intermediates arising in the primary stage). The kinetic model put forward by the author was experimentally verified.

*The impulse model*, developed by Ljachov, is based on the idea that the kinetics of the reaction is determined by the time in which substance is liable to be in contact with balls,

owing to the impulse effect of grinding balls on solid substance [1.31]. This time is different from the overall time of grinding and is connected to the temperature rise during the impulse. The author succeeded in determining the equivalent temperatures corresponding to the contact of grinding balls with solids and verified this idea. The impulse character of mechanical action was pointed out in Boldyrev's works [1.30, 1.32].

It was Heegn who has formulated *the theory of the energy balance* of grinding processes in mechanical activation [1.33-1.34]. It was shown that the individual mill parameters as well as the different mill types lead to characteristic changes of the crystal lattice of solids.

Later on Tkáčová published *an analogous model* based on similarity of energy transfer in mill with the energy transfer in an electric circuit [1.35]. This concept was experimentally verified with a great deal of minerals and has enabled a description of the mechanical action for variable specific energies of structural disordering of solids.

### 1.3.Mechanical activation

The term mechanical activation was introduced by Smékal [1.36] who regarded it as a process involving an increase in reaction ability of a substance which remains unchanged. Provided the activation brings about a change in composition or structure, it is a mechanochemical reaction. In this case, the mechanical activation precedes the reaction and has no effect during the course of this reaction. The definitions of mechanical activation published later were always dependent on the observed effect.

It was Butjagin [1.37] who contributed to a certain unification. He considered the behaviour of the solids exposed to the effect of mechanical energy from the view-point of three main aspects: structural disordering, structure relaxation and structural mobility. Under real conditions, three factors simultaneously affect the reactivity of a solid. Butjagin defines the mechanical activation as an increase in reaction ability due to stable changes in solid structure.

However, structural relaxation plays the important role in reactivity of solids. Ljachov [1.38] described the concept of slowly changing states after interrupting the action of mechanical forces by activation. He published a generalised relaxation curve for activated solids where different parts of the curve correspond to processes with different characteristic times of relaxation (Fig. 1.5).

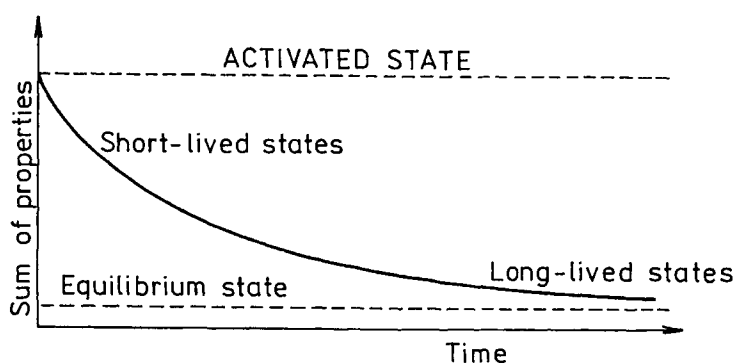


Fig. 1.5 A generalised relaxation curve of mechanically activated state [1.38].

By this theory there is no possibility of influencing the reactivity of activated solids via states whose relaxation time is less than characteristic time of reaction itself. On the contrary, some long-lived states (e.g. surface area) may be regarded as constant during the course of a reaction and their influence has to be a subject of mechanical activation studies.

As for the kinds of relaxation processes various processes were described: heating, formation of a new surface, aggregation, recombination, adsorption, imperfections, chemical reaction between adjoining particles, etc. [1.32, 1.39]. The rate of these relaxation processes may be vastly different and the processes can change from one way of relaxation to the other (Fig. 1.6).

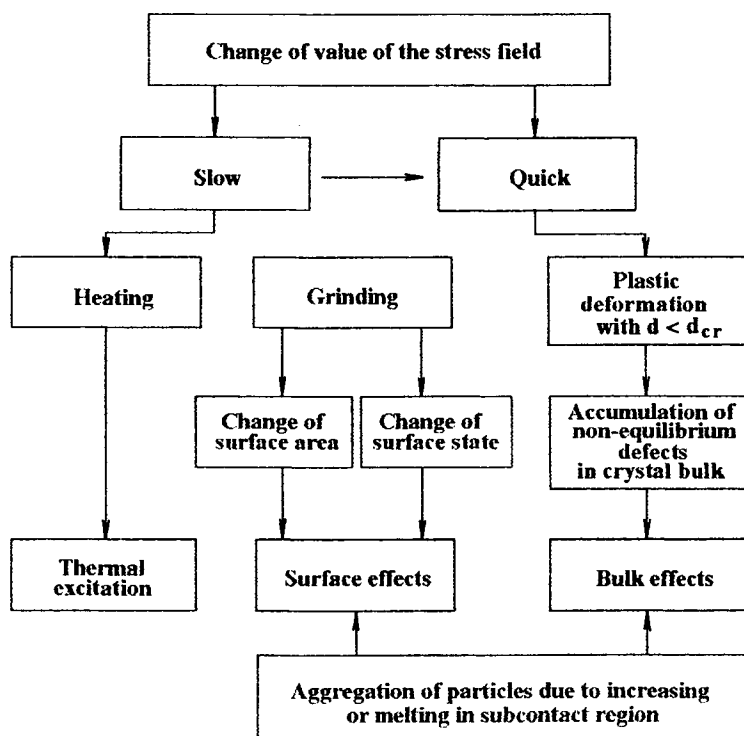


Fig. 1.6 Flowsheet of changes of relaxation processes [1.32].

Thus, mechanical activation can be regarded as a multi-step process with changes in the energetic parameters and the amount of accumulated energy of solids in each step.

Juhasz proposed that processes under the influence of mechanical activation can be subdivided into primary and secondary ones [1.39-1.40]. The primary process (e.g. increase of internal and surface energy, increase of surface area, decrease of the coherence energy of solids) generally increase the reactivity of the substance. The secondary processes (e.g. aggregation, adsorption, recrystallization) take place spontaneously in activated systems and may appear even during grinding or after grinding has been completed.

The multi-step character of mechanical activation was analysed by Molčanov [1.41]. It was assumed that the amount of accumulated energy changes in each step and four, potentially overlapping steps of mechanical activation were distinguished.

*Step I.* Precedes the structure disordering and is the effect of applying a force smaller than the strength limit of a given substance. In crystalline substances, the atoms are deflected from their “normal” positions. The crystal lattice is disordered and the intermolecular, interatomic and interionic distances as well as the angles of orientation in structure alter.

*Step II.* It involves the origination of new surface. The structural disordering and origination of cracks in solids is interesting for several reasons. It is interesting not only as a process resulting in a change in energetic state but also as a process producing transformation of the mechanical energy of mill into surface energy of the ground substance.

*Step III (fine grinding).* The formation of new surface and the accumulation of energy in surface layer at the interface significantly influence the thermodynamic properties of a substance and bring about significant change in structure and properties of the ground solid.

*Step IV (ultrafine grinding).* In this stage, the solid loses its original identity and turns into a substance showing different structure, properties and sometimes even different composition. The term mechanochemical activation instead of mechanical activation is better in this case [1.42].

#### 1.4.Equipments used for mechanical activation

The multi-stage character of mechanical activation requires the application of equipment (generally called mills) with different working regimes. The main stress types applied by activation are compression, shear (attrition), impact (stroke) and impact (collision) (Fig. 1.7).

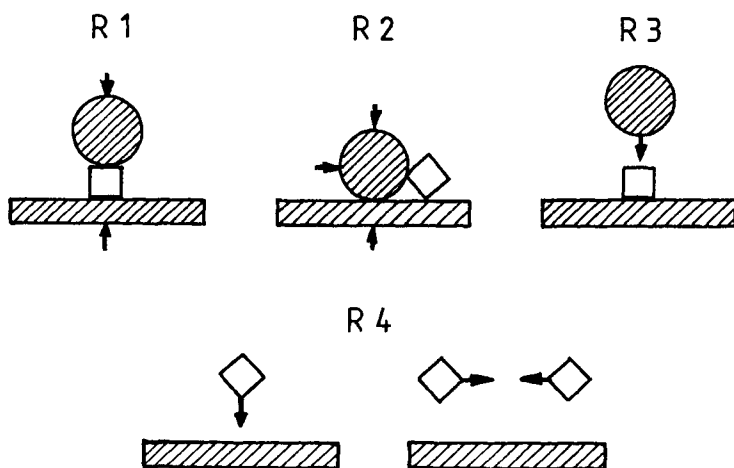


Fig. 1.7 Main stress types in mills, R1 - compression, R2 - shear (attrition), R3 - impact (stroke), R4 - impact (collision), ○ - mass of grinding media, □ - mass of material charge, ▨ - mass of mill wall [1.14].

In fact, there are various factors affecting the operation of the grinding process [1.43] such as

- types of mills (Fig. 1.8),
- types of grinding media (balls, rods or other shapes),
- material of grinding tools (e.g. stainless steel, tungsten carbide, zirconium oxide, aluminium oxide, silicon nitride),
- grinding atmosphere (e.g. air, inert gas, reductive gas),
- grinding mode (dry or wet),
- ball-to-activated material size ratio,
- ball-to-activated material weight ratio,
- grinding temperature,
- speed of the mill and
- grinding time.

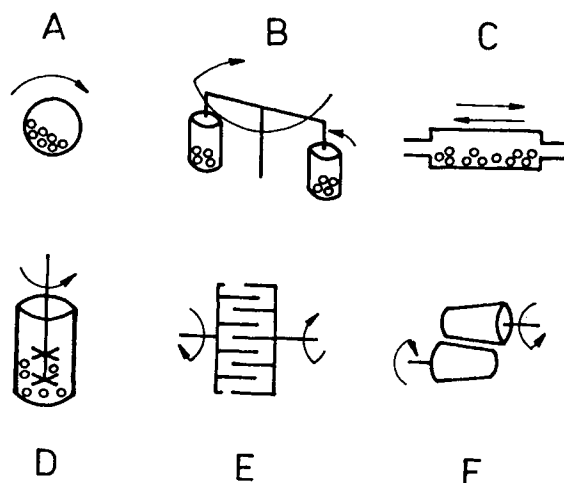


Fig. 1.8 Types of mills for mechanical activation and the stress types, A – ball mill (R1-R4), B – planetary mill (R1-R4), C – vibratory mill (R1-R4), D – stirring ball mill – attritor (R1-R4), E – pin mill (R4), rolling mill (R1-R2) [1.32].

The detailed description of mills for mechanical activation was published in special articles, e.g. [1.34] and monographs [1.14, 1.41, 1.44, 1.47-1.51, 1.53-1.54, 1.56-1.57].

There are a great number of publications on mechanical activation concentrated in many monographs [1.14, 1.20, 1.25, 1.29, 1.41, 1.44-1.60]. The last one on the topic being published in 1998 [1.60]. However, the unique work devoted to the application of mechanical activation in extractive metallurgy was written only in the Slovak language [1.59]. This monograph is a considerably expanded version of that book and is the only volume in which the major emphasis is on the application of mechanical activation in technology.

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## **Chapter 2 SELECTED METHODS FOR THE IDENTIFICATION OF CHANGES IN MECHANICALLY ACTIVATED SOLIDS**

- 2.1. Infrared spectroscopy**
- 2.2. Photoelectron spectroscopy**
- 2.3. Electron paramagnetic resonance**
- 2.4. Mössbauer spectroscopy**
- 2.5. X-ray diffraction**
- 2.6. References**

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During the history of development of mechanochemistry the number of applied identification methods gradually increased. At the beginning, these methods were directed to at obtaining the characteristics of mechanically activated solid substances, mostly in integral form. This activity encompassed for example, the measurement of specific surface area by sorption methods and the determination of the content of crystalline phase by the methods of X-ray diffraction, etc. At present, the number of methods applied in investigation of mechanically activated substances comprises a few tens. These methods are thoroughly analyzed in special monographs [2.1 –2.5].

This chapter is concerned with principles of five representative identification methods which have been used for characterizing the mechanically activated minerals described in subsequent chapters.

## 2.1. Infrared spectroscopy

The method of infrared spectroscopy is based on absorption of infrared radiation by molecules of gaseous, liquid or solid substances [2.6]. The molecules can exist in different energetic states and the transition from a lower level to a higher one necessitates the absorption of an amount of energy equal to the difference of energies between these two levels ( $\Delta E$ ). The ability of molecules to absorb radiation is due to changes in the energetic state of electrons, vibrational motion of atoms and rotation of whole molecules. The total energy of transition  $\Delta E$  is equal to the sum of energy differences between individual states

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_r \quad (2.1)$$

where  $e$  denotes electron state,  $v$  vibration state and  $r$  rotation state.

Infrared spectroscopy follows vibration and vibration-rotation spectra which occur in the wavelength range of 2.5 – 100  $\mu\text{m}$ . In spectroscopy it is more usual to use reciprocal wavelength (wavenumber). The wavenumber range for infrared spectroscopy is 4000 - 100  $\text{cm}^{-1}$ .

In an infrared spectrometer the sample is gradually exposed to radiation of different frequencies and it is determined at which frequencies  $\nu_j$  the absorption occurs (Fig. 2.1). The radiation of source Z goes through sample S and impinges on prism P where it is resolved in monochromatic components.



Fig. 2.1 The scheme of IR spectrometer. Z – source of radiation, S – sample, P – prism, D – detector, R – registration.

The gradual rotation of the prism results in radiation of different frequencies falling on the detector D where both the frequency and radiant flux is registered. The obtained spectrum expresses the dependence of absorption on radiation frequency. As to a double-beam instrument, absorbance  $A = -\log \Phi/\Phi_0$  is recorded instead of radiant flux  $\Phi$ . It is frequently usual to use wavenumber  $\bar{\nu}$  or wavelength  $\lambda$  ( $\bar{\nu} = 1/\lambda = c/\lambda$ , where  $c$  is light speed) instead of frequency  $\nu$ .

The application of infrared spectroscopy in examining sulfide minerals is associated with problems caused by the general application of solids and, in particular, with the structure of sulfides. These problems are reflected both in data collection and interpretation.

Sulfides are typically characterised by the low strength of interatomic bonds and these are excited in the low wavenumber range  $\bar{\nu} < 1000\text{--}400\text{ cm}^{-1}$  where IR spectroscopy is least efficient. These minerals have the main absorption bands in the region  $\bar{\nu} < 400\text{ cm}^{-1}$ , and only pyrite and arsenopyrite have high peaks at  $\bar{\nu} \sim 400\text{ cm}^{-1}$  [2.7 – 2.11]. The spectra of sulfides are characterised by broadened peaks due to the specific features of the crystalline structure and the nature of Me-S bonds. The form of the spectrum is greatly affected by the proportion of the metallic bond. The scatter and absorption of infrared radiation by free electrons causes smoothing and partial "broadening" of the peaks which overlap and the spectra becomes indistinct and complex to interpret.

The majority of currently available infrared spectrometers work in the regions above  $400\text{ cm}^{-1}$  with a few operating above  $200\text{ cm}^{-1}$ . Due to this restriction the IR method in solids is limited by the method of preparing samples for actual measurements. Satisfactory results have been obtained with the method of preparing tablets in a mixture with potassium bromide which uses the effect of plasticity of halides of alkali metals at elevated pressure [2.7]. The KBr method solves the problems associated with low transmission of sulfide powders but it is essential to overcome other procedural problems such as, for example, purity of KBr, evacuation of tablets, application of optimum pressure in tablet pressing, possible interaction of KBr with sulfides, etc.

Despite these restrictions, the IR spectroscopy method has been used in examining the effects resulting from mechanical activation of solids [2.1 – 2.4, 2.12 – 2.20]. The application possibilities of the method are utilised mainly for

- evaluating the particle size and disordering of their structure and
- identifying new compounds formed on the surface of solids.

The first case is concerned with the minerals of the oxide and silicate type [2.21 – 2.23] and is based on Rayleigh's relation which links the scatter of light  $S$  with the particle diameter  $d$

$$S = kd^3\lambda^{-4} \quad (2.2)$$

where  $\lambda$  is the wavelength of incident light. The effect of the particle size is then reflected in the situation in which the absorption band does not change frequently but becomes more intense and narrower with the reduction in particle size. Since the shape of the absorption band also depends on the orientation of the crystal lattice, polymorphism, etc. [2.22], it is also possible to evaluate the disordering of the structure of the minerals which takes place during their mechanical activation. The authors of paper [2.23] compared the methods of infrared spectroscopy and X-ray diffraction analysis in evaluating the degree of disordering of a series of oxide-type minerals. Certain correlations have been found between the particle size and the quantitative data obtained by means of these methods.

Since the low strength of bonds of sulfide minerals may, during mechanical activation cause their disordering or even fracture, it may be expected that intensive grinding in air will be accompanied by the formation of oxide compounds on the surface of minerals (for example, oxides, sulfates, oxysulfates, etc.) for which the IR spectroscopy method is a suitable identification tool because their typical wavelength is in the range  $\bar{\nu} = 2000\text{--}700\text{ cm}^{-1}$ . Fig. 2.2 shows the IR spectrum of mechanosynthesized zinc sulfide prepared by intensive grinding of zinc and sulfur in planetary mill in presence of air. The spectrum consists of a series of bands which correspond with the standard spectrum of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ .

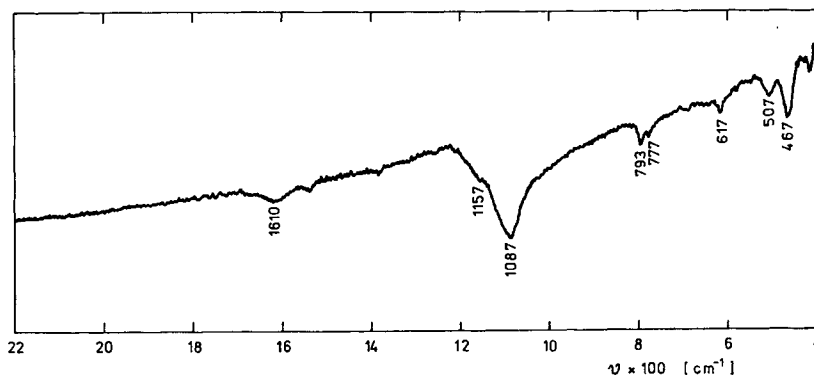


Fig. 2.2 IR spectrum of  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  [2.24].

## 2.2. Photoelectron spectroscopy

The method of photoelectron spectroscopy is commonly known as either XPS (X-ray Photoelectron Spectroscopy) or ESCA (Electron Spectroscopy for Chemical Analysis) and is based on the photoelectric effect which was described by Einstein (1905). If monochromatic X-rays of  $h\nu$  energy impinge the surface of sample photons of radiation are absorbed creating a metastable state. The metastable ion emits an electron with kinetic energy  $E_{\text{kin}}$ . The absorption of photon and the emission of electron are called photoelectric effect. The equation of energy conservation assumes the form

$$h\nu = E_{\text{kin}} + E_B \quad (2.3)$$

where  $E_B$  stands for the binding energy of valence or inner shell electron. The practical use of the photoelectric effect consists in the fact that the values of  $E_{\text{kin}}$  are characteristic of pertinent elements and sensitive to the bonding of these elements with environment. The theoretical elaboration of this observation was accomplished by Siegbahn [2.25] who was awarded the Nobel prize for his work in the field of photoelectron spectroscopy. The fact that the chemical environment of an element changes its energetic level as much as by 6 eV caused rapid development of this method.

The scheme of a spectrometer is represented in Fig. 2.3. A sample is irradiated with monoenergetic X-rays (most frequently  $\text{MgK}\alpha = 1\,486.6\text{ eV}$ ) and the energy of the emitted electrons is measured. The energy analyzer is, in principle, a monochromator of electrons which transmits only electrons of a certain kinetic energy. Equation (2.3) adapted for measurement on a spectrometer assumes

$$E_{\text{kin}} = h\nu - E_B - \phi_s \quad (2.4)$$

where  $\phi_s$  is the work function of spectrometer which is constant for a given spectrometer. For practical purposes, the values of  $h\nu$  and  $\phi_s$  are combined within the spectrometer constant and the value of  $E_B$  can be immediately calculated from the measured value of  $E_{\text{kin}}$ .

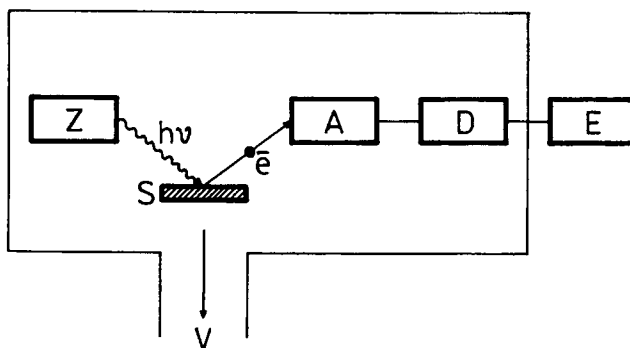


Fig. 2.3 The scheme of XPS spectrometer. Z – source of radiation, V – vacuum, S – sample, A – electron analyser, D – detector, E – electronic control.

The result of measurement is a XPS spectrum which gives the dependence of intensity of the detected signal on the kinetic energy of electron (Fig. 2.4). The spectral peaks correspond to different bonding states of electrons. The penetration depth of the exciting X-rays amounts to micrometers by decimal order. However, the escape pathlength of the emitted electrons and thus the thickness of the analyzed surface layer is substantially smaller due to interactions between the electrons and the components of the layer. The escape pathlength depends on kinetic energy of the electrons and is equal to 1-5 nm making XPS highly surface selective. Thus for studying the bulk characteristics of samples, identical chemical composition in surface and bulk is a necessary (but not sufficient) postulate [2.26].

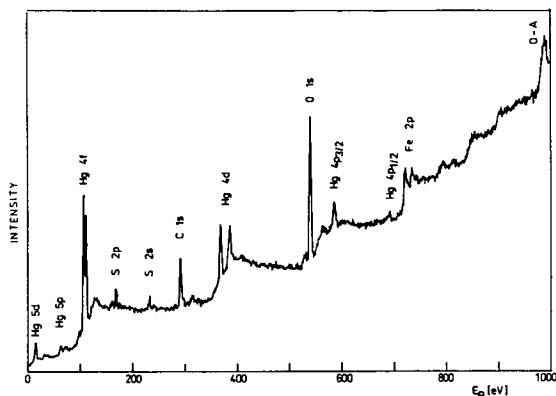


Fig. 2.4 Survey XPS spectrum of HgS [2.27].

Every line of a photoelectron spectrum is characterized by its binding energy, shape, width and, as the case may be, splitting. These data are a source of information about electron structure (e.g. oxidation state of the present elements) and chemical composition of the surface layer of the investigated sample. Thus, quantitative analysis is feasible, but owing to the microscopically heterogeneous structure of powdered sample it cannot be recommended as a method of estimating the bulk composition [2.28]. The typical error in quantitative analysis amounts to 30 % or in the most favourable cases 10-20 % [2.29].

If the values of binding energy are to be more precisely measured in the regime of high resolution the spectrometer is usually calibrated for two main lines: Au 4f<sub>7/2</sub> ( $E_B = 84.0$  eV)

and Cu 2p<sub>3/2</sub> ( $E_B = 932.7$  eV). Other than hydrogen and helium, all elements can be determined, most of them to the level of 0.1 atomic percentage. The amount of sample necessary for analysis is usually equal to a few milligrammes.

A potential complication in measuring the values of binding energy consists in accumulation of positive charge on the surface of sample, this cause the whole spectrum to shifted by the value of this charge towards higher values of binding energies. This effect is most problematical in electrically non-conductive samples. In order to ascertain the value of charging or to eliminate this phenomenon, a great number of methods have been put forward [2.30]. However, none of them is of universal use and corrections need to be made for each sample.

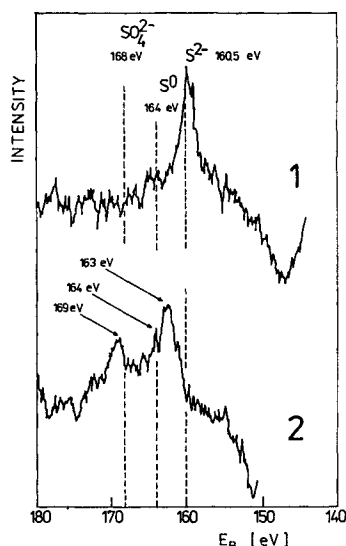


Fig. 2.5 XPS S 2p spectrum of PbS. 1 – natural PbS, 2 – synthetic PbS [2.31].

In the case of unknown samples, the first spectrum is usually taken over a wide energy interval ( $E_B = 0$ -1000 eV) as a survey spectrum (Fig. 2.4) which serves for identification of the elements present. The finding that non-equivalent atoms of a certain element give spectra with measurable difference between binding energies is of outstanding analytical importance. This difference was called chemical shift  $\Delta E_{ch}$  by analogy with the similar effect appearing in Mössbauer spectroscopy [2.30]. The non-equivalence of atoms may be due to the differences in their chemical environment or to different location of atoms in the lattice.

The structure of individual lines is examined at high resolution over a narrow energy interval. Besides the fundamental electron lines we may observe

- spin-orbital splitting which results in a doublet for all levels except s-electrons,
- multiplet splitting which may appear if there are unpaired electrons on valence levels of the system,
- satellite lines and bands of different origin and
- some peaks of low intensity which are due to non-monochromaticity and impurity of X-ray sources [2.30].

These structures frequently help us to interpret the measured results and in the case of multiplet splitting and satellites they are also a valuable source of additional information about the state of solids.

### 2.3. Electron paramagnetic resonance

Electron paramagnetic resonance EPR (also electron spin resonance ESR) is a sensitive physical method for studying electron paramagnetism of atoms, molecules, ions or chemical groups. The electron paramagnetism is a result of the existence of unpaired electrons which have magnetic moments. If a substance containing unpaired electrons is put into strong magnetic field two energy levels arise. These levels correspond to conformable and nonconformable orientation of the electron magnetic moment to the external magnetic field. The difference between energies of both levels satisfies the so-called resonance condition of EPR and is equal to

$$\Delta E = g \mu_B \overline{B_o} \quad (2.5)$$

where  $g$ ,  $\mu_B$  and  $\overline{B_o}$  stand for  $g$ -factor of spin-orbital interaction, magnetic moment of electron (Bohr magneton) and induction of magnetic field respectively. The  $g$ -factor of spin-orbital interaction is an important EPR characteristic and is isotropic for a free electron, its value being equal to 2.0023. In general, the  $g$ -factor is an anisotropic quantity with deviation from the mentioned value of  $g$  arising as a consequence of orbital contributions to the total magnetic moment of electron [2.32].

The most frequent paramagnetic ions are ions of transition metals of the 3d-group, ions of rare earth metals of the 4f-group and donor admixtures. These ions have unpaired electrons in incomplete orbitals. Natural substances often contain these ions which are either within their crystal structure, or are present in the form of admixtures.

However, the paramagnetic centres present are not always of genetic origin and can also originate from the breakage of chemical bonds giving rise to free radicals or from the trapping of electrons in defects of solids (colour centres). The colour centres were originally attributed to halides of alkali metals but were subsequently also identified in other solids. We distinguish centres F, V, N, Z<sub>1</sub> and others [2.33 – 2.34]. A F-centre and a V-centre are represented in Fig. 2.6. In principle, the electrons in F-centres are not bound and migrate between the cations surrounding the hole (vacancy) due to removal of an anion from the crystal lattice site. For instance, the formation of V-centre can be interpreted by the idea that the electrons are bound to a neutral atom formed by tearing an electron away from an anion. The neutral atoms fall into holes and thus form the V-centres [2.34].

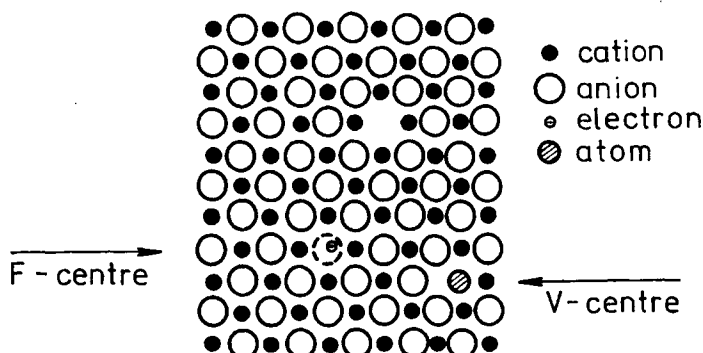


Fig. 2.6 F- and V-centre in the structure of crystalline substance.

In the field of study of mechanical activation the EPR method has proved to be very useful [2.2 – 2.5, 2.35 – 2.37]. In the course of intensive grinding the surface area of solid substances is disordered, the bonds between atoms are interrupted and radicals, atoms or molecules come into existence. These structures often cannot react rapidly with other and are therefore detectable by the EPR method. The point, linear and volume defects generated in the process of grinding represent a notable source of paramagnetism.

For instance, the vacancies which are due to breakage of chemical bonds belong among point defects. As a matter of fact, the F-centre represented in Fig. 2.6 is a new defect due to an electron trapped in an anion vacancy. The admixture centres which bring about considerable distortion of interatomic bonds also belong among point defects. They are frequently used as paramagnetic markers which are either introduced in the form of admixtures into the investigated object or are formed in this object in the process of technological operation. The addition of manganese is frequently employed for this purpose. The disturbances produced in this element are relatively small which brings about long times of relaxation and a good detectability [2.38]. The EPR spectrum is fairly distinguishable and its identification is facilitated by the fact that manganese exhibits a characteristic spectrum of hyperfine interaction comprising 6 lines. Each line of hyperfine structure contains 5 components of fine structure owing to which the total number of lines in the spectrum is equal to 30. In crystals subject to strain and in polycrystalline materials only one resonance line of manganese can usually be observed. In literature we can find information about the correlation of parameters of the EPR spectrum of bivalent manganese with particle size of mechanically activated periclase [2.39] or with concentration of defects in crystalline lattice of this mineral [2.40 – 2.41].

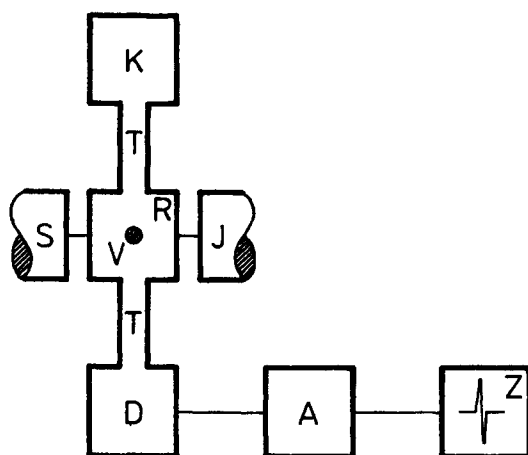


Fig. 2.7 The scheme of EPR spectrometer. K – clystron, T – waveguide, R – resonance hole, D – detector, SJ – magnet, V – sample, A – amplifier, Z – registration.

The experimental equipment for taking EPR spectra is represented in Fig. 2.7. The source of microwave radiation is a clystron K. The radiation is passed through a metallic waveguide T into the resonance hole R containing the sample V and subsequently to the detector D. This detector transforms the microwave radiation in direct current. The splitting of magnetic energy is achieved in the field of strong electromagnet SJ. After reaching the condition of resonance, i.e. when the microwave radiation is absorbed by the sample, the energy in the resonance hole

decreases. The obtained signal is amplified in an amplifier A and recorded. The record of signal Z expresses the dependence of absorption of radiation on variable magnetic field and for better resolution it is given in the form of the first derivative of absorption signal (Fig. 2.8).

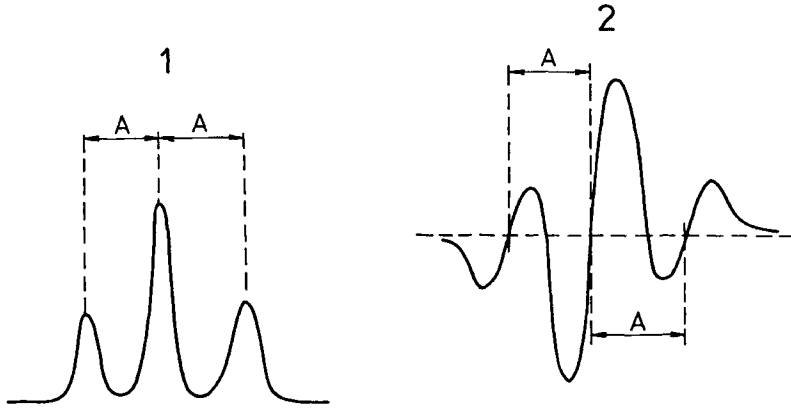


Fig. 2.8 Splitting of signal in EPR spectrum: 1 – normal spectrum, 2 – derivative spectrum.

## 2.4. Mössbauer spectroscopy

In 1957 Mössbauer detected that the gamma radiation of special nuclei could be emitted and resonantly absorbed without energy on certain conditions [2.42]. Owing to the high precision with which the energy of this radiation could be measured the phenomenon of recoil-force nuclear gamma resonance (Mössbauer effect) made it possible to investigate the static as well as dynamic hyperfine intractions and to lay foundations of a new type spectroscopy, the so-called Mössbauer spectroscopy.

A schematic illustration of the principle of the Mössbauer effect is given in Fig. 2.9. The gamma photons emitted from a special radioactive source are resonantly absorbed by the corresponding nuclei of a suitable absorber and registered by a detector. A thin foil (0.1 mm) containing a radionuclide, e.g.  $^{57}\text{Co}$  (half life of decay 270 days) usually works as a source.  $^{57}\text{Co}$  gradually decays according to the scheme  $^{57}\text{Co} \rightarrow ^{57}\text{Fe} \rightarrow ^{57}\text{Fe}^m \rightarrow ^{57}\text{Fe}$

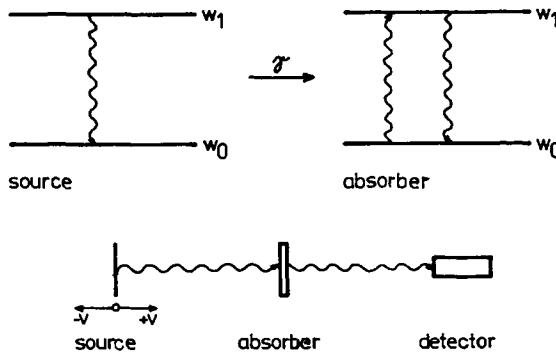


Fig. 2.9 Principle of the Mössbauer effect.

The excited iron isotope releases an energy quantum of 14.4 keV which is appropriate for the Mössbauer effect. The condition of resonance can be achieved by changing the energy of the primary source of gamma photons. The practical accomplishment of this consists of moving the gamma photons source towards and away from the sample thereby varying the energy of gamma radiation due to the Doppler effect. The absorber is a  $^{57}\text{Fe}$  nucleus which attains the excited state by absorbing a gamma photon of convenient energy. Thus the presence of the  $^{57}\text{Fe}$  isotope which occurs in the quantity of 2.2 % in iron is a precondition of application of this method (about 40 other nuclides, e.g.  $^{119}\text{Sn}$ ,  $^{197}\text{Au}$  also exhibit the Mössbauer effect as well). 5 mg  $\text{Fe}/\text{cm}^2$  of absorber area are used for measurement. Often a NaI crystal activated by thallium serves as detector of the transmitted or resonantly absorbed gamma-photons. The Mössbauer spectrum is then obtained on a recorder after accumulating the count-rates by means of a multichannel analyzer which gives the dependence of the measured number of impulses on the velocity of moving source. That enables us to establish two principal applications in phase analysis

- it is possible to identify a given substance (qualitative analysis),
- the relative area of spectrum gives information about the site occupations of atoms in a given component (quantitative analysis).

The deviations of the spectral peak profiles from the ideal form (Lorentz lines) manifest themselves by extension and deformation. They may be due to the presence of impurities and structural nonuniformity of the occurrence of defects.

A Mössbauer spectrum (Fig. 2.10) is mainly characterized by the following principal parameters

- isomer shift ( $\delta$  or IS),
- quadrupole splitting ( $\Delta E_0$  or QS) and
- magnetic hyperfine splitting ( $H_{\text{ef}}$ ).

The values of these parameters are dependent on kind and magnitude of the hyperfine interactions between charge distribution and magnetic moment of  $^{57}\text{Fe}$  and electric and magnetic fields acting on the nucleus.

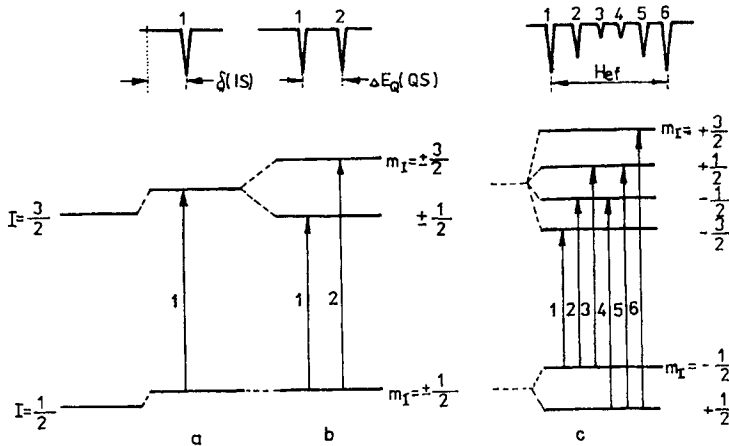


Fig. 2.10 Schematic diagram of shift and splitting of nuclear levels: a – isomer shift ( $\delta$  or IS), b – quadrupole interaction ( $\Delta E_0$  or QS), c – effective magnetic field ( $H_{\text{ef}}$ ).

The isomer shift (IS) provides information about the local chemical bonding. For this reason, it is frequently called chemical shift ( $\delta$ ). The magnitude of isomer shift increases with the decreasing density of the s-electrons surrounding the nucleus and with increasing density of the d-electrons (note: 3d-electrons screen 4s-electrons and thus reduce their density on nucleus). The isomer shift is a measure of the deviation of Mössbauer spectrum from the zero point on the scale of velocity  $v$  of the source (Fig. 2.9), the zero point is referred to a standard (usually elemental Fe). On the basis of the values of the isomer shift we can estimate the type of chemical bond, oxidation state and coordination number of iron.

The quadrupole splitting ( $\Delta E_0$  or QS) is a consequence of interaction between the nuclear quadrupole moment and the gradient of the electric field at the site of nucleus. Thus two lines instead of one line appear in Mössbauer spectrum (Fig. 2.10b). The value of the quadrupole splitting is proportional to the deviation of nuclear surroundings from cubic symmetry (note: if the symmetry of surroundings of the nucleus is cubic, then QS = 0). The neighbouring ions affect the wave functions around the nucleus and thus QS gives information about the size and symmetry of the surrounding crystal field.

The magnetic hyperfine splitting ( $H_{ef}$ ) is a consequence of the interaction between the nuclear magnetic dipole moment and internal magnetic field at the nucleus. Owing to splitting of the ground level of  $^{57}\text{Fe}$  into two sublevels and of the excited first level into four sublevels and taking the selection rules into account, six possible  $\gamma$ -energies arise. The allowed transitions between these produce a six-line spectrum (Fig. 2.10c). The distance between the first and sixth line of spectrum characterize the effective magnetic field of nucleus  $H_{ef}$  with QS = 0. The magnetic hyperfine splitting gives information about magnetic moments and their magnetic arrangement relative to the electric field gradient and is also important for qualitative analysis.

In mineralogy the application of Mössbauer spectroscopy is conditioned mainly by the presence of iron though there are records of the spectra of minerals with tin and tungsten as Mössbauer isotopes [2.43 – 2.47]. The outstanding sensitivity of Mössbauer spectroscopy enables the resolution of  $\text{Fe}^{2+}$  from  $\text{Fe}^{3+}$  with a relative precision of  $\pm 1\%$  which is a great advantage for determining the oxidation state of iron. The method is more sensitive when compared with chemical analysis and the results of measurements are not affected by the presence of accessory ions of transition metals which coincide, e.g. in the course of dissolution preceding a chemical analysis. The methods of XRD analysis as well as other methods, such as EDS analysis or electron microprobe analysis, however, are not able to distinguish between the above-mentioned oxidative states. The values of isomer shift IS for individual oxidation states of iron in sulfides are given in Table 2.1.

Table 2.1 Values of isomer shift IS for bivalent and trivalent iron in sulfides [2.48]

| Oxidation state of Fe     | + 2         | + 3         |
|---------------------------|-------------|-------------|
| IS ( $\text{mm s}^{-1}$ ) | 0.38 – 1.20 | 0.34 – 0.47 |

For iron it is also possible to determine electronic configurations (low or high spin), coordination symmetry (tetra- or octahedral positions) and the pertinent deviations.

The Mössbauer spectrum characteristic of a certain mineral can be used for the identification of individual minerals in a mixture (the so-called "fingerprint" technique). The spectra of sulfides, oxides, hydroxides, jarosites, silicates etc. are currently identified and quantitatively evaluated. The sensitivity of the hyperfine structure to deviations caused by surroundings of the Mössbauer atom enables the study of changes in the stoichiometry of minerals. In Table 2.2 the Mössbauer parameters for different sulfides are summarized.

Table 2.2 Mössbauer data for selected sulfides

| Mineral      | Temperature<br>(°C) | IS*<br>(mm s <sup>-1</sup> ) | QS<br>(mm s <sup>-1</sup> ) | H <sub>ef</sub><br>(kgauss) | Reference |
|--------------|---------------------|------------------------------|-----------------------------|-----------------------------|-----------|
| Sphalerite   | 27                  | 0.66                         | 0.80                        | -                           | 2.48      |
|              | -193                | 0.86                         | 2.04                        |                             | 2.48      |
|              | 27                  | 0.64-0.67                    | 0.62-0.67                   |                             | 2.49      |
| Wurtzite     | 27                  | 0.69                         | 0.80                        |                             | 2.48      |
|              | -193                | 0.91                         | 2.05                        |                             | 2.48      |
| Pyrite       | 27                  | 0.30                         | 0.60                        |                             | 2.50      |
|              | -196                | 0.31                         | 0.61                        |                             | 2.50      |
|              | 27                  | 0.31                         | 0.61                        |                             | 2.51      |
|              | -192                | 0.40                         | 0.62                        |                             | 2.51      |
| Marcasite    | 27                  | 0.27                         | 0.51                        |                             | 2.51      |
|              | -192                | 0.37                         | 0.50                        |                             | 2.51      |
| Arsenopyrite | 27                  | 0.25                         | 1.05                        |                             | 2.50      |
|              | -196                | 0.26                         | 1.07                        |                             | 2.50      |
| Chalcopyrite | 27                  | 0.20                         | 0                           | 350                         | 2.52      |
|              | -193                | 0.27                         | 0                           | 365                         | 2.48      |
|              | 27                  | 0.20                         | 0                           | 246                         | 2.53      |
|              | -196                | 0.37                         | 0.17                        | 206                         | 2.54      |
| Bornite      | 27                  | 0.38                         | 0                           |                             | 2.48      |
|              | -193                | 0.48                         | 0.20                        |                             | 2.48      |
|              | 27                  | 0.39                         | 0.16                        |                             | 2.52      |
|              | -196                | 0.52                         | 0.25                        |                             | 2.54      |

\* relative to metallic iron

## 2.5. X-ray diffraction

The X-ray beams consist of electromagnetic radiation of the wave length of  $10^{-10}$  m which originates from bombardment of a substance with charged particles of high energy. Their wave character was revealed by Max von Laue in 1912. Owing to their small wavelength they show high penetrating power. An X-ray spectrum represents a set of diffraction lines of different intensities. The position of a diffraction line is fixed and the overall pattern is characteristic for a given substance.

The X-ray diffraction is widely used in the study of solid state properties, e.g. for qualitative and quantitative phase analysis, the determination of parameters of unit cell and crystal structure as well as for the estimation of crystallite size and lattice distortion. It is a method suitable for investigating the transformations in solids caused by mechanical activation. In principle, these transformations manifest themselves by shift and/or broadening of lines (Fig. 2.11).

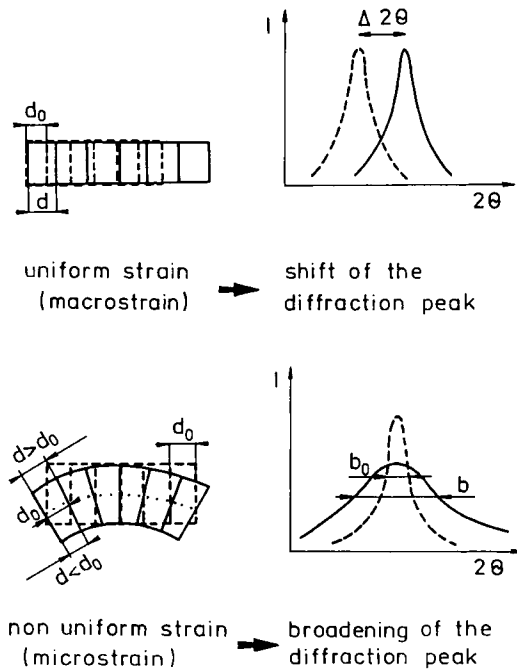


Fig. 2.11 Shift and broadening of an X-ray diffraction line [2.55].

The shift in a diffraction line is the result of uniform strain or macrostrain while the broadening of a diffraction line is due to non-uniform strain or microstrain. In real materials, the X-ray diffraction is affected by real structure of this material and further factors related to microstructure, such as chemical composition, phase boundaries, grain size, crystallographic orientation, grain boundaries, dislocations, point defects, etc. must be taken into consideration.

In practice, two methods of determination of diffraction line broadening are used for investigating the microstrain in mechanically activated solids (Fig. 2.12).

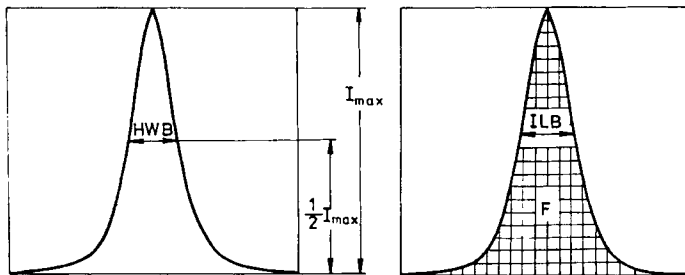


Fig. 2.12 Diffraction line broadening (HWB) and integral width (ILB) [2.56].

The HWB (diffraction line broadening) can be found out by measuring the width of diffraction line at half of its maximum intensity ( $I_{max}$ ) whereas ILB (integral width) has to be calculated from

$$ILB = \frac{F}{I_{\max}} \quad (2.6)$$

where  $F$  stands for the area under the diffraction peak whose maximum intensity is  $I_{\max}$ .

The diffraction line broadening depends on the experimental conditions used in the measurement of the diffraction peak (so-called instrumental line broadening) and on the properties of the measured solid phase (so-called physical line broadening). For obtaining further information from physical line broadening it is necessary to eliminate instrumental line broadening. The correction can be achieved by comparing the obtained result with the resulting diffraction of the sample that has not been disordered by mechanical activation [2.57] or by eliminating instrumental effects by means of correction coefficients [2.58].

The physical line broadening is dependent on two principal factors

- the crystallite size, called coherently diffracting domains and
- the lattice strain which is created by microstrain.

In mechanical activation these factors can be effective either jointly or separately. A serious problem that faces us is to distinguish the size effect from the strain effect. The possibility of determining the both coincident effects has been described in paper [2.58] and is represented in Fig. 2.13.

The quantities  $b \cos \theta$  and  $b/\tan \theta$  can be plotted against diffraction angle  $\theta$ . The change in  $b \cos \theta$  characterises the lattice strain while the crystallite size is responsible for the change in  $b/\tan \theta$ .

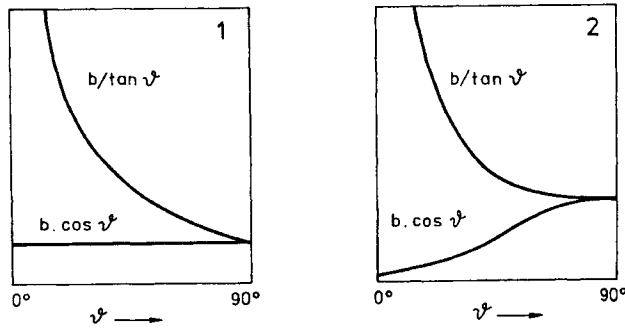


Fig. 2.13 Effect of crystallite size and lattice strain on diffraction line broadening; 1 – crystallite size, 2 – lattice strain and crystallite size.

Provided  $b \cos \theta$  is independent of  $\theta$ , then the physical line broadening  $b$  depends only on crystallite size  $\Lambda$  which can be expressed according to Scherrer [2.59]

$$\Lambda = \frac{Kr\lambda}{b \cos \theta} \quad (2.7)$$

where the symbols  $K$ ,  $r$  and  $\lambda$  stand for the shape factor varying between 1 and 1.25, the radius of goniometer and the wavelength, respectively.

Provided  $b/\tan \theta$  is independent of  $\theta$ , then the physical line broadening  $b$  is due only to lattice strain and the relative lattice strain  $\Delta \epsilon/\epsilon$  can be calculated from formula

$$\frac{\Delta\varepsilon}{\varepsilon} = \frac{b}{4r \tan \theta} 1000 \quad (2.8)$$

If the crystallite and the lattice strain are simultaneously present in mechanically activated solids, both values can be assessed on the basis of physical broadening of two diffraction lines by using the equations

$$\Lambda = \frac{Kr\lambda (b_2 \cos \theta_2 \sin \theta_2 - b_1 \cos \theta_1 \sin \theta_1)}{b_2 \cos \theta_2 b_1 \cos \theta_1 (\sin \theta_2 - \sin \theta_1)} \quad (2.9)$$

$$\frac{\Delta\varepsilon}{\varepsilon} = \frac{\lambda (b_2 \cos \theta_2 - b_1 \cos \theta_1)}{\Lambda (b_2 \cos \theta_2 \sin \theta_2 - b_1 \cos \theta_1 \sin \theta_1)} \quad (2.10)$$

where the symbols have the same meaning as in eq. (2.7). Subscripts 1 and 2 correspond to two diffraction lines for which  $\theta_2 > \theta_1$ .

In the literature there are also other relationships which estimate the change in real structure of mechanically activated crystalline substances [2.56].

Patzak [2.60] has defined the degree of disorder of structure F by formula

$$F = \frac{(ILB)_x}{(ILB)_0} \quad (2.11)$$

where  $(ILB)_x$  is integral width corresponding to disordered sample and  $(ILB)_0$  is integral width corresponding to non-disordered (reference) sample. Parameter F is a summary quantity for all factors which bring about a broadening of diffraction line (after elimination of instrumental line broadening). Thus we can obtain relative values in which the effect of activation on a given substance is reflected.

Another relative method serving for estimation of the degree of crystallinity (content of crystalline phase) X is the method put forward by Ohlberg and Strickler [2.61].

The effect of mechanical activation can be evaluated by a mass fraction of the crystalline phase in the activated sample, X compared with the reference substance (non-activated substance) which is assumed to correspond to 100 % crystallinity. Thus it holds that

$$X = \frac{U_0}{I_0} \frac{I_x}{U_x} 100 \quad (2.12)$$

where  $U_0$  and  $U_x$  denote the backgrounds of non-activated (reference) sample and activated sample while  $I_0$  and  $I_x$  are integral intensities of diffraction lines of non-activated (reference) sample and activated sample, respectively.

Equation (2.12) is based on the assumption that the mechanical activation is not accompanied by a texture error (e.g. due to preferential orientation where there was none in the non-activated sample). Sometimes, the complementary value of amorphization A (degree of amorphization or content of X-ray amorphous phase) is used. It is defined by equation

$$A = 100 - X \quad (2.13)$$

The precision of determination of individual X-ray – quantities varies and is dependent on a great number of factors. An important factor is elimination of the effect of primary extinction by removing the particles exceeding 40  $\mu\text{m}$  [2.62]. This limit has to be determined experimentally for every material [2.5]. The primary particle size can be determined with precision of 5-10 % up to the upper limit of 200 nm and in the case of lattice strain up to any small value. The precision of determination of the content of crystalline phase also varies within the range of a few percent.

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## **Chapter 3 PHYSICO-CHEMICAL PROPERTIES OF MECHANICALLY ACTIVATED MINERALS**

- 3.1. Disintegration of particles**
- 3.2. Formation of new surface and effect of aggregation**
- 3.3. Disordering of crystal structure**
- 3.4. Relationship between new surface area formation and disordering of crystal structure**
- 3.5. Physical and chemical changes of minerals during mechanical activation in organic liquids**
- 3.6. Mechanochemical surface oxidation**
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### 3.1. Disintegration of particles

The primary effect of mechanical activation is comminution of particles which results in changes in a great number of physico-chemical properties of a particular system. The analysis of comminuted particles is aimed at the study of their *size*, *shape* and *distribution* [3.1 – 3.3].

The size of particles can be measured by different techniques, which are tabulated together with their useful range of measurement in Table 3.1.

Table 3.1 Methods of particle size measurement [3.1]

| Method                        | Range ( $\mu\text{m}$ )            |
|-------------------------------|------------------------------------|
| Microscopy                    | 0.4-100                            |
| Ultramicroscopy               | 0.01-2                             |
| Electron microscopy           | 0.0005-5                           |
| Light-scattering              | 0.1-30                             |
| X-ray analysis                | 0.0005-1                           |
| Sieve classification          | over 40                            |
| Ultrafiltration               | over 0.002                         |
| Sedimentation                 | 1-50                               |
| Centrifugation                | 0.01-1                             |
| Ultracentrifugation           | 0.0005-0.01                        |
| Elutriation                   | 1-100                              |
| Diffusiometry                 | up to 0.1                          |
| Osmometry                     | up to 0.1                          |
| Gel permeation chromatography | up to 0.1                          |
| Viscometry                    | two dimensions smaller than 0.0001 |
| Permeametry                   | 0.5-100                            |
| Adsorption                    | 0.002-50                           |
| Conductometry                 | above 0.2                          |
| Radiometry                    | above 0.002                        |

The possibilities of electron microscopy are illustrated by Fig. 3.1 where chalcopyrite particles of different sizes are scanned. The method of particle size measurements of different minerals by sieve analysis is given in Table 3.2.

Examination of the mass yields  $\Delta R$  for mechanically activated minerals indicates a gradual increase in the portion of particles in the smaller size fractions and especially high in the less than  $< 10 \mu\text{m}$  fraction which is characteristic of ultrafine grinding. In this region we can obtain  $\Delta R > 50 \%$  for all minerals exposed to mechanical activation lasting a certain time. The fraction of the fines particles is dominant and determines the general behaviour of a particular polydisperse system. The time of mechanical activation necessary for attaining this mass recovery is different for individual particles. This phenomenon will be described in more detail later.

The extent of disintegration can also be quantified by means of the size of primary particles  $\Lambda$  calculated on the base basis of X-ray measurements (equation 2.7). The plot of the quantity against the time of mechanical activation is represented in Fig. 3.2 for individual sulfides.

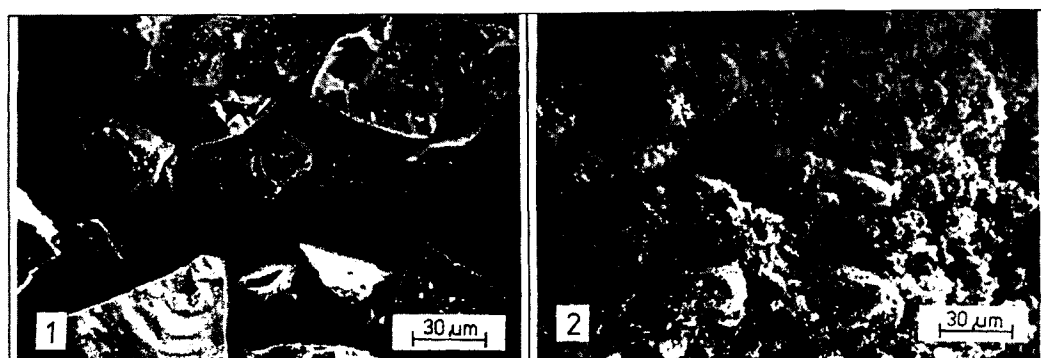


Fig. 3.1 Scanning electron micrographs of  $\text{CuFeS}_2$ , 1 – before mechanical activation, 2 – after mechanical activation.

Table 3.2 Particle size measurement of different mechanically activated minerals by sieve classification

| Mineral          | Sieve size range ( $\mu\text{m}$ ) | Mass yield $\Delta R$ (%) for samples mechanically activated in time $t_G$ (min) |         |          |          |          |          |
|------------------|------------------------------------|----------------------------------------------------------------------------------|---------|----------|----------|----------|----------|
|                  |                                    | $t_G=0$                                                                          | $t_G=5$ | $t_G=10$ | $t_G=15$ | $t_G=20$ | $t_G=30$ |
| $\text{CuFeS}_2$ | +71                                | 11.3                                                                             | 3.9     | 3.2      | 6.9      | 7.6      | 9.4      |
|                  | 71-40                              | 25.0                                                                             | 7.3     | 6.2      | 15.2     | 9.9      | 12.00    |
|                  | 40-30                              | 14.4                                                                             | 7.8     | 6.5      | 9.3      | 5.9      | 7.5      |
|                  | 30-20                              | 13.3                                                                             | 18.6    | 15.2     | 12.7     | 8.2      | 10.4     |
|                  | 20-10                              | 16.2                                                                             | 34.8    | 28.6     | 16.2     | 12.8     | 13.5     |
|                  | 10-5                               | 9.8                                                                              | 13.9    | 15.8     | 8.7      | 9.6      | 7.3      |
|                  | -5                                 | 10.0                                                                             | 13.7    | 23.6     | 31.2     | 46.1     | 40.1     |
| $\text{FeS}_2$   | +71                                | 58.1                                                                             | 2.7     | 2.8      | 2.9      | 3.8      | 3.9      |
|                  | 71-40                              | 29.3                                                                             | 14.1    | 4.0      | 4.4      | 5.3      | 5.8      |
|                  | 40-30                              | 4.2                                                                              | 12.3    | 4.3      | 4.8      | 5.3      | 6.0      |
|                  | 30-20                              | 3.4                                                                              | 16.5    | 9.9      | 10.6     | 13.8     | 9.0      |
|                  | 20-10                              | 3.0                                                                              | 16.2    | 26.7     | 26.3     | 28.3     | 22.8     |
|                  | 10-5                               | 2.4                                                                              | 8.7     | 21.3     | 16.7     | 15.4     | 24.6     |
|                  | -5                                 | 1.1                                                                              | 29.6    | 30.9     | 34.3     | 28.0     | 27.8     |
| $\text{PbS}$     | +71                                | 33.6                                                                             | 2.1     | 1.2      | 2.3      | 4.5      | 5.0      |
|                  | 71-40                              | 29.1                                                                             | 11.8    | 7.3      | 8.1      | 7.3      | 9.5      |
|                  | 40-30                              | 11.6                                                                             | 11.0    | 6.4      | 6.8      | 7.3      | 8.7      |
|                  | 30-20                              | 9.7                                                                              | 18.0    | 13.9     | 14.1     | 15.9     | 13.5     |
|                  | 20-10                              | 9.4                                                                              | 25.1    | 21.0     | 20.4     | 21.0     | 21.0     |
|                  | 10-5                               | 3.8                                                                              | 11.2    | 11.7     | 11.5     | 9.1      | 9.9      |
|                  | -5                                 | 2.9                                                                              | 20.7    | 38.6     | 36.8     | 34.8     | 32.4     |

It is evident for all minerals that the values of  $\Lambda$  decrease with increasing time of activation. Examination of this decrease over the initial thirty minutes shows different trends for different minerals:

- the course is linear ( $\text{Sb}_2\text{S}_3$ , partly  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ) and
- the course is not linear and the maximum rate of decrease of  $\Lambda$  occurs during the initial period of mechanical activation ( $\text{CuFeS}_2$ ,  $\text{FeS}_2$ ,  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{ZnS}$ , partly  $\text{Cu}_5\text{FeS}_4$ ).

These relationships also have a bearing upon the nature of aggregation.

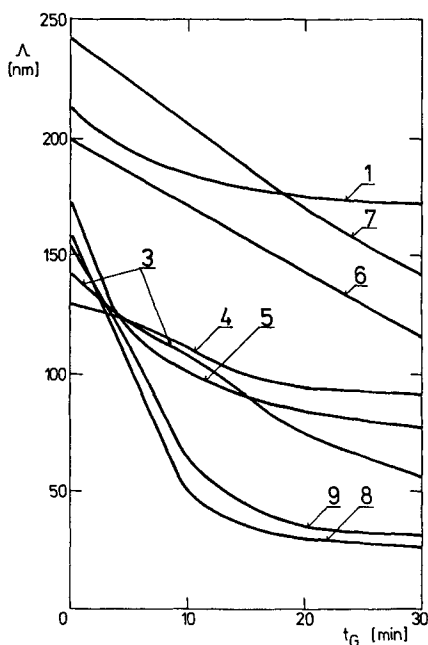


Fig. 3.2 Size of primary particles,  $\Lambda$  vs. time of mechanical activation,  $t_G$ : 1 –  $\text{CuFeS}_2$ , 3 –  $\text{Cu}_5\text{FeS}_4$ , 4 –  $\text{FeS}_2$ , 5 –  $\text{HgS}$ , 6 –  $\text{Sb}_2\text{S}_3$ , 7 –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 8 –  $\text{PbS}$ , 9 –  $\text{ZnS}$  [3.4].

The shape of particles can be described in qualitative terms which can give some indication about their form. The British Standard Institute has prepared a standard glossary of terms used in the description of fines (Table 3.3).

Table 3.3 Definitions of particle shape [3.2 – 3.3]

| Shape       | Description                                             |
|-------------|---------------------------------------------------------|
| Acicular    | needle-shaped                                           |
| Angular     | sharp-edged or having roughly polyhedral shape          |
| Crystalline | freely developed in a fluid medium of geometric shape   |
| Dendritic   | having a branched crystalline shape                     |
| Fibrous     | regularly or irregularly thread-like                    |
| Flaky       | plate-like                                              |
| Granular    | having approximately an equidimensional irregular shape |
| Irregular   | lacking any symmetry                                    |
| Modular     | having rounded, irregular shape                         |
| Spherical   | global shape                                            |

The great variability of particle shape for several sulfidic minerals is illustrated by Fig. 3.3.

It is necessary to measure and define shape quantitatively as the descriptions are clearly inadequate due to the range and variability of shapes. Different techniques have been described [3.1 – 3.3] for shape characterization, e.g. pattern recognition technique and dimensionless description of the profile of fine particle by a Fourier analysis of a waveform representing the profile.



Fig. 3.3 Scanning electron micrographs of  $\text{CuFeS}_2$ (1),  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ (2),  $\text{FeAsS}$ (3),  $\text{FeS}_2$ (4),  $\text{Sb}_2\text{S}_3$ (5),  $\text{HgS}$ (6),  $\text{PbS}$ (7),  $\text{Cu}_5\text{FeS}_4$ (8),  $\text{ZnS}$ (9).

The use of fractal dimensions as a descriptor of fine particle shape was introduced recently. Mandelbrot [3.5] has discussed the problem of describing highly rugged boundaries that typically occur in nature. Based on concepts drawn from non-Euclidean mathematics he came to the conclusion that a rugged curve was describable by a mathematical dimension that has fractional values between 1 and 2. Mandelbrot called this dimension the fractal dimension. The surface geometric irregularities of minerals are characterized by surface fractal dimension  $D_s$ , where  $2 \leq D_s < 3$  [3.6]. The concept of the fractal dimension of ground minerals has been

published by Mockovčiaková et al. [3.7]. The values of  $D_S$  based on specific surface area measurements were calculated for  $\text{CuFeS}_2$  and  $\text{PbS}$  treated using two different grinding modes – crushing and mechanical activation. The results are summarized in Table 3.4.

Table 3.4 Surface fractal dimension,  $D_S$  for  $\text{CuFeS}_2$  and  $\text{PbS}$  prepared by crushing and mechanical activation [3.7]

| Mineral          | $D_S$    |                       |
|------------------|----------|-----------------------|
|                  | Crushing | Mechanical activation |
| $\text{CuFeS}_2$ | 2.501    | 2.479                 |
| $\text{PbS}$     | 2.554    | 2.163                 |

The results in Table 3.4 indicate that fractal theory may well have some use in quantifying the different methods of particle comminution, including mechanical activation.

### 3.2. Formation of new surface and effect of aggregation

The disintegration of mineral particles by mechanical activation is accompanied by an increase in the number of particles and by generation of fresh, previously unexposed, surface. The measurement of specific surface area and particle size analysis are among the most frequently applied methods for quantitative analysis of mechanically activated fines. Several different methods of specific area measurement are applied, procedures based on gas adsorption (BET, Harkins-Jura, Kiselev, thermodesorption, etc. [3.2]) are very popular. The advantage of these methods is the potential for more precise determination of surface area compared with calculation from particle size distribution. This is because the separation of particles into size ranges is not always unambiguous [3.8 – 3.9], does not take account of surface roughness of particle shape (being typically based on spheres) and does not account for the presence of porosity.

However, the adsorption surface area  $S_A$  is closely related to the size of adsorbed gas and in case of aggregate formation may not be sensitive enough to measure the inner surface of small pores. The method of granulometric surface area  $S_G$  based on particle size distribution measurement is more adequate in this case. This is demonstrated in Figure 3.4 where aggregation phenomena prevail for mechanical activation lasting more than two hours.

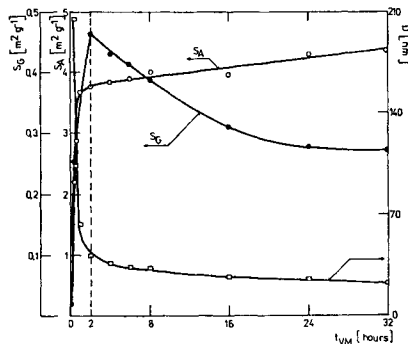


Fig. 3.4 Granulometric surface area,  $S_G$  adsorption surface area,  $S_A$  and size of primary particles,  $\Lambda$  of  $\text{CuFeS}_2$  vs. time of mechanical activation,  $t_{VM}$ .

The dependence of specific adsorption surface of the sulfidic minerals on the time of mechanical activation in a planetary mill is represented in Fig. 3.5. These traces show that the rate of formation of new surface is limited by both time of mechanical activation and type of sulfide. The experimental curves can be classified into two groups:

- sigmoidal (S-curve) – the rate of formation of new surface increases up to the inflection point of the curve and afterwards it decreases ( $\text{CuFeS}_2$ ,  $\text{HgS}$ ,  $\text{ZnS}$ ) and
- parabolic – the rate of formation of new surface is maximum at the beginning and subsequently decreases ( $\text{Cu}_5\text{FeS}_4$ ,  $\text{FeAsS}$ ,  $\text{FeS}_2$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ ).

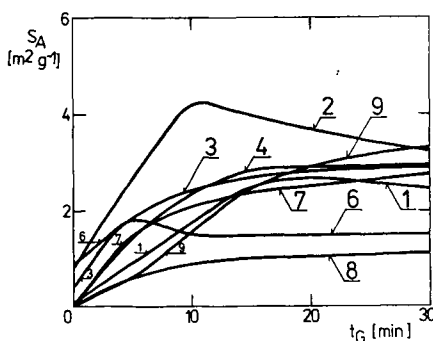


Fig. 3.5 Specific adsorption surface,  $S_A$  vs. time of mechanical activation,  $t_G$ : 1 –  $\text{CuFeS}_2$ , 2 –  $\text{Cu}_5\text{FeS}_4$ , 3 –  $\text{FeAsS}$ , 4 –  $\text{FeS}_2$ , 6 –  $\text{Sb}_2\text{S}_3$ , 7 –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 8 –  $\text{PbS}$ , 9 –  $\text{ZnS}$  [3.4].

The retardation of formation of new surface observed in both cases may be due to aggregation of fine particles as has been shown for several mechanically activated sulfides [3.4, 3.8].

The effect of aggregation can be investigated by the use of different methods [3.8]. The formation of new surface can be described by means of the value of  $S_A$ , the generation of agglomerates manifests itself as a near-constant area with increasing time. On the other hand, the value of  $S_G$  decreases owing to the generation of aggregates. The internal surface of the mineral becomes inaccessible for adsorbate. The temporal course of the values of  $S_G$  for sulfides is represented in Fig. 3.6.

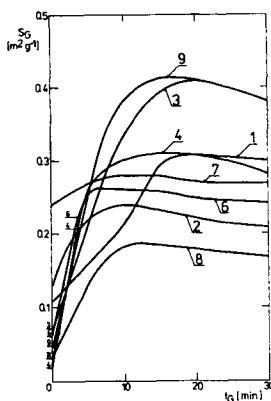


Fig. 3.6 Specific granulometric surface,  $S_G$  vs. time of mechanical activation: 1 –  $\text{CuFeS}_2$ , 2 –  $\text{Cu}_5\text{FeS}_4$ , 3 –  $\text{FeAsS}$ , 4 –  $\text{FeS}_2$ , 6 –  $\text{Sb}_2\text{S}_3$ , 7 –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 8 –  $\text{PbS}$ , 9 –  $\text{ZnS}$ .

## The mathematical description of new surface area formation

Chodakov [3.8] describes the process of new surface area formation by equation

$$S = S_{\max} (1 - e^{-k_2 t}) \quad (3.1)$$

where  $S$  is specific surface after time  $t$  and  $S_{\max}$  is maximum specific surface. Constant  $k_2$  implies the significance of rate constant of new surface formation. Equation (3.1) describes the processes in which the formation of new surface is limited by grinding equilibrium after a certain time of milling.

The description of new surface formation is problematic in the case of mechanically activated sulfides. Avvakumov states that high-intensity dry grinding of  $\text{FeS}_2$ ,  $\text{ZnS}$ ,  $\text{FeS}$  and  $\text{PbS}$  rapidly produces agglomerates (see Fig. 3.7) the formation of which hinders the correlation between the kinetic parameters of the process of new surface formation and the physical properties of sulfides [3.9].

Agglomerates are defined as groups of particles (so-called secondary particles) joined in point contacts. These secondary particles behave as a whole in real investigated processes (i.e. measurement of particle surface). The internal surface of the aggregates is not accessible for the molecules of adsorbate, e.g. nitrogen or argon [3.9, 3.11]. Aggregation can be either spontaneous or produced by external conditions. However, the opposite process – spontaneous decay of agglomerates can also proceed [3.12].

The strength of bonding between particles in agglomerates is high, however, the intermolecular bonding within the crystal lattice is stronger. For this reason, the harder is the mineral, the greater is its ability of aggregates formation. The plastic deformation of surface layers which occurs during mechanical activation plays an important role in the aggregation process. We may assume that the particles get joined not at points but also in contacts taking up a certain surface area. If the size of particles decreases, the total area of contacts per unit weight of material increases and the firmness of agglomerates rises.

As for external conditions, the formation of agglomerates is influenced by the regime of grinding. The formation of agglomerates during dry grinding is frequently described in the literature as more extensive than for grinding in a liquid medium. While the structure of mineral is preferentially destroyed during the course of dry grinding, the formation of new surface comes to the fore in the course of wet grinding [3.8, 3.13 – 3.15].

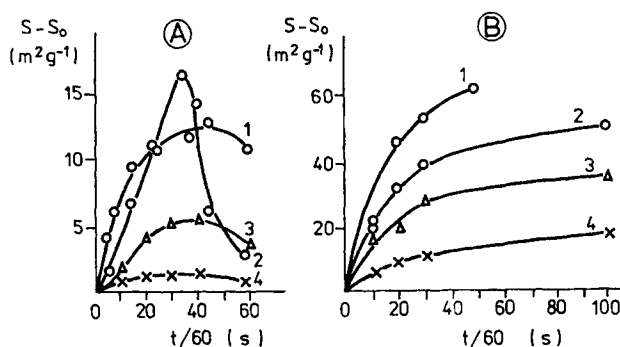


Fig. 3.7 Specific adsorption surface,  $S - S_0$  vs. time of mechanical activation,  $t$ : 1 –  $\text{FeS}_2$ , 2 –  $\text{ZnS}$ , 3 –  $\text{FeS}$ , 4 –  $\text{PbS}$ , A – dry grinding in air, B – wet grinding in water,  $S_0$  – specific adsorption surface of non-activated mineral [3.10].

The differences between dry and wet grinding are illustrated in Fig. 3.7 in which the dependence of specific adsorption surface of different sulfides on time of mechanical activation in a planetary mill is represented.

In these cases the specific adsorption surface of the sulfides exposed to mechanical activation reaches the maximum at a certain time and afterwards its value decreases to a constant value. This effect was first observed by Szantho during the long-term grinding of galena [3.16].

The effect of grinding time on the specific surface  $S$  of chalcopyrite is represented in Fig. 3.8. This relationship can be expressed by the analytical function

$$S = A + (B + kt) e^{\alpha t} \quad (3.2)$$

Where the meaning of individual parameters  $A$ ,  $B$ ,  $k$  and  $\alpha$  is as follows:  $A$  is the value of specific surface corresponding to mechanochemical equilibrium.  $B$  can be determined from the starting conditions: when  $t = 0$ , the initial surface is  $S_0$  and it results from rearranging eq. (3.2) that  $B = S_0 - A$ .  $k$  is surface increment in unit time and  $\alpha$  characterizes the rate of aggregation process [3.17]. The theoretical time  $t_M$  when the function given in (3.2) reaches its maximum can be determined as follows:

$$t_M = \frac{1}{\alpha} - \frac{B}{k}. \quad (3.3)$$

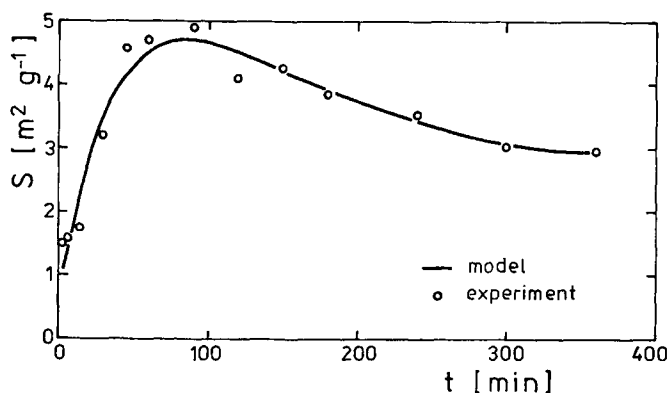


Fig. 3.8 Variation of specific surface of  $\text{CuFeS}_2$ ,  $S$  with time of planetary grinding,  $t$  [3.17].

The determination of the parameters of function (3.2) by the method of non-linear regression using the dependence of specific surface of chalcopyrite on grinding time given in Fig. 3.8 leads to the empirical function

$$S = 2.755 + (-2.066 + 0.106 t) e^{-0.014t} \quad (3.4)$$

The time  $t_M$  calculated from parameters of eq. (3.4) is in good agreement with experimental data.

The relationship between the adsorption and granulometric surface areas was deduced by Tkáčová [3.13] for various minerals. She expressed a simple parabolic relationship where the

parameter is a measure of the difference between quantities  $S_A$  and  $S_G$ . She stated that before the start of aggregation there is a linear relation between adsorption surface and granulometric surface of oxide minerals.

If we compare Fig. 3.5 with Fig. 3.6 we can state that the decrease in formation of new surface appears in case the aggregation showing itself by a decrease in the values of  $S_G$  becomes dominant.

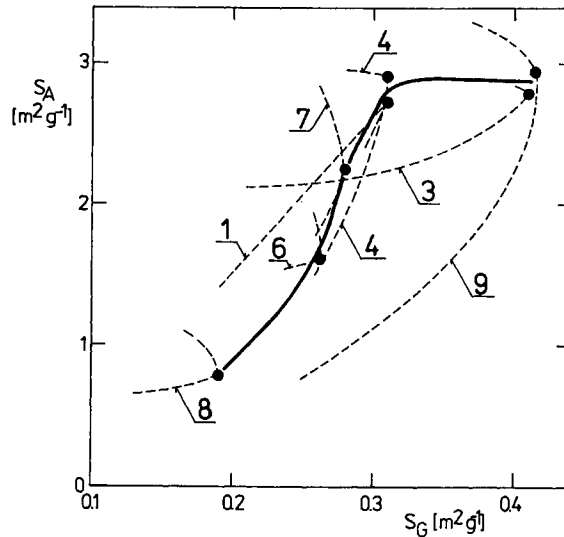


Fig. 3.9 Specific adsorption surface,  $S_A$  vs. specific granulometric surface,  $S_G$ : 1 –  $\text{CuFeS}_2$ , 3 –  $\text{FeAsS}$ , 4 –  $\text{FeS}_2$ , 6 –  $\text{Sb}_2\text{S}_3$ , 7 –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 8 –  $\text{PbS}$ , 9 –  $\text{ZnS}$  [3.4].

The values of specific adsorption surface  $S_A$  are plotted against the values of specific granulometric surface  $S_G$  for individual mechanically activated sulfides in Fig. 3.9. In agreement with the results of paper [3.13] we can observe the parabolic character of the plots (denoted with dashed lines) for all aggregating sulfides. It results from the presented data, using a certain grinding equipment and medium (planetary mill and grinding in air), that aggregation does not occur provided that the specific adsorption surface  $S_A$  is below about  $3 \text{ m}^2\text{g}^{-1}$ . Higher values of  $S_A$  cannot be achieved under these specific grinding conditions. The solid line in Fig. 3.9 joins the maximum values of specific granulometric surface  $S_G^{\max}$  with the corresponding values of specific adsorption surface  $S_A$ . While for  $\text{PbS}$ ,  $\text{Sb}_2\text{S}_3$  and  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  the specific adsorption surface  $S_A$  is sensitive to  $S_G^{\max}$ ,  $S_A$  is practically independent of  $S_G^{\max}$  in the case of  $\text{CuFeS}_2$ ,  $\text{FeS}_2$ ,  $\text{FeAsS}$  and  $\text{ZnS}$ . This fact is due to the hardness of the minerals with the Vickers hardness of the former group in the range  $\text{VHN} = 42\text{--}119 \text{ kgmm}^{-2}$  and those of the second group in the range from 174 to  $2056 \text{ kgmm}^{-2}$  [3.18].

The aggregation ability of ultrafine particles is caused by molecular forces within solid substances. In Fig. 3.10 the values of  $S_A^{\max}$  of sulfides activated by grinding in a planetary mill are plotted against the tabulated values of the Mohs hardness scale. A sensitivity of the maximum surface to hardness can be observed only in the region  $H < 4$ . For harder materials, the surface is independent of hardness and varies, as already mentioned, about the value equal to  $3 \text{ m}^2\text{g}^{-1}$ . This effect is a consequence of agglomerate formation and in accordance with the

theory [3.8] that the ability of aggregation of harder minerals exposed to grinding is greater than for softer minerals.

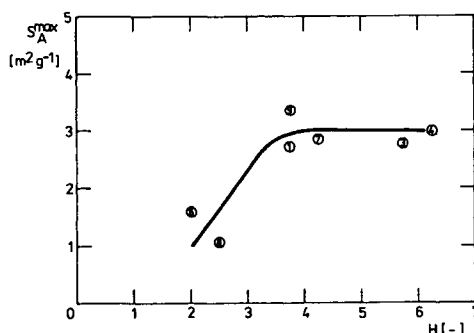


Fig. 3.10 Maximum specific adsorption surface,  $S_A^{\max}$  vs. Mohs hardness, H. 1 –  $\text{CuFeS}_2$ , 3 –  $\text{FeAsS}$ , 4 –  $\text{FeS}_2$ , 5 –  $\text{Sb}_2\text{S}_3$ , 7 –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 8 –  $\text{PbS}$ , 9 –  $\text{ZnS}$  [3.4].

Besides the indirect methods, e.g. the methods of determination of adsorption surface and granulometric surface, the agglomerates can be observed directly by the method of electron microscopy. The corresponding micrographs of  $\text{ZnS}$  and  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  for non-activated as well as for samples activated by dry grinding in planetary mill for 30 minutes are shown in Fig. 3.11. Besides the effect of disintegration resulting in a greater proportion of finer particles, we can also observe the formation of agglomerates which may have dimensions comparable to those of non-activated particles.

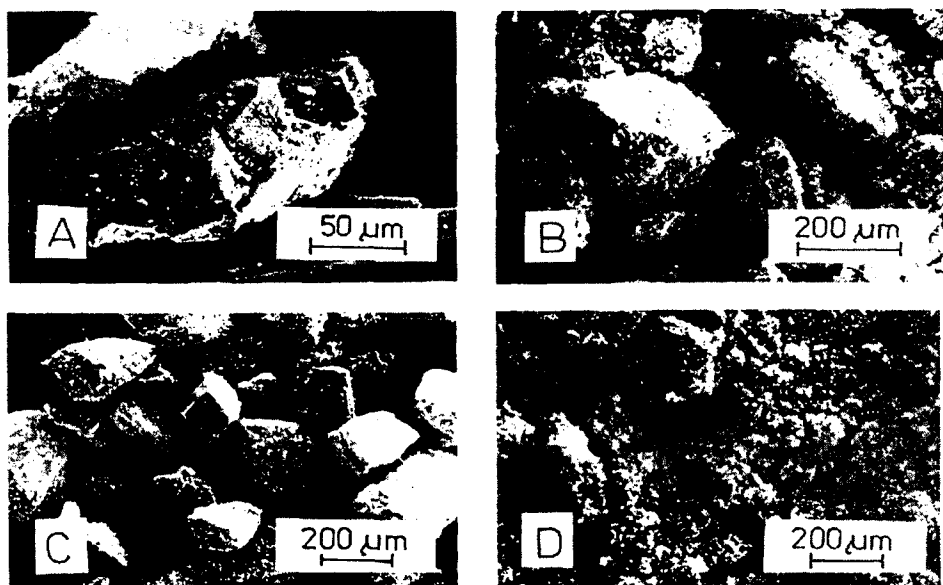


Fig. 3.11 Scanning electron micrographs of  $\text{ZnS}$  (A,B) and  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  (C,D): A,C – non-activated minerals, B – mechanical activation by vibratory grinding 240 min, D – mechanical activation by planetary grinding 30 min.

### 3.3. Disordering of crystal structure

To appreciate the defectiveness in the bulk of mineral we can use several physico-chemical methods. The application of diffraction methods enables us to investigate the disordering of crystal structure. The diffraction line (002) of mechanically activated molybdenite  $\text{MoS}_2$  is shown of Fig. 3.12 for illustration. The dependence of the shape of the lines changes with specific energy of grinding  $E_M$  [3.19] and at  $E_M = 2240 \text{ kWh t}^{-1}$  the diffraction line is almost completely absent.

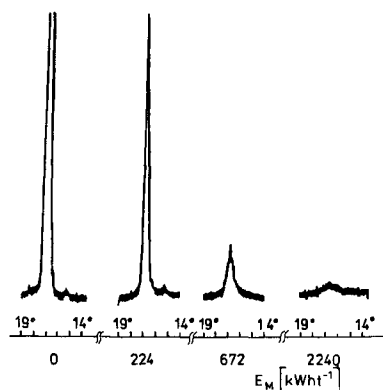


Fig. 3.12 Diffraction line (002) of  $\text{MoS}_2$ ,  $E_M$  – specific energy of grinding [3.19].

Different parameters can be calculated from the diffraction lines of mechanically activated minerals. While the calculations of amorphization  $A$  and crystallinity  $X$  is based on the integral intensities of the X-ray lines, the calculation of lattice deformation  $\epsilon$  is based on estimation of the halfwidths of these lines (see Chapter 2).

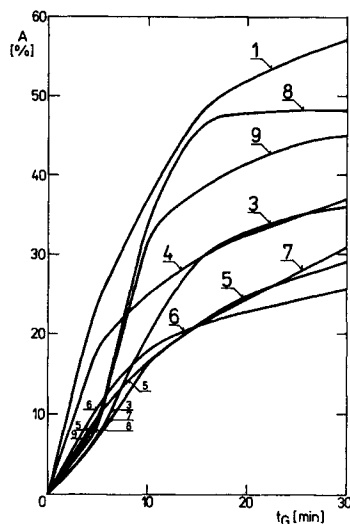


Fig. 3.13 Amorphization,  $A$  vs. time of mechanical activation,  $t_G$ : 1 –  $\text{CuFeS}_2$ , 3 –  $\text{FeAsS}$ , 4 –  $\text{FeS}_2$ , 5 –  $\text{HgS}$ , 6 –  $\text{Sb}_2\text{S}_3$ , 7 –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 8 –  $\text{PbS}$ , 9 –  $\text{ZnS}$  [3.4].

The dependence of amorphization and lattice deformation on the time of mechanical activation for individual sulfides is shown in Figs 3.13 and 3.14. Disordering in the bulk of mineral increases with the time of mechanical activation. However, as in the estimation of surface changes, the dependence on the time of mechanical activation is different for individual minerals. In general, we may state that the rate of formation of bulk defects decreases with increasing grinding time.

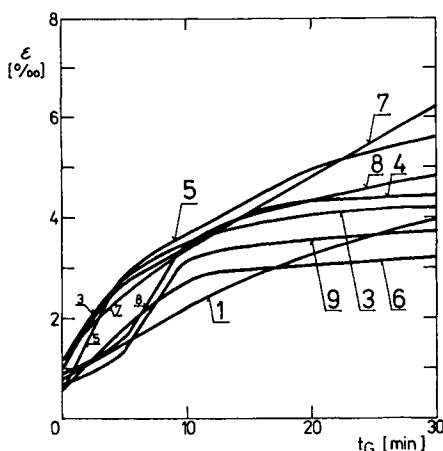


Fig. 3.14 Lattice deformation,  $\varepsilon$  vs. time of mechanical activation,  $t_G$ : 1 –  $\text{CuFeS}_2$ , 3 –  $\text{FeAsS}$ , 4 –  $\text{FeS}_2$ , 5 –  $\text{HgS}$ , 6 –  $\text{Sb}_2\text{S}_3$ , 7 –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 8 –  $\text{PbS}$ , 9 –  $\text{ZnS}$  [3.14].

### 3.4. Relationship between new surface area formation and disordering of crystal structure

It follows from the preceding paragraphs that both specific adsorption surface  $S_A$  and lattice deformation  $\varepsilon$  increase with the time of mechanical activation.

In order to compare the values  $S_A$  and  $\varepsilon$  with each other over the same interval we can define their reduced dimensionless equivalents by means of the following equations

$$S_A^r = \frac{S_A^t - S_A^0}{S_A^{\max} - S_A^0} \quad (3.5)$$

$$\varepsilon^r = \frac{\varepsilon^t - \varepsilon^0}{\varepsilon^{\max} - \varepsilon^0} \quad (3.6)$$

where symbols  $S_A^r$ ,  $\varepsilon^r$ ,  $S_A^t$ ,  $\varepsilon^t$ ,  $S_A^0$ ,  $\varepsilon^0$ ,  $S_A^{\max}$ ,  $\varepsilon^{\max}$  and  $t$  stand for reduced specific adsorption surface, reduced lattice deformation, specific adsorption surface in the time  $t$ , lattice deformation in the time  $t$ , specific adsorption surface of the non-activated sample, lattice deformation of the non-activated sample, maximum specific adsorption surface, maximum lattice deformation and time of mechanical activation, respectively.

In Fig. 3.15 the reduced specific adsorption surface  $S_A^r$  is plotted against the reduced lattice deformation  $\varepsilon^r$  of mechanically activated sulfides.

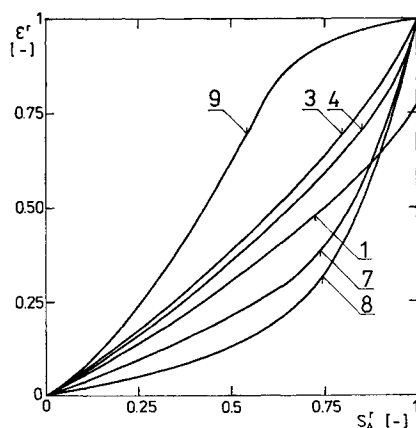


Fig. 3.15 Reduced lattice deformation,  $\varepsilon^r$  vs. reduced specific adsorption surface,  $S_A^r$  for mechanically activated sulfides: 1 –  $\text{CuFeS}_2$ , 3 –  $\text{FeAsS}$ , 4 –  $\text{FeS}_2$ , 7 –  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 8 –  $\text{PbS}$ , 9 –  $\text{ZnS}$  [3.4].

Except for sphalerite, all investigated minerals exhibit a parabolic relationship which can be described by the equation

$$\varepsilon^r = (S_A^r)^n \quad (3.7)$$

The deviation observed for sphalerite is a consequence of rapid agglomeration (Fig. 3.6, 3.7) and stagnation of the values of lattice deformation in this mineral during mechanical activation (Fig. 3.14 and 3.7). Provided the disordering in bulk and surface of the investigated minerals is uniform, the plots of  $\varepsilon$  against  $S_A$  should be linear. The deviation from linearity indicates that lattice deformation and formation of new surface do not advance at an equal rate. The observed parabolic course is due to the start of aggregation effects and deviation of the exponent  $n$  from unity may serve as a measure of departure from the proportional disordering in bulk and surface of the mineral. The values of this exponent calculated for individual sulfides are given in Table 3.5. Confrontation of these results with Fig. 3.10 enables us to suggest that the values of exponent  $n$  may be related to the Mohs hardness values of the minerals, except for the discussed zinc sulfide.

Table 3.5 Values of exponent  $n$  in the equation (3.7) for mechanically activated sulfides ( $S_A^r = 0.2-0.6$ )

|                                          | $n$  | Regression coefficient | Mohs hardness |
|------------------------------------------|------|------------------------|---------------|
| ZnS                                      | 1.40 | 0.99996                | 3-4           |
| FeAsS                                    | 1.15 | 0.99939                | 5.5-6         |
| $\text{FeS}_2$                           | 1.15 | 0.99987                | 6-6.5         |
| $\text{CuFeS}_2$                         | 1.10 | 0.99936                | 3-4           |
| $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ | 0.87 | 0.93631                | 3-4           |
| PbS                                      | 0.33 | 0.99842                | 2-3           |

Both the formation of new surface as well as the disordering of crystal structure of mechanically activated sulfides have significant influence on their reactivity in consecutive treatment in either gaseous or liquid medium. We shall analyze the theoretical aspects and the possible technological applications of these processes in further chapters.

### 3.5. Physical and chemical changes of minerals during mechanical activation in organic liquids

It has been demonstrated throughout the history the grinding in a liquid was more effective for new surface formation than dry grinding [3.15]. In the case of grinding in water, chemical reactions between broken surface bonds and water molecules occur [3.20]. A reduction in hardness was discovered in the case of such minerals as oxides, silicates and carbonates. A more detailed study of the effect of the quality of wet grinding environment on the properties of minerals has been given by Rebinder [3.21]. He used such liquids as inorganic salt solutions (NaCl, NaOH, Na<sub>2</sub>CO<sub>3</sub> and AlCl<sub>3</sub>) and organic polar compounds. In the latter case, it was found that the hardness of the ground substances decreased with an increase in the number of carbon atoms in the molecules of organic compounds.

Grinding in organic liquids is often more effective than in water [3.15, 3.22 – 3.25]. It is assumed that during grinding in this environment a slowing down of the formation of agglomerates and enhanced material flow occurs and as a result, improved grinding is achieved. Chemical additives can influence grinding for a number of further reasons, e.g. hindering agglomeration of the freshly produced fines, modifying interactions between mineral particles and balls and mill wall, influencing the interparticle frictional characteristics and altering the strength of the mineral, etc. [3.26]. Ikazaki et al. [3.27 – 3.28] studied the interaction between the ground material and organic liquids and introduced the term "chemically-assisted comminution", meaning that particles which are to be ground are made fragile or more easily broken by chemical interaction of the particles in the grinding environment.

New surface formation and amorphization for sulfides mechanically activated in different organic liquids (alcohols with 1-5 carbon atoms) were studied in paper [3.29]. Properties of liquids used as grinding medium are given in Table 3.6.

Table 3.6 Physico-chemical properties of organic liquids used as grinding medium in mechanical activation of sulfides by planetary grinding

| Liquid         | Molecular formula                 | Molecular weight<br>M | Molecular density<br>$\rho$<br>(kgm <sup>-3</sup> ) | Molecular volume<br>$V=M/\rho$<br>(m <sup>3</sup> kg <sup>-1</sup> ) | Dipole moment<br>$\mu \times 10^{-30}$<br>(C m) | $\mu/V \times 10^{-29}$<br>(C kg m <sup>-2</sup> ) |
|----------------|-----------------------------------|-----------------------|-----------------------------------------------------|----------------------------------------------------------------------|-------------------------------------------------|----------------------------------------------------|
| Methanol       | CH <sub>3</sub> OH                | 32.04                 | 792                                                 | 0.04045                                                              | 5.64                                            | 13.94                                              |
| Ethanol        | C <sub>2</sub> H <sub>5</sub> OH  | 46.07                 | 789.2                                               | 0.05838                                                              | 5.67                                            | 9.71                                               |
| Propanol       | C <sub>3</sub> H <sub>7</sub> OH  | 60.10                 | 804.4                                               | 0.07471                                                              | 5.47                                            | 7.32                                               |
| i-Propanol     | C <sub>3</sub> H <sub>7</sub> OH  | 60.10                 | 785.5                                               | 0.07651                                                              | 5.27                                            | 6.89                                               |
| Butanol        | C <sub>4</sub> H <sub>9</sub> OH  | 74.12                 | 810                                                 | 0.09151                                                              | 5.54                                            | 6.05                                               |
| i-Butanol      | C <sub>4</sub> H <sub>9</sub> OH  | 74.12                 | 805                                                 | 0.09208                                                              | 5.44                                            | 5.91                                               |
| i-Amyl alcohol | C <sub>5</sub> H <sub>11</sub> OH | 88.15                 | 880                                                 | 0.10021                                                              | 5.54                                            | 5.53                                               |

In Fig. 3.16 the values of specific surface area for mechanically activated sulfides were plotted against  $\mu/V$  values, where  $\mu$  is the dipole moment and  $V$  is the molecular volume. This ratio has been calculated for the individual organic liquids and the results are given in Table 3.6. From these data it follows that they can be described by an empirical linear function

$$S_A = a + b \frac{\mu}{V} \quad (3.8)$$

where  $S$  is the specific surface of the ground specimens,  $\mu/V$  is a value describing the individual organic liquids and  $a$ ,  $b$  are parameters. The linear character of this empirical function shows that the increase of surface is directly proportional to  $\mu/V$ . Ikazaki et al. [3.27] found a similar relationship between the median diameter of silicon nitride, alumina and soda glass powders ground in vibration mill and  $\mu/V$  values. It follows then, that the increase of surface area is dependent also on the number of carbon atoms. The higher the number of atoms, the more space filling adsorption is evident and the greater the surface area.

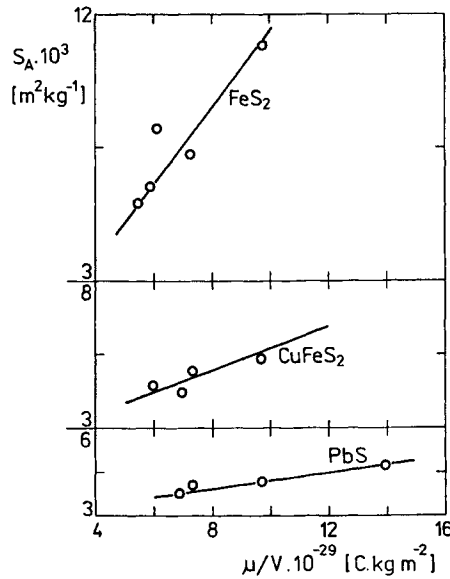


Fig. 3.16 Specific adsorption surface area,  $S_A$  vs.  $\mu/V$ . Mechanical activation 10 min [3.29].

For the propagation of cracks formed during mechanical activation, the value of  $\mu/V$  can be used as a means of assessing the grinding ability of the liquid and to characterize the grinding environment [3.31]. We assume that the use of organic liquids which apart from supporting the formation and propagation of cracks also hinders the aggregation of freshly produced fines.

The slopes in Fig. 3.16 depend on the properties of the minerals. Fig. 3.17 shows the relationship between parameter  $b$  and the values of Vickers microhardness (VHN). The parameter  $b$  was calculated by linear regression for all the minerals selected and shows that the rate of surface area production changes with respect to  $\mu/V$  and is greater for harder minerals. Also the organic liquid chosen as the grinding medium has a greater influence on surface growth in the case of harder materials.

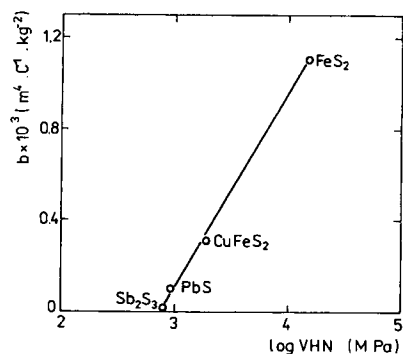


Fig. 3.17 Variation of the parameter  $b$  from equation (3.8) with the values of Vickers microhardness VHN.

The relationship between amorphization and  $\mu/V$  value for two selected sulfides, chalcopyrite and pyrite, ground in  $\text{C}_1\text{-C}_5$  organic liquids is shown in Figs. 3.18-3.19. The degree of amorphization of the investigated sulfides decreases as  $\mu/V$  increases. The lowest values (i.e., the highest proportion of the crystalline phase in the material) were observed in case of using methanol.

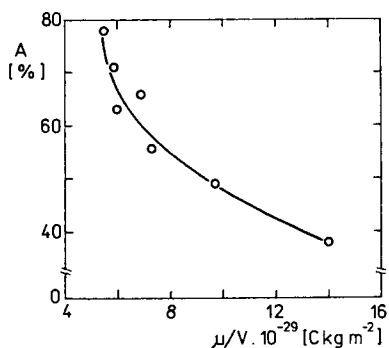


Fig. 3.18 Amorphization,  $A$  vs.  $\mu/V$  for  $\text{CuFeS}_2$ , mechanical activation 10 min.

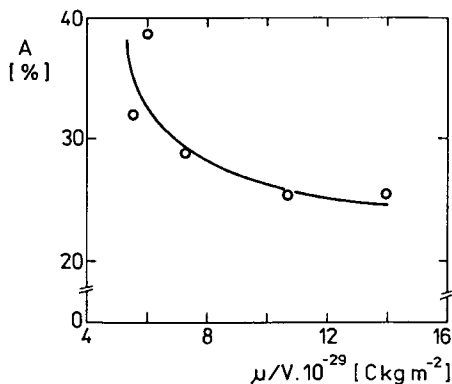


Fig. 3.19 Amorphization,  $A$  vs.  $\mu/V$  for  $\text{FeS}_2$ , mechanical activation 10 min.

The increase in the rate of formation of new sulfide surfaces is facilitated by organic liquids of low molecular density (high  $\mu/V$  values) which allow a free flow of pulp in the planetary mill. The disordering of their structure is facilitated if organic liquids with greater molecular density and lower  $\mu/V$  values (as well as higher number of C atoms) are applied. In this case, the interaction between the sulfide particles and grinding environment is facilitated, so that the crack propagation reaches subsurface zones and the bulk structure of the material.

The change in crystal disordering relative to  $\mu/V$  of the grinding medium can be characterized by the difference  $\Delta A$

$$\Delta A = A_{\max} - A_{\min} \quad (3.9)$$

where  $A_{\max}$  is the amorphization for  $\mu/V = 5.53 \times 10^{-29}$  (i-amyl alcohol) and  $A_{\min}$  is the amorphization for  $\mu/V = 13.94 \times 10^{-29}$  (methanol). The relationship between  $\Delta A$  and VHN is shown in Fig. 3.20. It can be seen that by organic liquids considered here the greatest structure disordering occurs with the softest sulfides (i.e., those having the lowest VHN hardness values).

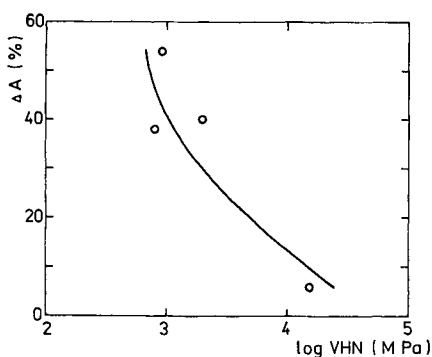


Fig. 3.20 Variation of  $\Delta A$  values with the value of Vickers microhardness VHN for different minerals, mechanical activation 10 min.

### 3.6. Mechanochemical surface oxidation

The disordering of surface layers of sulfide minerals occurs during mechanical activation by dry grinding in the presence of air oxygen. The first surface layers of these sulfides are degraded to some extent [3.32]. However, this disordering is not uniform and a great variety of different species are formed on surface of disordered sulfides e.g. oxides, hydroxioxides, hydroxides, sulfites, thiosulfates, oxisulfates, hydroxisulfates and sulfates have all been reported. The methods of photoelectron spectroscopy (XPS) and infrared spectroscopy (IR) serve as reliable tools for the identification of the species.

#### *Chalcopyrite CuFeS<sub>2</sub>*

The distribution of elements in the surface layer of non-activated CuFeS<sub>2</sub> is represented in the form of XPS spectrum in Fig. 3.21. Besides copper, iron and sulfur, other elements such as carbon, nitrogen and oxygen can be identified as well. The occurrence of carbon and to a certain extent of oxygen is customary for minerals owing to adsorption of CO<sub>2</sub> from air atmosphere.

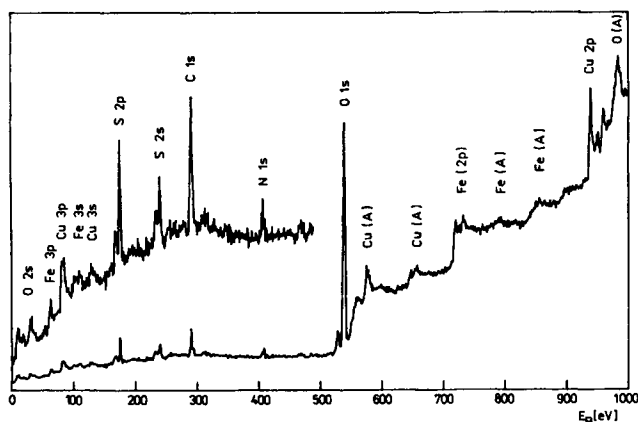


Fig. 3.21 XPS survey spectrum of  $\text{CuFeS}_2$  [3.33].

The method of photoelectron spectroscopy allows not only to ascertain the distributions of individual elements but also to obtain information about oxidation states of these elements [3.34 – 3.35]. The spectra of copper  $\text{Cu}2p_{3/2}$  and  $\text{Cu}2p_{1/2}$  in the regime of high resolution are represented in Fig. 3.22. In the region  $E_B = 950\text{--}970$  eV of the spectrum of mechanically activated sample (spectrum 2) we can observe the so-called satellite peaks the presence of which indicates that bivalent copper prevails over the univalent [3.36 – 3.37].



Fig. 3.22  $\text{Cu}2p$  XPS spectrum of  $\text{CuFeS}_2$ , mechanical activation: 1 – 0 min, 2 – 60 min [3.36].

The XPS method gives many possibilities of determining the different oxidation states of sulfur with characteristic peaks occurring in the region  $E_B = 161\text{--}170$  eV [3.38]. In Fig. 3.23 we can see the  $\text{S}2p$  spectrum  $\text{CuFeS}_2$  subjected to mechanical activation in air of up to 360 min. We can observe two different peaks, the intensities of which change with the time of mechanical activation [3.37]. While the peak at  $E_B \sim 161\text{--}166$  eV corresponds to bivalent sulfur, the peak at  $E_B \sim 166\text{--}169$  eV is typical of hexavalent sulfur and is present in all activated samples. (Note: hexavalent sulfur also appears in the case of reference sample – curve 1 – which was the partially oxidized as-received mineral).

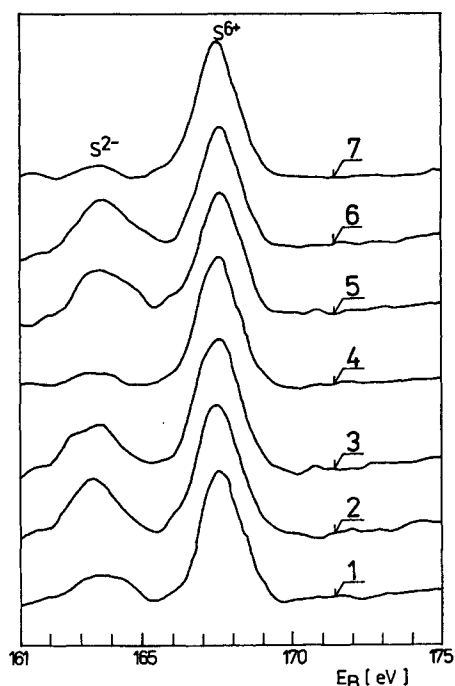


Fig. 3.23 S2p XPS spectrum of CuFeS<sub>2</sub>, mechanical activation: 1 – 0 min, 2 – 7.5 min, 3 – 15 min, 4 – 60 min, 5 – 120 min, 6 – 240 min, 7 – 300 min [3.37].

The atomic ratio  $S^{6+}/S^{2-}$  obtained by processing the spectra in Fig. 3.23 is presented as a function of time of mechanical activation in Fig. 3.24.

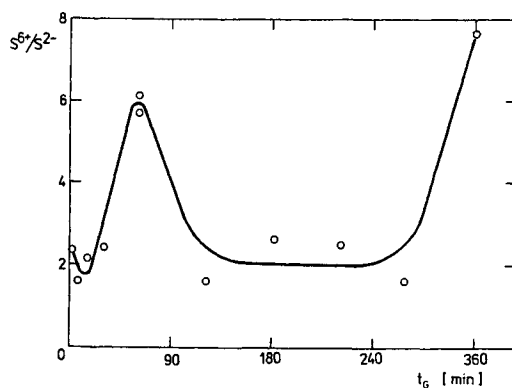


Fig. 3.24  $S^{6+}/S^{2-}$  ratio of CuFeS<sub>2</sub> vs. time of mechanical activation,  $t_G$  [3.37].

In the region  $t_G < 60$  min there is a parallel increase in the values of  $S^{6+}/S^{2-}$  and specific surface  $S_A$  (Fig. 3.25). In this region, it is clear that the extent of oxidation is a function of the surface area. For activation times up to 300 min, the formation of new surface stagnates due to aggregation of particles and formation of agglomerates as shown by particle size analysis and electron microscopy described in the paper [3.36]. In the region of agglomerate formation, the dispersing process is retarded, the mechanochemical oxidation is inhibited and the atomic

ratio  $S^{6+}/S^{2-}$  remains practically constant. Beyond 300 min of activation, the damage to the structure of  $CuFeS_2$  assumes critical values and transformation of the structure from ordered to disordered occurs. Simultaneously, the conditions favourable for mechanochemical oxidation are restored which manifests itself by increasing values of  $S^{6+}/S^{2-}$  (Fig. 3.24).

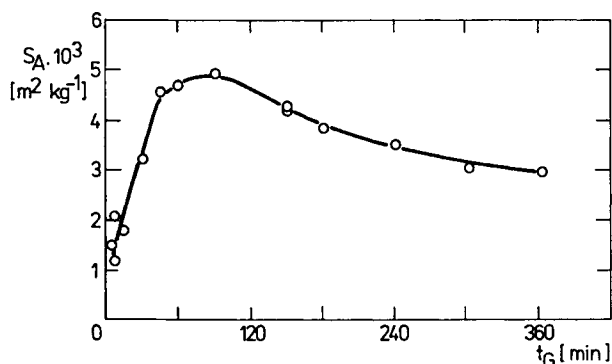


Fig. 3.25 Specific adsorption surface area,  $S_A$  of  $CuFeS_2$  vs. time of mechanical activation,  $t_G$  [3.37].

The presence of sulfate was also proven by infrared spectroscopy [3.39] with  $(SO_4^{2-})$  identified in chalcopyrite, ground in different media, by means of its characteristic peaks  $\bar{\nu}_3(SO_4) = 1085 \text{ cm}^{-1}$ ,  $\bar{\nu}_4(SO_4) = 600\text{--}625 \text{ cm}^{-1}$  and  $\bar{\nu}_2(SO_4) = 473 \text{ cm}^{-1}$ . The most extensive formation of sulfates was observed if  $CuFeS_2$  was ground in a ball mill for 15 hours (Fig. 3.26, curve 5).

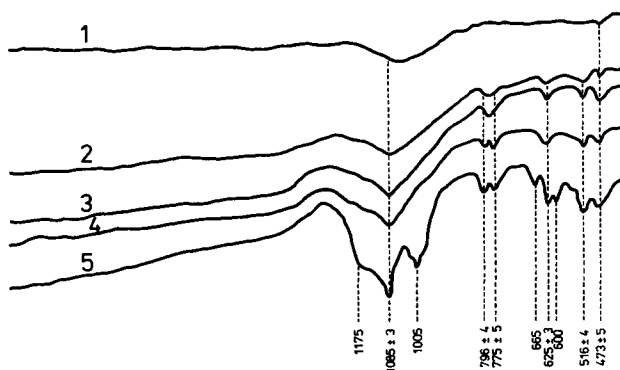


Fig. 3.26 Infrared spectra of mechanically activated  $CuFeS_2$ , 1 – non-ground sample, 2 – grinding in air (3 hours), 3 – grinding in methanol (3 hours), 4 – grinding in water (3 hours), 5 – grinding in water (15 hours) [3.39].

The extent of sulfate formation in the products of planetary grinding of chalcopyrite in air was estimated by measuring the area of the  $\bar{\nu}_3(SO_4)$  peak. The relationship between the logarithm of reciprocal value of transmittance  $1/T$  and the time of planetary grinding is presented in Fig. 3.27 and is clearly linear. The infrared spectra represented in Fig. 3.26 are completed by the bands at 1175, 1005, 796, 777 and  $516 \text{ cm}^{-1}$  which correspond to admixed quartz [3.40].

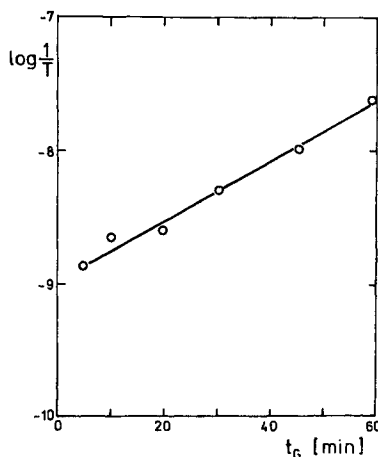


Fig. 3.27 Changes of the logarithmic reciprocal value of transmittance  $T$  of the  $1144\text{ cm}^{-1}$  band of  $\text{SO}_4^{2-}$  for  $\text{CuFeS}_2$  vs. time of mechanical activation,  $t_G$  [3.36].

Brion [3.32] published data about the compounds that are generated on the surface of sulfides during grinding. It is rather difficult to attribute individual species to  $\text{CuFeS}_2$  because we can expect any (or all) of the following compounds:  $\text{Fe}_3\text{O}_4$ ,  $\text{FeO}$ ,  $\alpha\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{FeO}(\text{OH})$ ,  $\text{Fe}(\text{OH})\text{SO}_4$ ,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{CuS}$  and  $\text{Cu}_2\text{S}$ . For chalcopyrite, the author disclosed an increase in content of the  $(\text{SO}_4)^{2-}$  group with grinding time as well as an increase in atomic ratio  $\text{Fe}/\text{Cu}$ . Formation of elemental sulfur as an intermediate of the oxidation  $\text{S}^{2-}$  to  $\text{S}^{6+}$  is not mentioned in literature [3.41] and was not observed in experiments with mechanically activated chalcopyrite.

### Pyrite $\text{FeS}_2$

The survey XPS spectrum of non-activated  $\text{FeS}_2$  is represented in Fig. 3.28. Besides the basic elements iron and sulfur also additional elements, i.e. carbon, oxygen, nitrogen and indium show itself in the region  $E_B \sim 550\text{ eV}$ . The peak of indium  $\text{In}3d$  does not correspond to an admixture in pyrite, but it was put in pyrite surface during the sample preparation for XPS measurement.

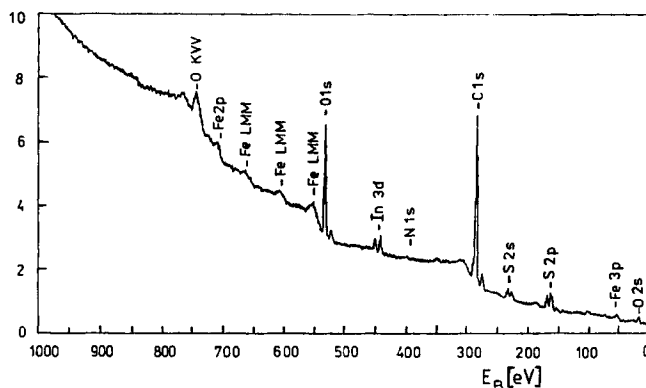


Fig. 3.28 XPS survey spectrum of  $\text{FeS}_2$  [3.42].

The XPS spectra of iron Fe2p and sulfur S2p taken in the regime of high resolution are represented in Figs 3.29 – 3.30 for non-activated sample and for pyrite subjected to 5, 10 and 30 minutes activation. The surface chemistry of the non-activated sample significantly differs from the surface of the activated samples. Analysis of the S2p spectrum indicates that sulfur at the surface of non-activated FeS<sub>2</sub> occurs in the forms S<sup>2-</sup>, S<sup>0</sup> and S<sup>6+</sup>, their ratio being 0.12:0.03:0.81. For higher times of activation all sulfur is transformed into the S<sup>6+</sup> form (curves 3 and 4 in Fig. 3.30). The generation of sulfates can also be observed in the spectrum of iron Fe2p (Fig. 3.29). From the literature the values E<sub>B</sub> = 706.7 eV and 725.7 eV may correspond to pyrite while the value E<sub>B</sub> = 711.7 eV is to be attributed to FeSO<sub>4</sub>·7H<sub>2</sub>O [3.32]. In the case of activated samples the peak at E<sub>B</sub> = 713.2 – 713.25 eV predominates. According to [3.32] this peak unambiguously corresponds to trivalent iron in Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

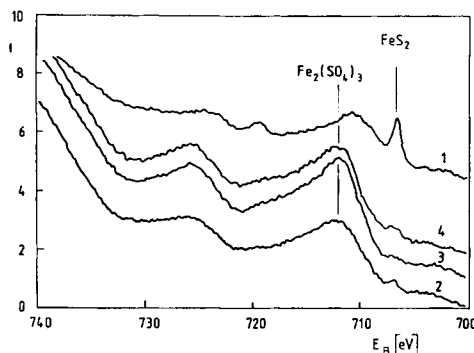


Fig. 3.29 Fe2p XPS spectrum of FeS<sub>2</sub>, mechanical activation: 1 – 0 min, 2 – 5 min, 3 – 10 min, 4 – 30 min [3.42].

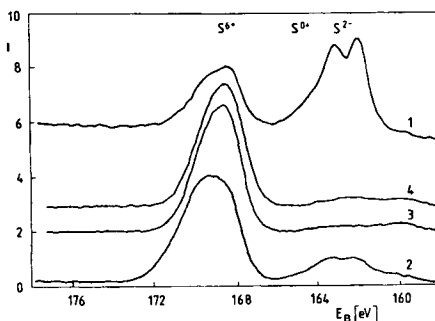


Fig. 3.30 S2p XPS spectrum of FeS<sub>2</sub>, mechanical activation: 1 – 0 min, 2 – 5 min, 3 – 10 min, 4 – 30 min [3.42].

The infrared spectra of the non-activated sample and the samples ground in a planetary mill for 5, 10 and 30 minutes are shown in Fig. 3.31. In the region 410-420 cm<sup>-1</sup> we can observe a peak corresponding to vibration of the S – S bond of pyrite. The admixed quartz can be identified by the bands at 808-820 and 1057-1081 cm<sup>-1</sup>, the admixed hematite by the bands at 570-593 cm<sup>-1</sup> [3.43] and 1103-1170 cm<sup>-1</sup> [3.44]. The bands at 637-653 cm<sup>-1</sup> might correspond to magnetite [3.45] and the bands at 1610-1623 cm<sup>-1</sup> indicate the traces of moisture in the tablet of KBr.

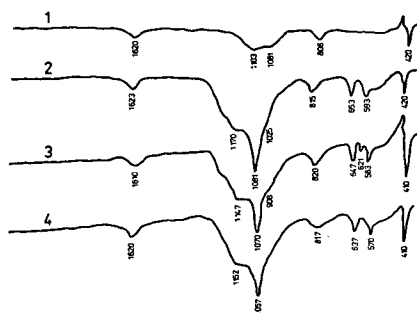


Fig. 3.31 IR spectrum of  $\text{FeS}_2$ , mechanical activation: 1 – 0 min, 2 – 5 min, 3 – 10 min, 4 – 30 min [3.46].

The infrared spectra of  $\text{FeS}_2$  mechanically activated by wet grinding in water and by dry grinding in the air was studied by Kulebakin [3.45, 3.47]. Magnetite  $\text{Fe}_3\text{O}_4$  and small amounts of pyrrhotite  $\text{FeS}$  were identified among the products by dry grinding (Fig. 3.32).  $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  prevailed among the products of wet grinding.

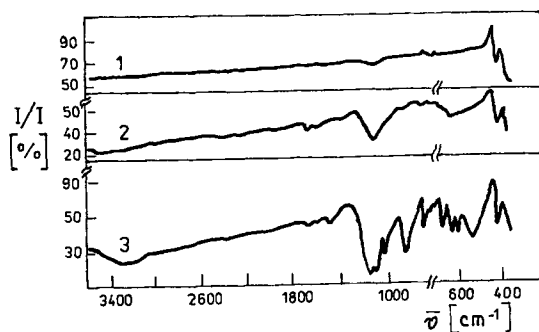


Fig. 3.32 IR spectrum of  $\text{FeS}_2$ , mechanical activation: 1 – 0 min, 2 – 7 min (wet grinding), 3 – 7 min (dry grinding) [3.45, 3.47].

### ***Stibnite $\text{Sb}_2\text{S}_3$***

Antimony, sulfur and contaminating carbon occur in the surface layer of stibnite (Fig. 3.33). The presence of  $\text{Si}2p$  corresponding to admixed quartz was found.

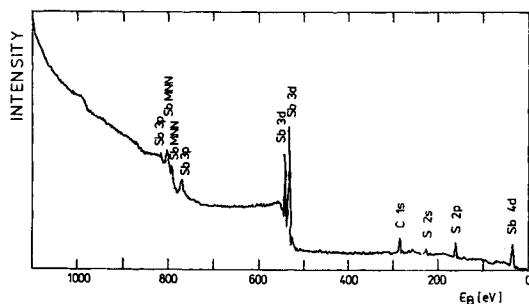


Fig. 3.33 XPS survey spectrum of  $\text{Sb}_2\text{S}_3$

A complex S2p spectrum was identified in the region  $E_B = 160\text{--}170$  eV (Figs 3.34, 3.35, full lines). It was resolved into two superimposing peaks by using computer data treatment (Figs 3.34, 3.35, dashed lines). If we compare the sample mechanically activated for 30 min (Fig. 3.35) with a non-activated one (Fig. 3.34), we may state that the position of S2p band of activated sample is slightly shifted to higher values of bond energy ( $E_B = 160\text{--}166$  eV for non-activated  $\text{Sb}_2\text{S}_3$  and  $E_B = 162\text{--}168$  eV for activated  $\text{Sb}_2\text{S}_3$ ).

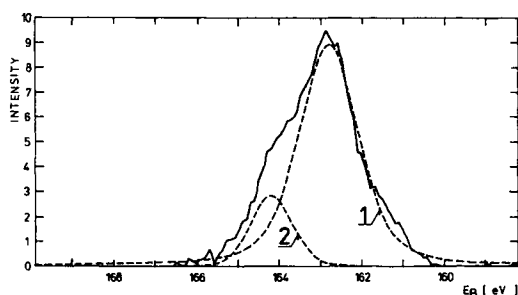


Fig. 3.34 S2p XPS spectrum of non-activated  $\text{Sb}_2\text{S}_3$ .

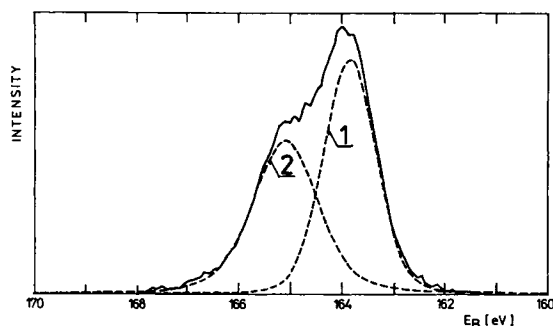


Fig. 3.35 S2p XPS spectrum of mechanically activated  $\text{Sb}_2\text{S}_3$ .

The area of second fitted peak was somewhat larger than the first peak in the activated sample than in the standard. No peak was observed in the region  $E_B \sim 169$  eV characteristic of the presence of the  $\text{S}^{6+}$  form of sulfur. The form of the peak of antimony Sb3d which overlaps the peak of oxygen O1s is consistent with this fact. Moreover, the calculated content of oxygen amounts only to a few atomic per cent which confirms the absence of the  $\text{S}^{6+}$  form. The Sb3d peak reaches its maximum at  $E_B = 539.6$  eV or  $E_B = 529.9$  eV for standard or activated sample which is in good agreement with the value tabulated for  $\text{Sb}_2\text{S}_3$  [3.48].

The values of atomic concentrations of antimony and sulfur in the investigated samples are listed in Table 3.7. The presented values of atomic ratios  $\text{Sb}/\text{S} = 0.80$  and  $\text{Sb}/\text{S} = 0.97$  show that the surface layer of activated  $\text{Sb}_2\text{S}_3$  was deprived of antimony when compared with non-activated  $\text{Sb}_2\text{S}_3$ . In agreement with literature [3.49] we assume that stibnite undergoes surface oxidation producing  $\text{Sb}_2\text{O}_3$  in the course of mechanical activation. Antimony (III) oxide is a volatile compound [3.50] which is likely to escape in the process of evacuation of spectrometer. In this way the surface layer of stibnite is deprived of antimony. The absence of oxide compounds is also confirmed by absence of the oxygen peak O1s.

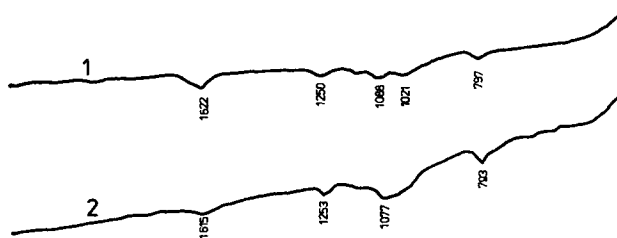


Fig. 3.36 IR spectrum of  $\text{Sb}_2\text{S}_3$ , mechanical activation: 1 – 0 min, 2 – 30 min [3.46].

Table 3.7 Atomic concentrations of Sb and S in surface layer of  $\text{Sb}_2\text{S}_3$

| Mechanical activation<br>(min) | Atomic concentrations (%) |       |      |
|--------------------------------|---------------------------|-------|------|
|                                | Sb                        | S     | Sb/S |
| -                              | 49.14                     | 50.86 | 0.97 |
| 30                             | 44.51                     | 55.49 | 0.80 |

The infrared spectra (Fig. 3.36) exhibit indistinct bands in the regions 793-797, 1021, 1077-1088, 1250-1253 and 1615-1622  $\text{cm}^{-1}$ . As  $\text{Sb}_2\text{S}_3$  only has bands at  $\bar{\nu} \leq 338 \text{ cm}^{-1}$  [3.51], the bands at higher wave numbers may be attributed to admixtures or the products of mechanochemical oxidation. The bands at 793-797  $\text{cm}^{-1}$  and 1077-1088  $\text{cm}^{-1}$  correspond to quartz. The admixed moisture is responsible for the bands at 1615-1622  $\text{cm}^{-1}$ . Sulfates were not found by infrared spectroscopy which is consistent with the results obtained by XPS.

### ***Tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$***

The survey XPS spectra of tetrahedrite are represented in Figs 3.37 – 3.38. The spectra disclose only copper, antimony and sulfur in the surface layer of the mineral and contamination by carbon and oxygen. Other admixed elements present in the mineral, e.g. Fe, As, Hg and Zn do not appear under the described experimental conditions [3.52].

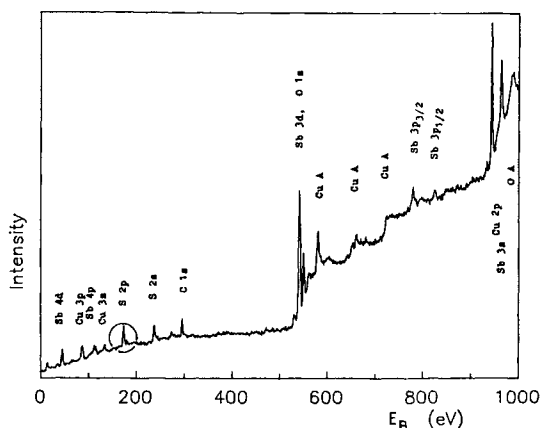


Fig. 3.37 XPS survey spectrum of non-activated  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ .

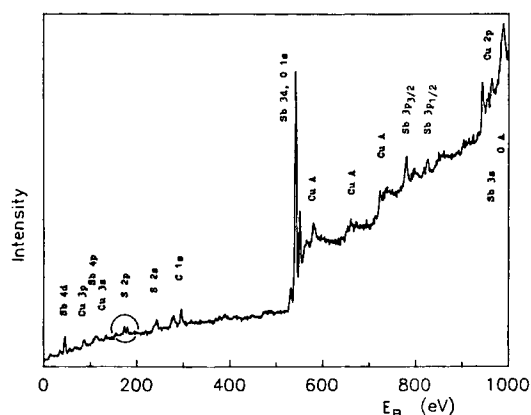


Fig. 3.38 XPS survey spectrum of mechanically activated  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  for 30 min.

In order to determine the distribution of copper and antimony in the surface of tetrahedrite, the  $\text{Cu}2p_{2/3}$  spectra were analysed (Fig. 3.39 – 3.40).

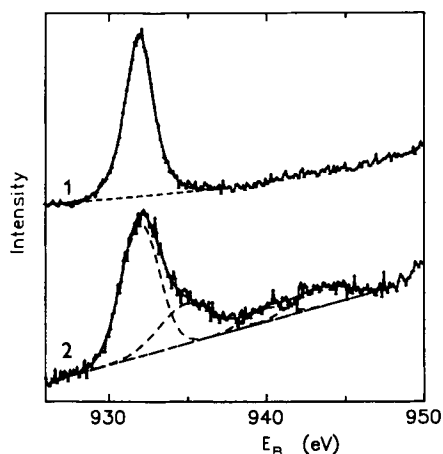


Fig. 3.39  $\text{Cu}2p_{2/3}$  XPS spectrum of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , mechanical activation: 1 – 0 min, 2 – 30 min [3.53].

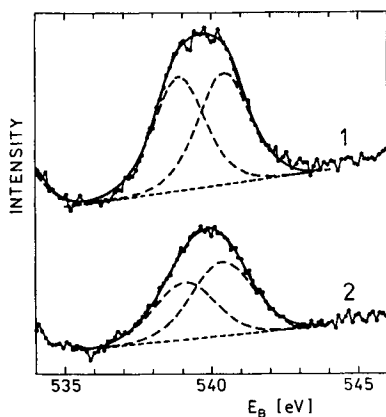


Fig. 3.40  $\text{Sb}3d_{3/2}$  XPS spectrum of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , mechanical activation: 1 – 0 min, 2 – 30 min [3.53].

In the case of copper, the surface of the reference (i.e. non-activated) sample (Fig. 3.39, line 1) contains practically only  $\text{Cu}^{1+}$ . Mechanical activation leads to generation of paramagnetic  $\text{Cu}^{2+}$ , the presence of which is indicated by appearance of a satellite structure (Fig. 3.39, line 2 at binding energy exceeding 940 eV). The  $3d_{3/2}$  antimony spectrum presented in Fig. 3.40 is a composite of two overlapping peaks. The lower binding energy peak corresponds to Sb in tetrahedrite while that for higher binding energy belongs to antimony oxide and/or antimony sulfate. The more intensive  $3d_{5/2}$  antimony line cannot be used for identification of the antimony valence states because it overlaps the oxygen line. The antimony peak with higher binding energy is of greater intensity for the mechanically activated sample (Fig. 3.40, line 2). In agreement with the results obtained by measuring the infrared spectra of mechanically activated sulfides [3.46] as well as with literature data [3.54] we can deduce that the formation of oxide ( $\text{Sb}_2\text{O}_3$  or  $\text{Sb}_4\text{O}_6$ ) is more likely than that of sulfate.

The ratios of the atomic concentrations of copper and antimony were calculated for the surface of tetrahedrite. The ratio Cu/Sb was 1.5 for the non-activated sample and 0.75 for a sample mechanically activated for 30 min. The enrichment of the surface of mechanically activated tetrahedrite with antimony confirms the qualitative results obtained by the method of cyclic voltammetry in paper [3.53].

The infrared spectrum of both investigated samples of tetrahedrite (Fig. 3.41) is poor in distinct bands and differs only a little from the infrared spectrum of stibnite (Fig. 3.36). Liese quotes the value  $\bar{\nu} = 330 \text{ cm}^{-1}$  [3.55] for tetrahedrite of Rudňany containing slight amount of mercury. The observed bands at  $797\text{--}803 \text{ cm}^{-1}$  and  $1077\text{--}1091 \text{ cm}^{-1}$  can be attributed to quartz while the bands at  $1620\text{--}1622 \text{ cm}^{-1}$  correspond to moisture in the tablet of KBr used for sample preparation.

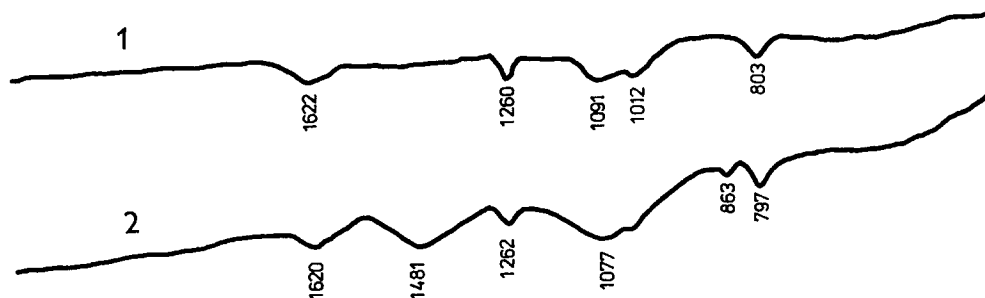


Fig. 3.41 IR spectrum of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , mechanical activation: 1 – 0 min, 2 – 30 min [3.46].

### ***Arsenopyrite $\text{FeAsS}$***

The S2p band of arsenopyrite XPS spectrum (Fig. 3.42) is characterized by a high noise which is a consequence of a low concentration of sulfur. The presence of some sulfur in a different oxidation state cannot be ruled out. However,  $\text{S}^{2-}$  and  $\text{S}^{6+}$  predominate (Table 3.8) with sulfate sulfur prevailing for mechanically activated samples.

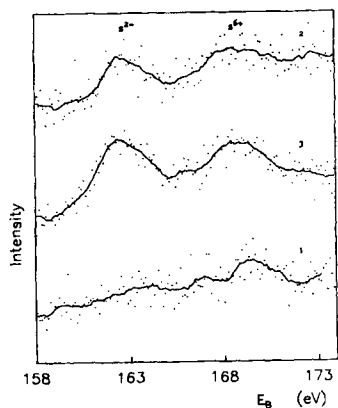


Fig. 3.42 Cu2p XPS spectrum of FeAsS, mechanical activation: 1 – 0 min, 2 – 5 min, 3 – 30 min.

Table 3.8 Percentage of sulfidic and sulfate forms of sulfur in the surface layer of FeAsS

| Mechanical activation (min) | S <sup>2-</sup> | S <sup>6+</sup> |
|-----------------------------|-----------------|-----------------|
| -                           | 100             | 0               |
| 5                           | 47              | 53              |
| 30                          | 31              | 61              |

### *Galena PbS*

The survey XPS spectrum of this mineral is represented in Fig. 3.43 [3.4]. High resolution traces of the lead 4f and sulfur S2p peaks are presented for the non-activated mineral in Figs 3.44 and 3.46 and for PbS activated for 30 min in Figs. 3.45 – 3.47.

The dashed lines in the spectra are synthetic curves obtained by computer data treatment of the measured data which are shown as solid lines.

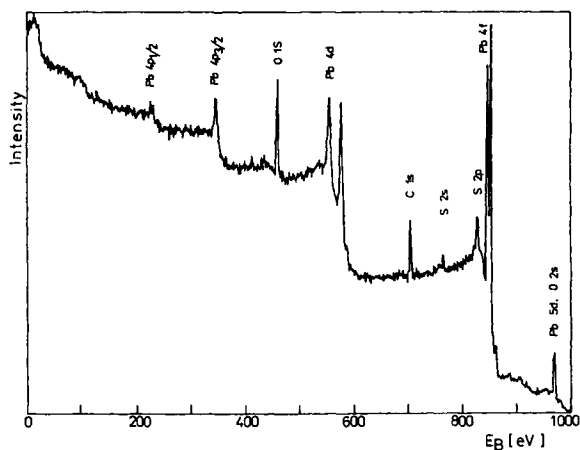


Fig. 3.43 XPS survey spectrum of non-activated PbS.

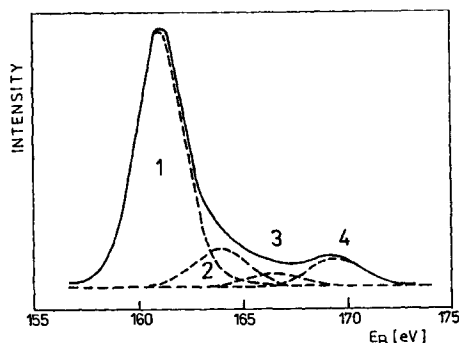


Fig. 3.44 S2p XPS spectrum of PbS, non-activated sample.

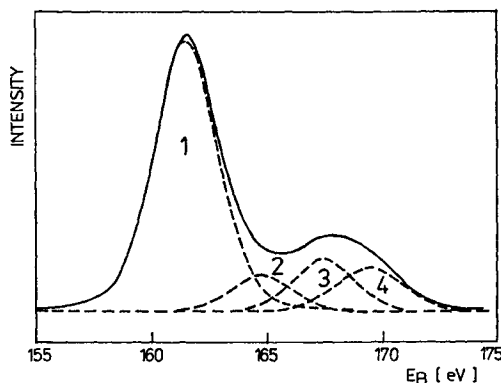


Fig. 3.45 S2p XPS spectrum of PbS, mechanical activation 30 min.

The sulfur S2p spectra have been resolved on the assumption that sulfur at the surface of galena occurs in different oxidation states (Table 3.9). This element is predominantly present in the sulfide form (Figs 3.44, 3.45, peaks 1) though the sulfate form can also be detected (Figs 3.44, 3.45, peaks 4). The intermediate oxidation products  $S^0$  and  $S^{4+}$  (peaks 2 and 3) can be detected in both samples as well. The content of sulfur in higher oxidation states is clearly higher in the mechanically activated sample.

Table 3.9 Atomic concentrations of S in surface layer of PbS

| Mechanical activation<br>(min) | Ratio of atomic concentrations |                    |                    |
|--------------------------------|--------------------------------|--------------------|--------------------|
|                                | $S^0/S$ (total)                | $S^{4+}/S$ (total) | $S^{6+}/S$ (total) |
| -                              | 0.13                           |                    | 0.06               |
| 30                             | 0.09                           | 0.19               | 0.11               |

The spectrum of lead Pb4f is represented in Figs 3.46 and 3.47. The minority doublets (denoted by 2) are to be assigned to  $PbSO_4$ . The spectrum of mechanically activated sample (Fig. 3.47) is considerably wider which is a consequence of increasing disorder of the mineral [3.56].

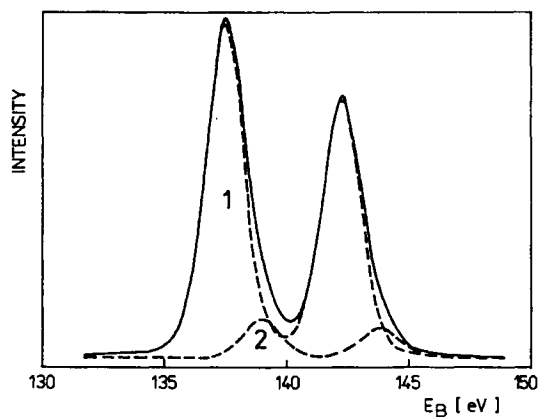


Fig. 3.46 Pb4f XPS spectrum of PbS, non-activated sample.

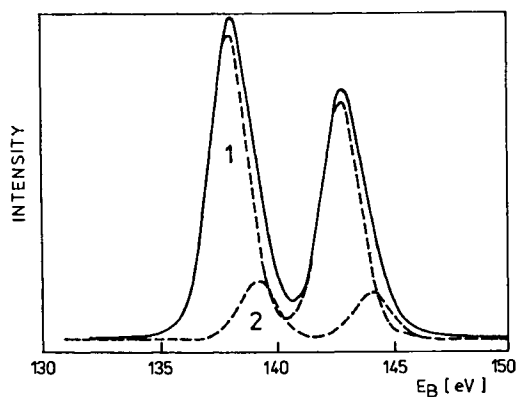


Fig. 3.47 Pb4f XPS spectrum of PbS, mechanical activation 30 min.

The understanding the surface oxidation chemistry of PbS is far from complete. In particular, there is uncertainty concerning the species present at surfaces exposed to air [3.57].

In literature [3.57 – 3.59] there are communications concerning the oxidation of non-ground PbS due to its long-termed exposure to air with sulfur oxidized to higher oxidation states. However, the linkage of elemental sulfur to the surface of mineral is rather weak owing to which it may escape from the surface to the vacuum before taking the XPS spectra.

Clifford [3.60] examined the mineral after it had been ground in air. Based on Pb4f peaks, he indicated that the sample exposed to air for less than 15 min had oxidised. Mechanical activation is a factor which intensifies the galena oxidation.

The infrared spectra (Fig. 3.48) complete the results obtained by the method of photoelectron spectroscopy as regards the presence of oxidation products at the surface of galena. Lead (II) sulfate can be identified ( $\bar{\nu} = 450 - 500 \text{ cm}^{-1}$  and  $1066-1083 \text{ cm}^{-1}$ ) while the band at higher wave number may belong to oxysulfate  $\text{PbO} \cdot \text{PbSO}_4$  [3.61].

The bands at  $787-793 \text{ cm}^{-1}$  are due to quartz and the bands at  $1620-1630 \text{ cm}^{-1}$  correspond to water in the tables of KBr.

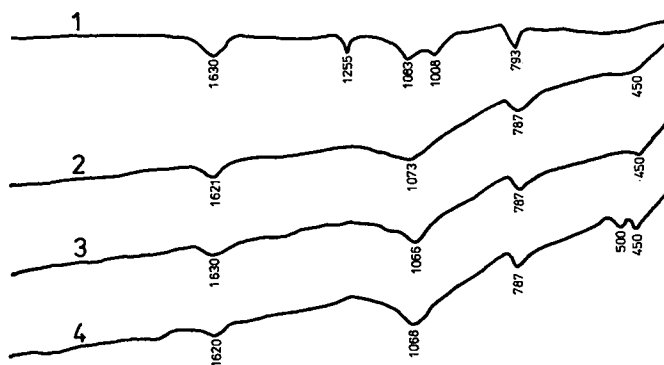


Fig. 3.48 IR spectrum of PbS, mechanical activation: 1 – 0 min, 2 – 10 min, 3 – 30 min, 4 – 60 min [3.46].

### *Sphalerite ZnS*

The XPS spectrum of sphalerite mechanically activated for 240 minutes (curve 1) together with the spectrum of a non-activated sample (curve 2) are presented in Fig. 3.49. We have ascertained from high resolution spectra of samples activated in a vibration mill for 7.5-240 min that the surface composition differs from that a non-activated sample in the distribution of zinc, iron, sulfur and oxygen [3.62].

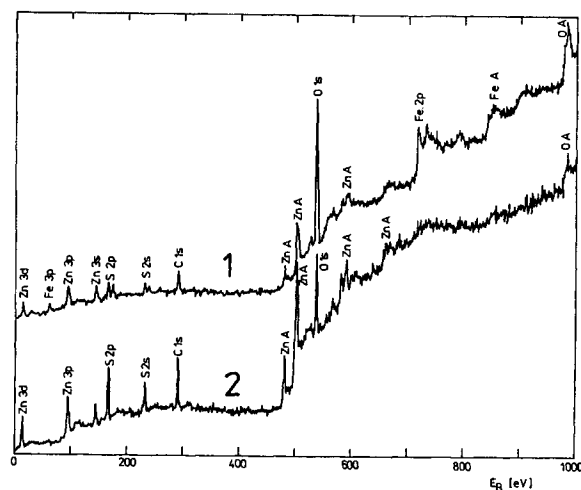


Fig. 3.49 XPS survey spectrum of ZnS, 1 – mechanical activation 240 min, 2 – non-activated sample [3.62].

Sulfur is present at the surface of non-activated sample only as  $S^{2-}$  whereas in activated samples the sulfate sulfur is also present at the surface (Fig. 3.50). The activated samples also differ from non-activated by the presence of iron, the content of which rapidly increases in the samples ground for a long time. Oxygen is present in all samples but its relative proportion in ground samples is greater. A quantitative evaluation of the presence of individual elements, expressed as the ratio of their atomic concentrations, is given in Table 3.10.

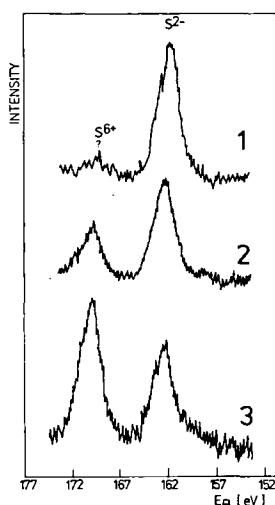


Fig. 3.50 S2p XPS spectrum of ZnS, mechanical activation 1 – 0 min, 2 – 7.5 min, 3 – 60 min [3.62].

Table 3.10 Atomic concentrations of Fe, Zn, O and S in surface layer of ZnS [3.62]

| Mechanical activation<br>(min) | Ratio of atomic concentrations |      |                                  |
|--------------------------------|--------------------------------|------|----------------------------------|
|                                | Fe/Zn                          | O/Zn | S <sup>6+</sup> /S <sup>2-</sup> |
| 0                              | 0                              | 1.55 | 0                                |
| 7.5                            | 0.2                            | 3.37 | 0.49                             |
| 15                             | 0.2                            | 3.89 | 0.63                             |
| 60                             | 0.2                            | 4.80 | 1.30                             |
| 150                            | 0.4                            | 5.79 | 1.12                             |
| 240                            | 0.5                            | 5.16 | 0.77                             |

A sulfate layer arises on the surface of sphalerite during mechanical activation. At longer times of activation ( $t_G > 60$  min) the surface mechanochemical oxidation is retarded because the transport of oxygen to the reaction surface is limited by the process of agglomeration of sphalerite particles. The generation of agglomerates of sphalerite during mechanical activation was demonstrated in papers [3.62 – 3.63]. The interpretation of the ratio Fe/Zn in Table 3.10 is not unambiguous. We may take into account the abrasion of iron from the balls used for mechanical activation. However, a continuous acceleration of diffusion of the iron atoms into surface zone of sphalerite must not be ruled out because of a high degree of stress of the mineral. The first interpretation is based on general laws of abrasion during intensive grinding [3.13] while in the second case we consider an analogous to the results published in paper [3.64] which are concerned with the different diffusion rates of iron and copper in mechanically activated chalcopyrite.

The complexity of surface transformations of sphalerite due to mechanical activation is documented by infrared spectra (Fig. 3.51). Sphalerite exhibits a band at  $\bar{\nu} = 305 - 310 \text{ cm}^{-1}$  while other bands correspond to admixed quartz, moisture in the tablet of KBr and to sulfate as product of mechanochemical oxidation.

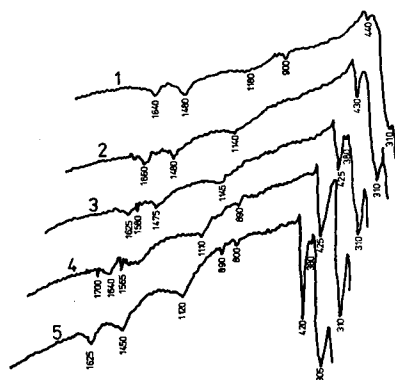


Fig. 3.51 IR spectrum of ZnS, mechanical activation: 1 – 0 min, 2 – 5 min, 3 – 10 min, 4 – 30 min, 5 – 60 min [3.62].

### 3.7. Paramagnetic centres in mechanically activated minerals

#### *Chalcopyrite $\text{CuFeS}_2$*

The EPR spectra of mechanically activated  $\text{CuFeS}_2$  are represented in Fig. 3.52. The form of these spectra significantly changes with the time of mechanical activation. A non-activated sample (curve 0) gives an indistinct spectrum with apparent splitting which is likely to correspond to the presence of the  $\text{Cu}^{2+}$  ions [3.4]. A new line at  $g = 2.000$  begins to appear after the sample was activated for 15 min (curve 2). For longer activation times, this line forms an asymmetric spectrum which becomes a dominant part of the complete EPR record. The appearance of this spectrum may be due to the presence of superparamagnetic particles arising by intensive grinding of  $\text{CuFeS}_2$  [3.65]. However, it is not possible to decide by using only the EPR method whether the presence of superparamagnetic particles is a consequence of the damage to the chalcopyrite structure or due to the formation of new magnetic phase.

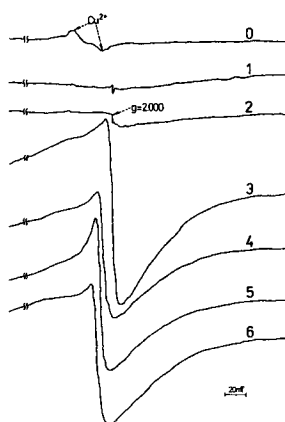


Fig. 3.52 EPR spectra of  $\text{CuFeS}_2$ , mechanical activation: 0 – 0 min, 1 – 7.5 min, 2 – 15 min, 3 – 30 min, 4 – 60 min, 5 – 90 min, 6 – 120 min [3.65].

## Pyrite $\text{FeS}_2$

The EPR spectrum of the non-activated  $\text{FeS}_2$  exhibits a hyperfine sextet corresponding to bivalent manganese which is present in this mineral as impurity. In agreement with literature [3.66] and the results obtained for pyrite by Mössbauer spectroscopy (see Chapter 3.8) we may assume that the  $\text{Mn}^{2+}$  ion occurs in the low-spin state in cationic places of pyrite. In the course of mechanical activation the spectrum of  $\text{Mn}^{2+}$  gradually disappears as another appears, the emergence of this line depends upon the intensity of mechanical stress. For a sample activated in planetary mill at relative acceleration  $b/g = 12.8$  it appears at grinding time  $t_{\text{PM}} = 5$  min while for a less intensively activated sample ( $b/g = 10.3$ ) it does not appear before  $t_{\text{PM}} = 15$  min. The shape of this line is represented in Fig. 3.53A and the dependence of its intensity on the time of mechanical activation  $t_{\text{PM}}$  is depicted in Fig. 3.53B.

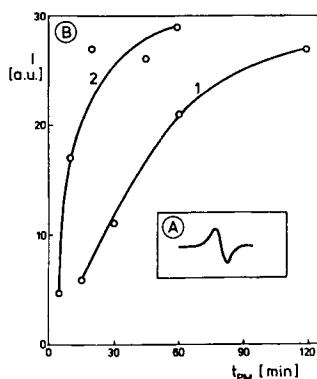


Fig. 3.53 EPR parameters of  $\text{FeS}_2$ , A: shape of EPR line, B:  $I$  – intensity of EPR line (in relative units) vs. time of mechanical activation,  $t_{\text{PM}}$ ; relative acceleration of planetary mill,  $b/g$ : 1 = 10.3, 2 = 12.8 [3.4].

Further experiments were aimed at identification of this line [3.4]. These experiments were based on the idea that paramagnetic resonance requires the intensity ratio of EPR line  $r = I_1/I_2$  equal to 3.8 ( $I_1$  intensity of EPR line at 77 K,  $I_2$  intensity of this line at 293 K). In our experiments we found the value  $r = 2.7$  for relative acceleration of mill  $b/g = 12.8$  and the value  $r = 3.4$  for  $b/g = 10.3$ . Both values are lower than the theoretical value which means that magnetic arrangement in pyrite takes place at low temperatures. In this region the width of line increases for both values of  $b/g$  which is also consistent with the phenomenon of magnetic arrangement at low temperatures. The increase is about 15 % for  $b/g = 12.8$  and 26 % for  $b/g = 10.3$ . With certainty, it is possible to attribute the new EPR line to the  $\text{Fe}^{3+}$  ions. Quantitative measurements allow determination of the concentration of the  $\text{Fe}^{3+}$  ions at  $\sim 10^{20}$ /gram for the sample of pyrite mechanically activated for  $t_{\text{PM}} = 120$  min ( $b/g = 10.3$ ).

## Cinnabar $\text{HgS}$

The EPR spectrum of cinnabar (Fig. 3.54) is a superposition of a wide line A and a narrow line B. The parameters of both lines (width  $\Delta H$  and amplitude  $I$ ) change by the effect of mechanical activation.

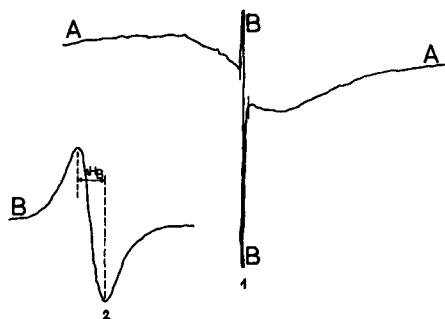


Fig. 3.54 EPR spectrum of HgS [3.4].

The width of the wide line A decreases from the value  $\Delta H = 900 \text{ kgs}^{-2}\text{A}^{-1}$  for non-activated sample to  $500 \text{ kgs}^{-2}\text{A}^{-1}$  for the sample activated for 30 min. The contraction of the line is accompanied by an increase in its amplitude which is especially obvious in the case of the sample activated for 30 min. We assign this line to the presence of admixed hematite.

The narrow line B with the parameters  $g = 2.0026$  and  $\Delta H = 5.3 \text{ kgs}^{-2}\text{A}^{-1}$  for the non-activated sample corresponds to a concentration of EPR centres of  $10^{17}/\text{gram}$ . The width of line  $\Delta H$  increases with the time of mechanical activation to  $\Delta H = 6.8 \text{ kgs}^{-2}\text{A}^{-1}$  for the sample subjected to 30 minutes activation. Simultaneously, the intensity of this line decreases. This decrease is most significant in the case of the sample activated for 5 minutes (approximately halved when compared with the non-activated sample). As for cinnabar activated at higher temperatures the intensity is practically equal. We consider the line B to be due to the presence of the  $\text{Mn}^{2+}$  ions in the diamagnetic matrix of cinnabar. The constant of hyperfine splitting is  $\sim 95 \text{ kgs}^{-2}\text{A}^{-1}$ .

The relationship between the width of EPR line of the admixed manganese ion  $\Delta H_{\text{Mn}}^{2+}$  and broadening of the diffraction line (101) of cinnabar  $\beta$ , presented in Fig. 3.55, is clearly linear as follows from equation (3.10)

$$\Delta H_{\text{Mn}}^{2+} = 3.30 + 96.32 \beta \quad (3.10)$$

where  $\Delta H_{\text{Mn}}^{2+}$  is expressed in  $\text{kgs}^{-2}\text{A}^{-1}$  and  $\beta$  in metres. The calculated value of regression coefficient  $r = 0.9783$  indicates a tight correlation of the pertinent parameters.

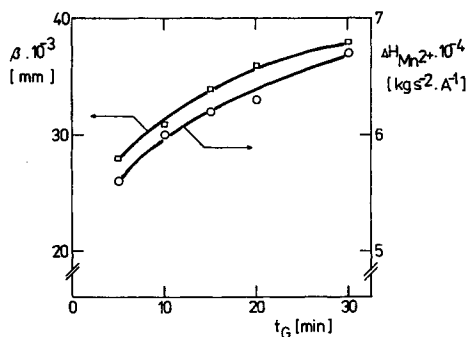


Fig. 3.55 Broadening of diffraction line (101) of HgS,  $\beta$  and the width of EPR line of admixed  $\text{Mn}^{2+}$ ,  $\Delta H_{\text{Mn}}^{2+}$  vs. time of mechanical activation,  $t_G$  [3.4].

## Galena PbS

It has been found that because of its brittleness and plastic properties galena rapidly becomes amorphous during mechanical activation [3.4, 3.9]. For this reason, a significant influence of planetary grinding on hyperfine structure of this mineral is also to be expected. In [3.4] it was detected by the EPR method the presence of the ions of bivalent manganese which occupy the positions of lead in the lattice of PbS.

The amplitude of the resonance line of manganese decreases with time of mechanical activation from 61.5 for the non-activated sample to 13.5 for a sample activated for 60 minutes. After 20 minutes activation a new, unspecified magnetic phase came into existence. The appearance of this line may be connected either with the presence of the  $O_2$  radical which originates from the reaction between galena and air oxygen [3.67 – 3.68] or with the phase transition which was described for galena and undergoes at high pressures [3.69].

## Sphalerite ZnS

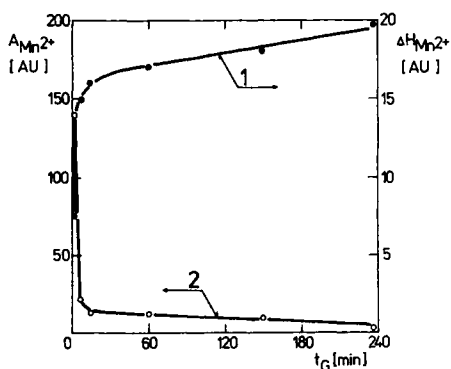


Fig. 3.56 Line width,  $\Delta H_{Mn^{2+}}$  and amplitude,  $A_{Mn^{2+}}$  of admixed  $Mn^{2+}$  vs. time of mechanical activation,  $t_G$  for ZnS [3.62].

The EPR spectrum of sphalerite demonstrates the complexity of ultrafine structure of this mineral. Its paramagnetic centres were intensively studied, especially in connection with its luminescence ability [3.70 – 3.72]. For a non-activated sample we can identify the main spectrum of the admixed  $Mn^{2+}$  ions, the centre of which is characterized by the value  $g = 2.001$ . The spectrum is characterized by hyperfine splitting at 6.7 mT, and on the basis of its form we assume that the  $Mn^{2+}$  ions occupy cationic positions in the lattice of sphalerite [3.73]. In the course of mechanical activation the amplitude of the line of manganese rapidly decreases and its width simultaneously increases (Fig. 3.56). The change in the parameters  $A$  and  $\Delta H$  of the EPR spectrum is a consequence of different local electric fields produced by mechanical activation. On the basis of the shape of this spectrum and its sensitivity to admixed ions it was possible to evaluate the quality of flotation sphalerite concentrates with varying content of iron [3.74]. In the case of the sample activated for  $t_G = 180$  min another spectrum appears, indicating the presence of a new manganese phase [3.63]. The centre of the spectrum corresponds to the value  $g = 2.020$  with hyperfine splitting at 9.5 mT. The new phase is probably amorphous and characterized by the manganese ions in interstitial positions of the lattice of sphalerite.

**Relationship between disordering of mechanically activated sulfides and changes in hyperfine structure**

The disordering of mechanically activated sulfides may be appreciated on the basis of deformation of their structure. The lattice deformation  $\epsilon$  is a quantitative measure of the deformability of solid substances. Manganese which is a common admixture in sulfidic minerals is virtually a point defect and is very sensitive to the deformations of interatomic bonds produced by mechanical stress. These deformations manifest themselves in the amplitude and halfwidth of the line of this metal, as detailed for individual sulfides in the preceding parts.

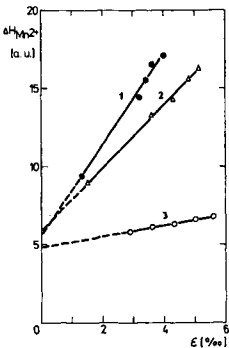


Fig. 3.57  $\Delta H_{Mn}^{2+}$  vs. lattice deformation,  $\epsilon$  for mechanically activated minerals, 1 – ZnS, 2 – PbS, 3 – HgS [3.14].

In Fig. 3.57 the halfwidths  $\Delta H_{Mn}^{2+}$  for sphalerite, galena and cinnabar are plotted against the lattice deformation due to mechanical activation. These relationships exhibit a linear character with the value  $\epsilon$  varying from 1.5 to 5.5 ‰ (in arbitrary units). The slopes of the function  $H_{Mn}^{2+}(\epsilon)$  calculated by linear regression are listed in Table 3.11. This table also contains data about standard enthalpy of atomization  $\Delta H_{298}^A$  and Mohs hardness. The quantity  $\Delta H_{298}^A$  is used instead of lattice energy  $E_m$  which is of limited use. While  $E_m$  is rigorously valid only for the crystals of halides, the quantity  $\Delta H_{298}^A$  is more universal because it can be used for arbitrary type of bond. It is defined by the energy released if the crystal is formed from infinitely dilute gas consisting of individual atoms [3.75]. It results from the data in Fig. 3.57 and Table 3.11 that there is a direct proportionality between the value  $\Delta H_{298}^A$  which represents the structural stability of mineral and the value  $\epsilon$  which is a measure of disordering of hyperfine structure (for a unit of deformed volume).

Table 3.11 Values of a, b and regression coefficient, r for dependence  $\Delta H_{Mn}^{2+} = a + b \epsilon$  calculated for mechanically activated ZnS, PbS and HgS in comparison with standard enthalpy of atomization,  $\Delta H_{298}^A$  and hardness by Mohs,  $H_M$

| Mineral | a     | b     | r     | $\Delta H_{298}^A$ (kJmol <sup>-1</sup> )<br>[3.76] | $H_M$ (rel.units)<br>[3.76] |
|---------|-------|-------|-------|-----------------------------------------------------|-----------------------------|
| ZnS     | 5.495 | 2.951 | 0.993 | 611.5                                               | 4.00                        |
| PbS     | 6.010 | 1.992 | 0.998 | 566.6                                               | 2.75-3.00                   |
| HgS     | 5.146 | 0.308 | 0.898 | 392.4                                               | 2.50-3.00                   |

### 3.8. Mössbauer effect in mechanically activated minerals

Mössbauer spectroscopy is one of the main techniques used to understand structural and magnetic properties of mechanically activated solids. The application is especially useful for characterization of disordered solids with iron content. In addition to phase and size characterization Mössbauer spectra can provide information on particle size and surface effects [3.77]. The increased incidence of Mössbauer spectroscopy over the past years in this field is indicated by several review articles [3.78 – 3.84].

#### *Chalcopyrite CuFeS<sub>2</sub>*

The Mössbauer spectrum of non-activated chalcopyrite (Fig. 3.58a) consists of a sextet of hyperfine magnetic splitting  $H_1$  and is a consequence of magnetically ordered iron in the structure of the mineral. The iron is present in the form of  $Fe^{3+}$  ions in high spin state located in tetrahedral positions [3.85 – 3.86]. The sextet is accompanied by a doublet  $D_2$  which corresponds to iron in the associated pyrite. With increasing time of mechanical activation the sextet gradually degenerates (Fig. 3.58 b-d). It can be approximated by three sextets ( $H_1$ ,  $H_2$  and  $H_3$ ). Besides the doublet  $D_2$ , further doublets  $D_1$  and  $D_3$  are formed corresponding to  $Fe^{3+}$  or  $Fe^{2+}$  ions. Their presence may be attributed to transition of ferric ions from high to low spin state and/or to the occurrence of  $Fe^{2+}$  ions in pyrite which are in high spin state with a much lower symmetry than observed for non-activated pyrite.

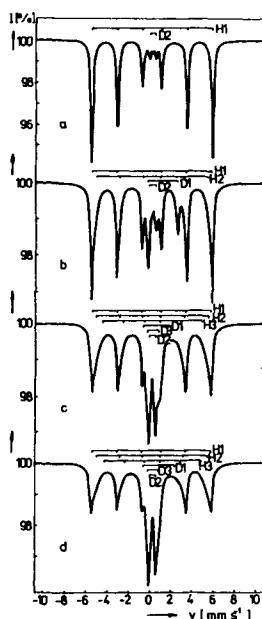


Fig. 3.58 Mössbauer spectra of  $CuFeS_2$ , mechanical activation: a – 0 min, b – 15 min, c – 240 min, d – 240 min [3.65].

Detailed analysis of the spectrum (Fig. 3.59) of an mechanically activated chalcopyrite has revealed that plastic deformation because of mechanical activation leads to a crystallographic shear in the sulfur sublattice and hence to a change of the cation distribution among octa- and tetra-positions [3.87 – 3.88].

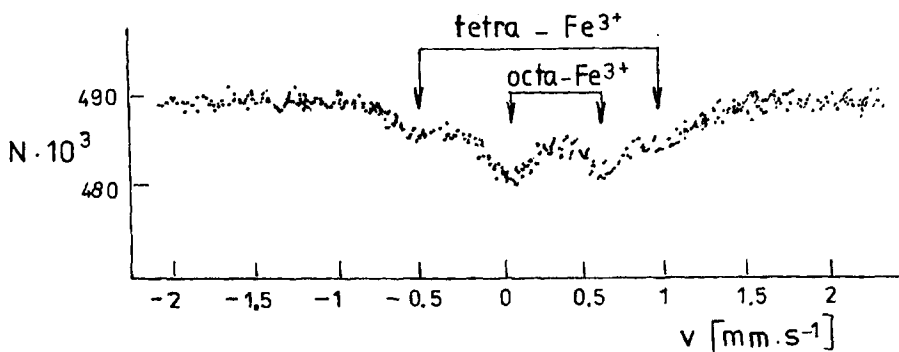


Fig. 3.59 Detail of Mössbauer spectrum of  $\text{CuFeS}_2$ , mechanical activation 120 min [3.4].

### Pyrite $\text{FeS}_2$

The Mössbauer spectrum of non-activated pyrite (Fig. 3.60a) is produced by a paramagnetic component approximated by doublet  $\Delta_1$  which corresponds to bivalent iron. Pyrite exhibits very small values of the isomer shift  $\text{IS} = 0.40 \text{ mm.s}^{-1}$  which indicates a high degree of bond covalency and the presence of low-spin  $\text{Fe}_6^{2+}$ . The value of quadrupole splitting  $\text{QS} = 0.69 \text{ mm.s}^{-1}$  indicates the deviations from cubic symmetry [3.86, 3.89].

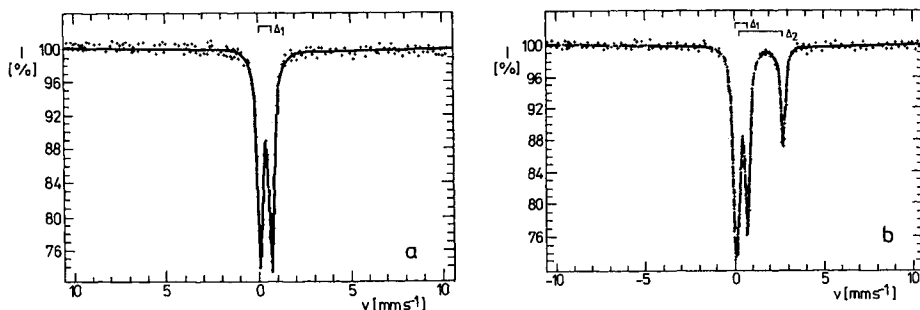


Fig. 3.60 Mössbauer spectra of  $\text{FeS}_2$ , mechanical activation: a – 0 min, b – 30 min [3.42].

The Mössbauer parameters for pyrite do not change with the time of mechanical activation. However, if the samples are activated for 15 min and longer, another doublet  $\Delta_2$  appears (Fig. 3.60b). Its parameters ( $\text{IS} = 1.5 \text{ mm.s}^{-1}$  and  $\text{QS} = 2.49 \text{ mm.s}^{-1}$ ) indicate the presence of iron in the high-spin  $\text{Fe}_6^{2+}$  state.

### Tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$

The Mössbauer spectra in Fig. 3.61 are formed by three resonance maxima which were fitted by three doublets  $\Delta_1$ ,  $\Delta_2$  and  $\Delta_3$ . The doublet  $\Delta_1$  corresponds to admixed pyrite. The doublet  $\Delta_2$  has the parameters identical with the parameters of the doublet observed for cinnabar with iron content [3.90]. In accordance with [3.91] the doublet  $\Delta_3$  can be attributed to tetrahedrite in which copper ions are partly replaced by iron atoms.

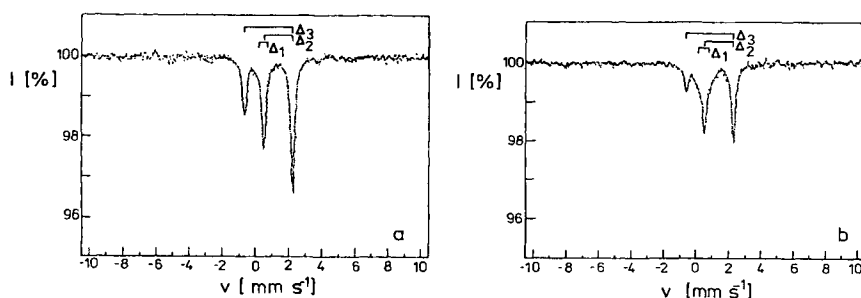


Fig. 3.61 Mössbauer spectra of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , mechanical activation: a – 5 min, b – 30 min [3.4].

Mössbauer parameters of mechanically activated samples are summarized in Table 3.12.

Table 3.12 Mössbauer parameters for  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$

| Mechanical<br>activation<br>(min) | $\Delta_1$                  |                             |      | $\Delta_2$                  |                             |      | $\Delta_3$                  |                             |      |
|-----------------------------------|-----------------------------|-----------------------------|------|-----------------------------|-----------------------------|------|-----------------------------|-----------------------------|------|
|                                   | QS<br>( $\text{mms}^{-1}$ ) | IS<br>( $\text{mms}^{-1}$ ) | %    | QS<br>( $\text{mms}^{-1}$ ) | IS<br>( $\text{mms}^{-1}$ ) | %    | QS<br>( $\text{mms}^{-1}$ ) | IS<br>( $\text{mms}^{-1}$ ) | %    |
| 0                                 |                             |                             | 3-4  | 1.76                        | 1.38                        | 52.4 | 2.86                        | 0.77                        | 47.6 |
| 5                                 | 0.54                        | 0.46                        | 9.6  | 1.75                        | 1.36                        | 51.3 | 2.90                        | 0.78                        | 39.1 |
| 10                                | 0.55                        | 0.46                        | 18.2 | 1.74                        | 1.36                        | 49.1 | 2.90                        | 0.78                        | 32.7 |
| 15                                | 0.58                        | 0.40                        | 24.8 | 1.76                        | 1.36                        | 46.8 | 2.88                        | 0.79                        | 28.4 |
| 20                                | 0.67                        | 0.48                        | 28.2 | 1.77                        | 1.40                        | 48.5 | 2.89                        | 0.84                        | 23.3 |
| 30                                | 0.63                        | 0.46                        | 33.1 | 1.79                        | 1.37                        | 45.5 | 2.86                        | 0.78                        | 21.4 |

### Sphalerite ZnS

The Mössbauer spectrum of mechanically activated sphalerite (Fig. 3.62) is similar to that of the standard and originates from a paramagnetic component. This component was approximated by two doublets  $\Delta_1$  and  $\Delta_2$ . Doublet  $\Delta_1$  corresponds to  $\text{Fe}^{2+}$  substituted in cation positions of the lattice of sphalerite, while the parameters of doublet  $\Delta_2$  are identical to those of pyrite the presence of which was confirmed by X-ray diffractometry.

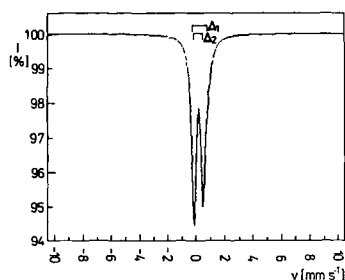


Fig. 3.62 Mössbauer spectrum of ZnS, mechanical activation 15 min [3.62].

The width of both doublets, which is a measure of the disruption of magnetic arrangement, as a function of grinding time is shown in Fig. 3.63. The broadening of the spectrum shows that the symmetry of local field near Mössbauer active atoms is significantly changing because of the influence of mechanical activation [3.10]. The greater sensitivity of this crystal field symmetry disordering is clear in the case of sphalerite (curve 1) in comparison with pyrite (curve 2).

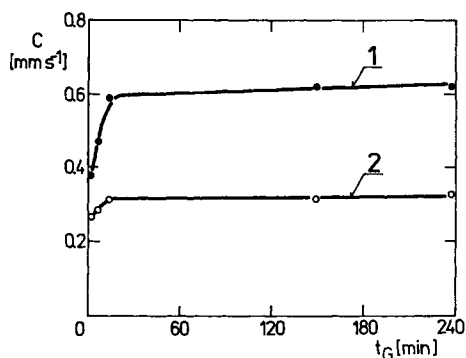


Fig. 3.63 The width of Mössbauer line,  $C$  for doublets  $\Delta_1(1)$  and  $\Delta_2(2)$  of ZnS vs. time of mechanical activation,  $t_G$  [3.63].

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## **Chapter 4 POLYMORPHOUS TRANSFORMATIONS INDUCED IN MINERALS BY MECHANICAL ACTIVATION**

**4.1. Chalcopyrite  $\text{CuFeS}_2$**

**4.2. Zinc sulphide  $\text{ZnS}$**

**4.3. Cinnabar  $\text{HgS}$**

**4.4. Greenockite  $\text{CdS}$**

**4.5. References**

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It is known that the action of mechanical forces on solid substances frequently leads to polymorphism, i.e. transformation of one crystal structure into another one without chemical change. In this process, the more ordered phases come into existence [4.1].

According to thermodynamics a system at constant pressure and temperature shows a tendency to reach the minimum value of its free energy. If it holds  $G_A > G_B$  for two phases, then phase A is liable to turn into phase B. The relationship between pressure  $p$  or temperature  $T$  and the volumes of both phases is described by the Clausius-Clapeyron equation

$$\frac{dp}{dT} = \frac{S_A - S_B}{V_A - V_B} \quad (4.1)$$

where  $S_A$  and  $V_A$  are the entropy and molar volume of phase A. Provided  $V_A > V_B$ , then it holds  $dp/dT > 0$  (the pressure increases with temperature) and the equilibrium shifts to formation of the phase with smaller volume. If  $V_A < V_B$  then  $dp/dT < 0$  and formation of the phase with larger volume is favoured.

The laws of polymorphous transformations of solid substances were described by Buerger in context with coordination of the structure of these substances [4.2]. Later on the description was founded on the transformation mechanism [4.3].

The course of mechanically stimulated phase transformations of some minerals was analyzed by Avvakumov [4.1]. He has alleged that the high local pressures and temperatures at contact surface of the mechanically activated particles as well as the presence of volume defects are responsible for the phase transformations. A peculiarity of mechanically stimulated phase transformations is the formation of phases with higher density, unlike thermal transformations where a phase with lower density usually arises.

#### 4.1. Chalcopyrite $\text{CuFeS}_2$

Chalcopyrite is a classic cupriferous mineral. Its relatively complicated structure and industrial importance explain why in recent decades it has become an attractive model and has stimulated the joint research efforts of metallurgists and chemists interested in problems of the solid phase.

The mineral occurs in several modifications. The, naturally occurring, low-temperature modification, the  $\alpha$ -phase, is tetragonal. When heated in an inert atmosphere, thermal decomposition starts at temperatures over  $400^\circ\text{C}$  forming the cubic  $\beta$ -phase. Heating at  $550^\circ\text{C}$  results in a further transformation to the tetragonal  $\gamma$ -phase occurring. Both of these phases result from the volatilisation of sulfur from the matrix leaving sulfur deficient phases i.e.  $\text{CuFeS}_{2-x}$ . The  $\gamma$ -phase is unstable and turns into the cubic  $\beta$ -phase [4.4]. The  $\gamma$ -phase may also occur if the  $\beta$ -phase is heated to temperatures over  $300^\circ\text{C}$ . In some publications the formation of the  $\gamma$ -phase at  $550^\circ\text{C}$  is not mentioned, and only the transformation of the  $\alpha$ -phase into the cubic  $\beta$ -phase is taken into consideration [4.5-4.6].

Figure 4.1 presents the DTA records of chalcopyrite either non-activated or activated in a vibration mill for different grinding times. In order to prevent oxidation the DTA measurements were performed in argon atmosphere.

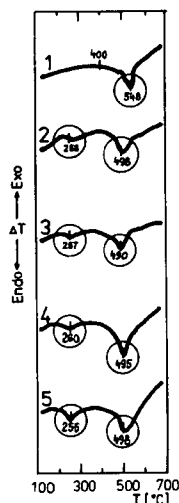


Fig. 4.1 DTA records of chalcopyrite mechanically activated for:  
1 - 0 min, 2 - 15 min, 3 - 20 min, 4 - 25 min, 5 - 30 min activation [4.7].

In the DTA record of the non-activated chalcopyrite there is an endothermic peak at 548°C, which in line with [4.5-4.6], corresponds to the  $\beta$ -phase. A new peak at  $257 \pm 3^\circ\text{C}$  and a decrease in the temperature of the above-mentioned peak characterize the DTA records of the mechanically activated samples. The mechanical activation brings about a decrease in temperature of the  $\beta$ -phase peak from 548°C (non-activated sample) to 490°C (optimally activated sample).

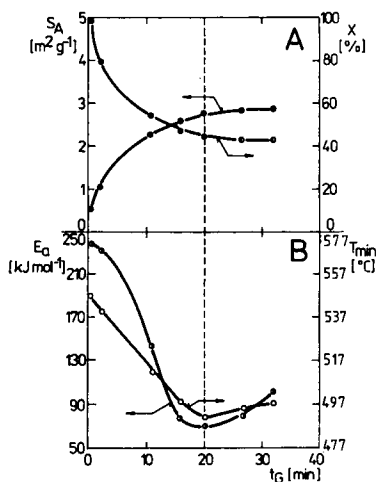


Fig. 4.2 A - Variations in specific surface,  $S_A$  and crystalline phase content,  $X$  of  $\alpha$ - $\text{CuFeS}_2$  with time of mechanical activation,  $t_G$ ,  
B - Variations in apparent activation energy,  $E_a$  of thermal transformation of  $\text{CuFeS}_2$  and temperature,  $T_{\min}$  of endothermic DTA peak of  $\beta$ - $\text{CuFeS}_2$  with time of mechanical activation,  $t_G$  [4.7].

The apparent activation energy of the polymorphous transformation of chalcopryrite falls from  $238 \text{ kJ mol}^{-1}$  to  $72 \text{ kJ mol}^{-1}$ . The decrease in both activation energy  $E_m$  and temperature of the  $\beta$ -phase peak  $T_m$  takes place in the first twenty minutes (Fig. 4.2). It is obvious that this region is characterized by the intensive formation of a new surface  $S_A$  and by a decrease in content of the crystalline phase X of chalcopryrite owing to transformation to the amorphous phase in the course of grinding. The aggregation of the particles during dry vibration grinding and their sticking on the grinding media lead to constant specific surface and crystalline phase content values when ground in excess of 20 min. The unfavourable influence of particle aggregation on the kinetics of thermal transformation manifests itself in slight increases in the values of  $E_a$  and  $T_{min}$  for longer grinding times. Although the appearance of the  $\beta$ -phase is structure-sensitive, the endothermic peak at  $257^\circ\text{C}$  does not change with surface area and crystalline fraction in the course of grinding. In order to explain this fact, we rely on papers [4.8-4.9], which report that  $\beta$ -chalcopryrite is produced by the intensive grinding of  $\text{CuFeS}_2$ , among other effects. The existence of the endothermic peak at  $257^\circ\text{C}$  for the mechanically activated samples may therefore be explained by the formation of the  $\gamma$ -phase from the  $\beta$ -phase, in agreement with the literature.

The existence of the  $\beta$ -phase was verified also by X-ray diffraction and chemical leaching methods [4.10]. The broadening of (112) line of  $\alpha$ -chalcopryrite due to the existence of (221) line of  $\beta$ -chalcopryrite was observed in dependance on the energy input  $EN$  (Fig. 4.3). The  $\beta$ - $\text{CuFeS}_2$  is less refractory for leaching in comparison of  $\alpha$ - $\text{CuFeS}_2$  and may be leached out by the sulfuric acid [4.11].

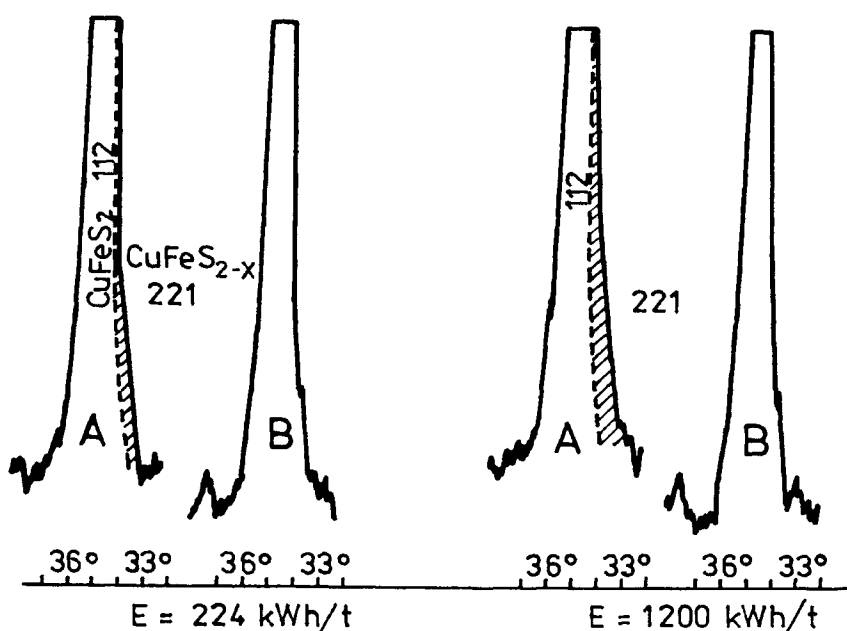


Fig. 4.3 XRD pattern of the chalcopryrite polymorphs, A:  $\alpha$ -chalcopryrite (112) and  $\beta$ -chalcopryrite (221), B:  $\alpha$ -chalcopryrite (112), [4.10].

Phase transformations originating by chalcopryrite heating in argon atmosphere are illustrated in Fig. 4.4.

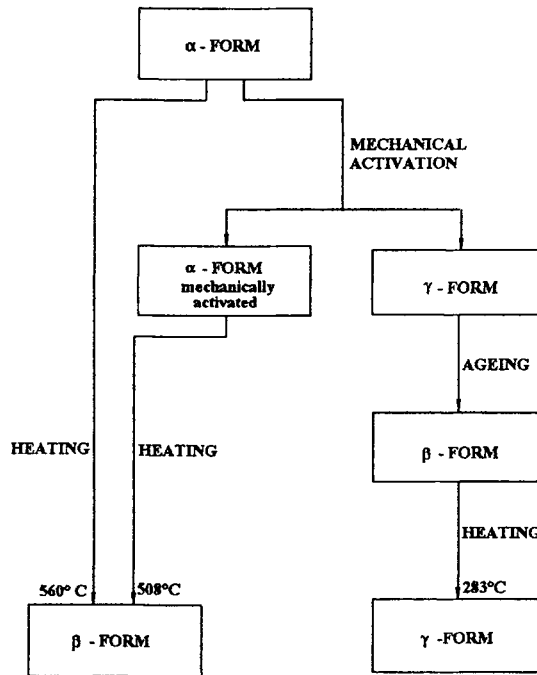


Fig. 4.4 Relations between polymorphs of  $\text{CuFeS}_2$ .

## 4.2. Zinc sulphide $\text{ZnS}$

Zinc sulphide occurs in two main structural forms, i.e. as cubic sphalerite and hexagonal wurtzite. These two minerals represent the terminal members of the series of compounds called polytypes [4.12]. The structure of individual polytypes is variable because of different sequence of layers and different periodicity [4.13]. It is known that such structures contain dislocations the frequency of which is in many cases dependent on the energy needed for mutual displacement of individual layers [4.14].

The cubic form is thermodynamically stable at low temperature and the hexagonal form is stable at high temperature. The transition of one form to another one can be produced by high temperature (Fig. 4.5). The cubic form originates from the hexagonal form at  $850^\circ\text{C}$  and slowly cooling, the reverse transformation arises from quenching the cubic form at  $1020^\circ\text{C}$  [4.15]. In nature, the cubic form is considerably more common than the hexagonal form confirming the greater stability at low temperature of sphalerite. The transformation of wurtzite to sphalerite at low temperatures is extremely slow with both phases being present in some mineral assemblages.

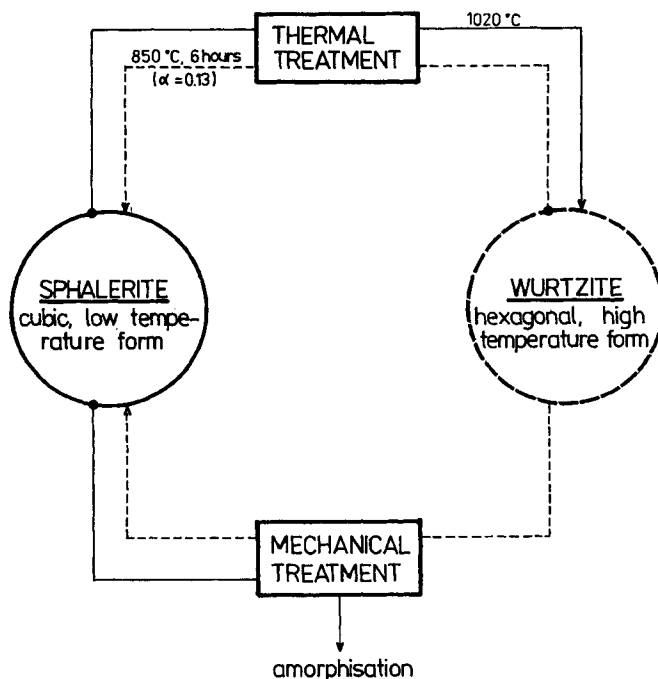


Fig. 4.5 Relations between polymorphs of ZnS.

The influence of mechanical activation on phase transformations was carefully studied [4.1, 4.16-4.19]. It was found that the mechanism of the polymorphous transformations stimulated by mechanical activation differs from the mechanism (Fig. 4.5). While the effect of mechanical stress on sphalerite results only in its amorphization, the mechanical activation of wurtzite can bring about transformation into sphalerite (with an associated density increase from  $3.48 \text{ g cm}^{-3}$  to  $4.09 \text{ g cm}^{-3}$ ). Senna assumes that the mechanochemical transformation is energetically more profitable than that produced by thermal processing [4.18]. While the thermal transformation requires that all atoms in the structure of wurtzite should be excited approximately to an equal degree, only a limited number of nucleation centers is able to start the mechanochemical transformation. We may assume that the driving force of the mechanochemical transformation of wurtzite to sphalerite is motion of the dislocations in the activated solid phase [4.1].

### 4.3. Cinnabar HgS

Cinnabar is present in nature in different polymorphs: trigonal  $\alpha$ -HgS, cubic  $\beta$ -HgS (often called metacinnabar) and hexagonal HgS. The polymorphous phase transition temperature  $\alpha \rightarrow \beta$  depends on sample purity, for pure  $\alpha$ -HgS states  $362^\circ\text{C}$  [4.20-4.21].

The influence of mechanical activation on the transformation of cinnabar was studied by differential scanning calorimetry (DSC) [4.22].

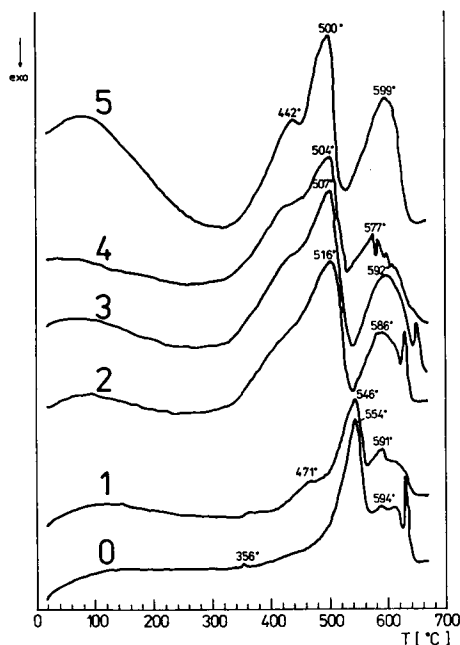


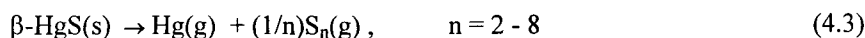
Fig. 4.6 DSC curve of a non-activated sample of  $\alpha$ -HgS (curve 0) and curves of  $\alpha$ -HgS samples activated for various grinding times: 1 - 5 min, 2 - 10 min, 3 - 15 min, 4 - 20 min, 5 - 30 min [4.22].

The DSC curves (Fig. 4.6) represent an association of endothermic effects which differ from each other in shape and values of the extreme temperatures. We can observe subpeaks in temperature region I (320-560°C) and strongly structured peaks at temperatures over 560°C (region II).

For a non-activated sample we observe a small endo effect at 356°C, a suggestion of which also appears in the case of a sample activated for 5 min. The occurrence of this endo effect cannot be excluded even for more disordered samples. In this case, it can, however, be blurred with the subsequent dominant endo effect. According to the literature [4.21, 4.23-4.24] this temperature can be attributed to the polymorphous transformation



Provided that  $T > 360^\circ\text{C}$ , we observe a large exothermic peak with a maximum at 554°C for a non-activated sample. This peak is probably due to the dissociative sublimation of  $\beta$ -HgS [4.25-4.26]



which leads to a considerable decrease in the weight of the sample.

It was found by X-ray diffraction phase analysis of the mineral sample under study [4.22] that this sample contained hexagonal cinnabar  $\alpha$ -HgS (JCPDS 6-256) as a major component and pyrite (JCPDS-710) and quartz  $\alpha$ -SiO<sub>2</sub> (JCPDS-490) as minor constituents.

Provided that  $T > 500^\circ\text{C}$ , pyrite undergoes dissociation [4.27]



The temperature of the polymorphous transformation  $\alpha$ -SiO<sub>2</sub>  $\rightarrow$   $\beta$ -SiO<sub>2</sub> (573°C) is also situated in this temperature region. Both processes overlap and their unambiguous interpretation from the course of the DSC curve in Fig. 4.5 for a non-activated sample is not possible.

The mechanical activation brings about a shift in temperatures of the above mentioned endo effects to lower values and also manifests itself in their form (Fig. 4.6).

The maximum temperature of the dominant endo effect  $T_{\text{max}}$  decreases with increasing activation time from 554°C in the non-activated sample to 500°C after 30 min activation.

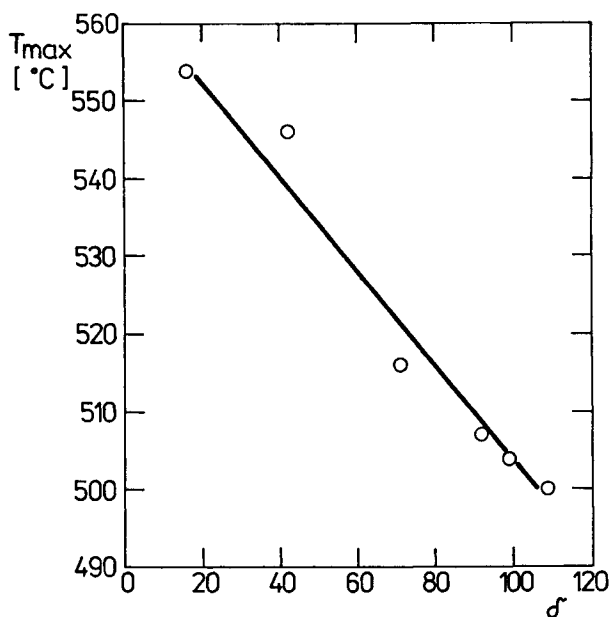


Fig. 4.7 Dependence of the maximum temperature of the dominant DSC effect,  $T_{\text{max}}$  on the coefficient of disorder of mechanically activated samples,  $\delta = S_A/(100-A)$ ,  $S_A$  - specific surface,  $A$  - amorphization [4.22].

The dependence of the values of the temperature of the individual endo effects on the empirical coefficient of disorder of mechanically activated samples  $\delta$  is represented in Fig. 4.7. The sensitivity of thermal decomposition of cinnabar to violation of its structure documented by this relationship confirms the structural sensitivity of the decomposition of sulfides as presented for copper and zinc sulfides in papers [4.7, 4.19, 4.28].

#### 4.4. Greenockite CdS

The most frequent crystalline form of occurrence of the mineral is hexagonal (wurtzite) CdS, this is more stable the cubic (sphalerite) form. This is the opposite of the zinc sulphide system.

The polymorphous transformations of cadmium sulfides during mechanical activation were investigated in papers [4.17-4.18, 4.29-4.31]. The grinding of the stable wurtzite CdS phase brings about its transformation into disordered cubic phase of the sphalerite type. The amount of the cubic phase arising from the hexagonal CdS in the course of grinding for 1, 6, 15 and 30 minutes is represented in Fig. 4.8.

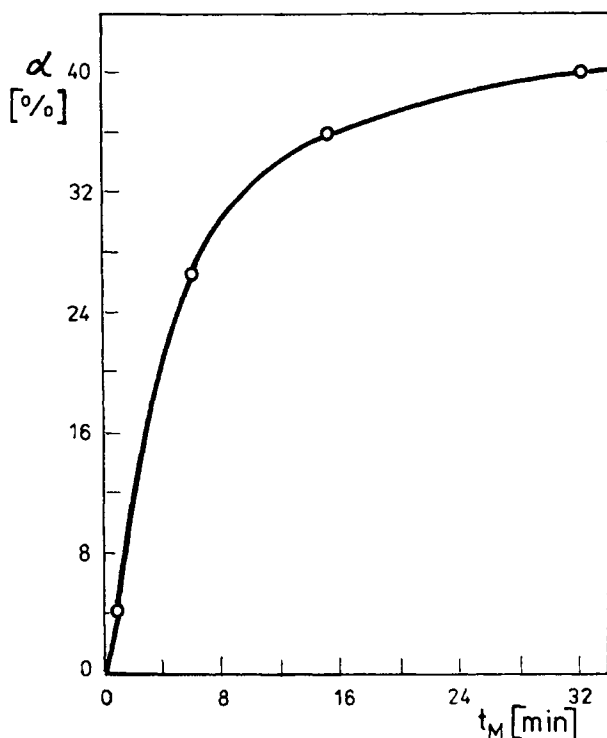


Fig. 4.8 Variation in cubic phase,  $\alpha$  with grinding time,  $t_M$  of hexagonal CdS [4.31].

The grinding also resulted in reduction of the particle size to the average value of 0.25  $\mu\text{m}$ . It has been found that the annealing of the ground samples at temperatures above 450°C leads to partial regeneration of the hexagonal phase. A sample ground for 30 minutes and annealed at 530°C for one hour in argon atmosphere underwent total regeneration.

The rate of transformation of the hexagonal phase into the cubic phase during mechanical activation is dependent on the method of preparation of the cadmium sulfide subjected to mechanochemical transformation. The formation of the new phase is accompanied by an increase in its enthalpy content [4.30].

The „frozen“ metastable state of the solid substance is released by subsequent heating as the mobility of atoms increases. The heat liberated by rearrangement of the mechanically activated CdS can be determined by calorimetry.

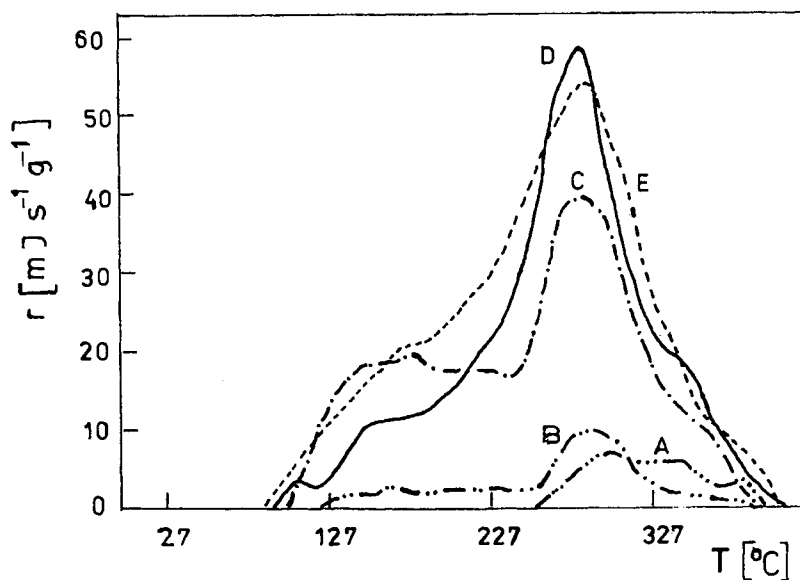


Fig. 4.9 DSC curves of CdS mechanically activated for: A - 30 min, B - 60 min, C - 180 min, D - 360 min, E - 540 min,  $r$  - rate of heat evolution [4.30].

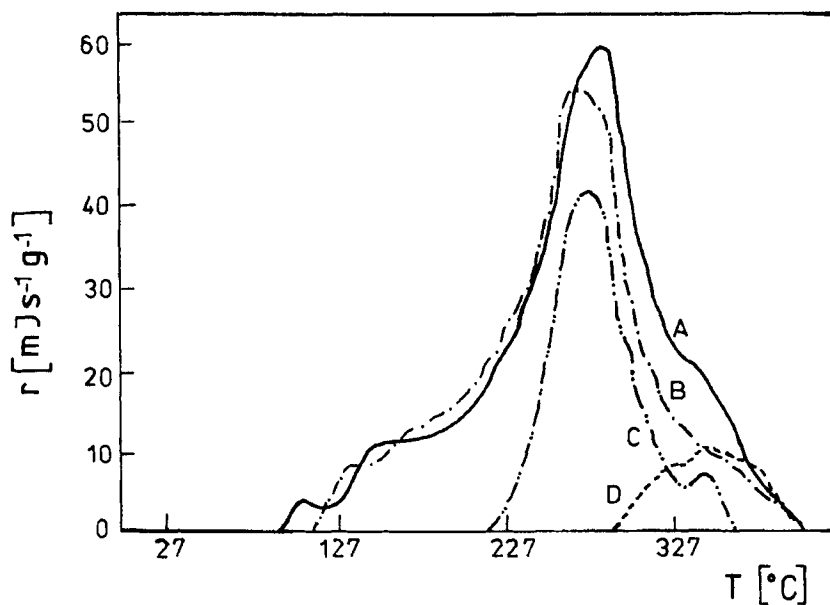


Fig. 4.10 DSC curves of CdS mechanically activated for 360 min and annealed for 60 min at temperature  $T$ : A - as -ground, B -  $T = 100^{\circ}C$ , C -  $T = 200^{\circ}C$ , D -  $T = 300^{\circ}C$  [4.30].

A DSC record of the CdS mechanically activated for 30-540 minutes is represented in Fig. 4.9. It is clear that the traces are practically independent of grinding time, although the energy

associated with the peak at 280°C increased with grinding, no change in peak temperature was evident. Therefore, although the extent of structural disordering increases quantitatively with grinding time, no qualitative changes take place.

However, the energy associated with the peak and the shape of the curve changes if the ground sample has been annealed prior to DSC (Fig. 4.10). This confirms that the degree of activation may differ, even if the overall enthalpy content is equal. For instance, if the rate determining step of the transformation is nucleation, a disordered region of the solid substance with high energy concentration may be necessary for the transformation to occur. On the other hand, an equal amount of accumulated energy in a less disordered region need not be sufficient for nucleation. This heterogeneity was demonstrated for CdS ground in cyclohexane and in air by Senna [4.32].

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## **Chapter 5 THERMAL DECOMPOSITION OF MECHANICALLY ACTIVATED MINERALS**

**5.1. Oxidative decomposition**

**5.2. Decomposition in an inert atmosphere (pyrolysis)**

**5.3. Reductive decomposition**

**5.4. Solid state exchange reactions**

**5.5. References**

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Sulfides exhibit a great variety of chemical and physical properties. They display similar structural defects as oxides with cation vacancies, interstitial cations or anionic defects all possible. However, the concentration, structure and mobility of these defects are much more varied in the case of sulfides [5.1].

The cationic vacancies change their properties according to conditions. For instance, their influence on electric properties and character of the chemical bond of sulfides is dependent on temperature [5.2]. The formation of interstitial defects, in which metal ions are displaced from a normal lattice position to an intermediate position, depends on strength of the metal-sulfur bond. The Me-S and S-S bond in sulfides are similar to each other and the difference between them decreases with increasing temperature. However, if sulfur is released, the metal present in the normal crystallographic position remains without a partner and the defectiveness of sulfide increases. The influence of defects on solid phase reactions is frequently more significant than the influence of the sulfide structure [5.3].

The defectiveness of the structure of solid substance can be affected by different treatments prior to thermal decomposition. The potentials for forming different defects by pretreatment of the solid phase are presented in Table 5.1. Mechanical activation belongs among the effective processes enabling us to control and regulate the course of thermal decomposition of sulfides via formation of different defects.

Table 5.1 Relationship between different types of defects and pretreatment of the solid phase [5.4]

| Preparative treatment            | Crystal defects |       |                        |              | Lattice defects |               |
|----------------------------------|-----------------|-------|------------------------|--------------|-----------------|---------------|
|                                  | Surface         | Habit | Heterophase Inclusions | Dislocations | Doping ions     | Point defects |
| Control of crystal growth        | +               | +     |                        | +            | +               | +             |
| Doping                           |                 |       |                        |              | +               | +             |
| Physical aging                   |                 |       |                        | +            |                 |               |
| Chemical aging                   |                 |       | +                      |              | +               |               |
| Preliminary chemical treatment   |                 |       | +                      |              |                 |               |
| Preliminary radiative treatment  |                 |       | +                      | +            | +               | +             |
| Preliminary mechanical treatment | +               |       | +                      | +            |                 | +             |

### 5.1. Oxidative decomposition

#### *Chalcopyrite CuFeS<sub>2</sub>*

The decomposition of chalcopyrite in an oxidizing environment is widely used as a preparatory operation in both hydro- and pyrometallurgical process routes. The complicated mechanism and technological importance of this process has attracted attention for a long time [5.5].

Thermoanalytical study of the oxidative decomposition of chalcopyrite and X-ray diffraction of the intermediates and products have provided much information about the sequence of reactions occurring in this process. It has been revealed that the exothermic oxidation reactions prevail in the low temperature region [5.6-5.7]. One of the intermediates is copper (II) sulfate,

the desulfurization of which is an endothermic process. It has also been found that the final product is a mixture of copper ferrites ( $\text{CuO} \cdot \text{Fe}_2\text{O}_3$ ,  $\text{Cu}_2\text{O} \cdot \text{Fe}_2\text{O}_3$ ).

Contemporary opinions concerning the nature of the exothermic reactions taking place at low temperatures may be classified into two main groups. According to the first group, the precursor of copper (II) sulfate is copper (II) oxide, formed by oxidation of  $\text{Cu}_2\text{S}$  [5.8] or  $\text{Cu}_2\text{O}$  [5.9] while the second view is that copper (II) sulfate originates in the oxidation of bornite  $\text{Cu}_5\text{FeS}_4$  [5.6-5.7].

The lack of consistency in the papers dealing with the oxidative decomposition of chalcopyrite suggests that the nature of products formed at a given temperature depends on a internal factors including the chemical character and structure of the reacting substance.

The actual structure of chalcopyrite may vary as well as a consequence of a great many external factors which increases the reaction surface and the concentration of irreversible defects in the bulk of the comminuted grains.

A thermoanalytical study of mechanically activated chalcopyrite were studied by Huhn [5.10]. For mechanically activated samples a distinct structuralization of the exothermic effect in the DTA records was observed, along with a shift in the characteristic maxima towards lower temperatures. The proportion of  $\text{CuSO}_4$  in the products of low-temperature decomposition increased with the mechanically induced disorder in chalcopyrite. A satisfactory explanation of these facts has not yet been presented.

Starting from the above analysis, the changes in the oxidative thermal decomposition of chalcopyrite and its mixture with pyrite (which frequent accompanies chalcopyrite in nature) were studied in paper [5.11].

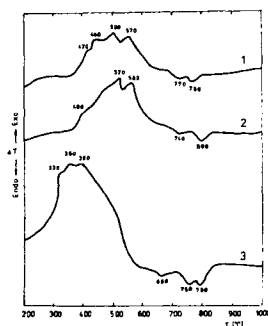


Fig. 5.1 DTA curves of non-activated  $\text{CuFeS}_2$  (1), a  $\text{CuFeS}_2$ - $\text{FeS}_2$  mixture (2), and a  $\text{CuFeS}_2$ - $\text{FeS}_2$  mixture mechanically activated for 60 minutes (3) [5.11].

The low temperature decomposition of chalcopyrite in an oxidizing atmosphere is characterized by exothermic effects in the DTA curves (Fig. 5.1) with maxima at 420, 460, 500 and 570°C. These maxima are accompanied by minima at 340, 380, 440, 490 and 550°C in the DTG curves, and by a gradual mass decrease in the TG curves on Fig. 5.2. X-ray phase analysis of the products of decomposition at 400°C revealed the presence of hematite  $\alpha\text{-Fe}_2\text{O}_3$  in addition to chalcopyrite. Bornite was identified together with chalcopyrite and hematite at 470°C. The diffraction lines of chalcopyrite are impaired at 540°C, and the presence of  $\text{CuSO}_4$  is indicated. In the temperature interval 570-680°C, the TG record indicates a mass increase due to the oxidation of bornite to  $\text{CuSO}_4$ . As the temperature increases to 660-800°C, two endothermic effects are observed in the DTA curve, with a mass increase in the TG curve. According to X-ray diffraction analysis, a gradual desulfatization of  $\text{CuSO}_4$  to oxysulfate  $\text{CuO} \cdot \text{CuSO}_4$ ,  $\text{CuO}$  and  $\text{SO}_2$  proceeds in this temperature region. The presence of oxysulfate,

which is a product of partial desulfatization, was confirmed at 770°C. The desulfatization is completed at 1000°C with only iron and copper oxides and copper ferrite present in the product.

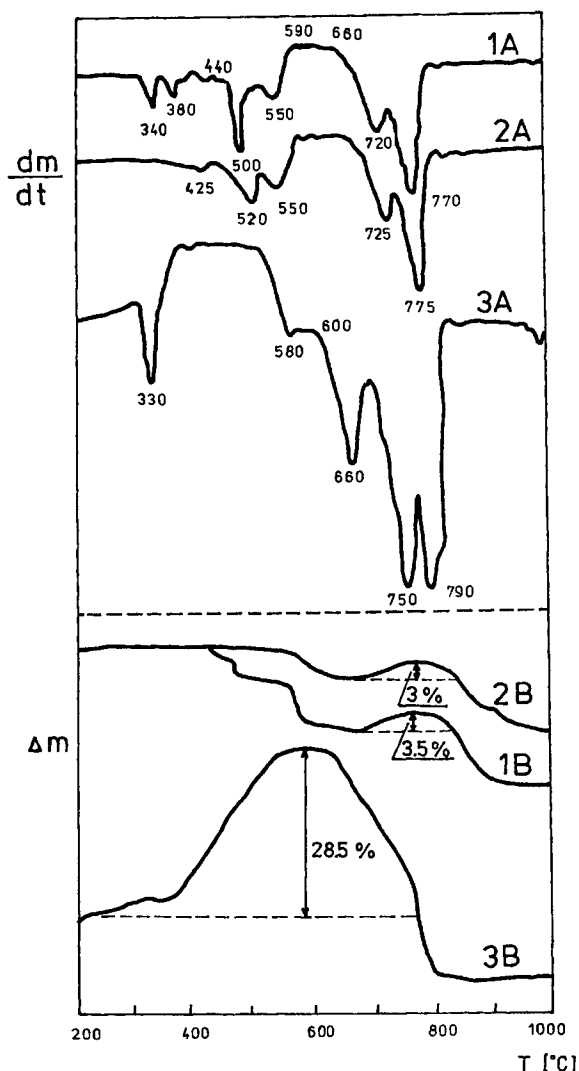
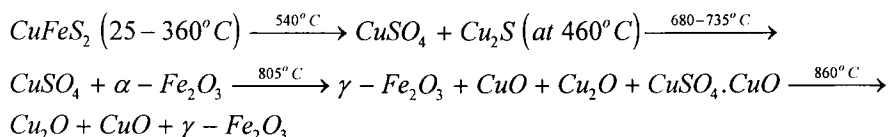


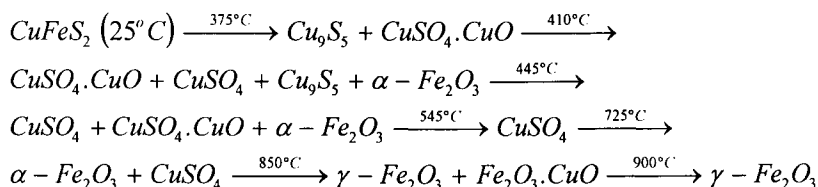
Fig. 5.2 TG and DTG curves of non-activated  $\text{CuFeS}_2$  (1A, 1B), a  $\text{CuFeS}_2\text{-FeS}_2$  mixture (2A, 2B), and a  $\text{CuFeS}_2\text{-FeS}_2$  mixture mechanically activated for 60 minutes (3A, 3B) [5.11].

The influence of mechanical activation of  $\text{CuFeS}_2$  in different media (grinding in air or in water) was investigated by Kulebakin [5.12]. The author has found that the processing of the mineral in different media results in different decomposition mechanisms and in the shift of maximum temperatures of DTA effects, in the course of which different phases come into existence. The situation can be illustrated by the following schemes:

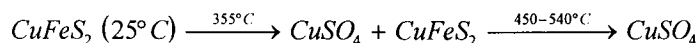
### Non activated CuFeS<sub>2</sub>



### Mechanically activated CuFeS<sub>2</sub> (water, 7 min)



### Mechanically activated CuFeS<sub>2</sub> (air, 7 min)



The addition of pyrite affects the character of the endothermic processes taking place at low temperature by suppressing the structural effect on the thermoanalytical curves and shifting to higher temperatures the characteristic maxima in the DTA and DTG curves. The presence of bornite in the products of oxidative decomposition was not proven. The first solid products of oxidation are CuSO<sub>4</sub> and α-Fe<sub>2</sub>O<sub>3</sub>. The endothermic desulfatization and the product composition from high temperature decomposition are not affected by the addition of pyrite. Similarly, the mass increase in the region of CuSO<sub>4</sub> formation is approximately equal to that observed for pure chalcopyrite.

Mechanical activation of the chalcopyrite-pyrite mixture has a significant influence on the thermoanalytical curves and the composition of the reaction products at different temperatures. According to the DTA record, the endothermic oxidation reaction begin at temperatures as much as 180 degrees lower than for non-activated samples with two indistinct peaks evident at approximately 360°C and 390°C. The oxidative decomposition of chalcopyrite is accompanied over a wide temperature range by a mass increase, which proceeds in two steps. The maximum mass increase is almost 10 times greater than that observed with non-activated sample and is Δm ~ 28.5 %. Only CuSO<sub>4</sub> and α-Fe<sub>2</sub>O<sub>3</sub> are present in the solid residue, as products of the oxidative decomposition in the temperature region 310-700°C. The gradual desulfatization of a large quantity of CuSO<sub>4</sub> is manifested as a mass decrease in the TG curve, and by three endothermic peaks, at 660, 750 and 790°C in the DTA record. The presence of oxysulfate, which is a product of partial desulfatization, was observed as for the non-activated sample at 770°C. The desulfatization is completed at 870°C with only CuO and the copper ferrites present in the products - hematite is no longer present. These facts indicate that the decrease in the temperature at which the primary oxidation processes take place is associated with a decrease in the temperature at which ferrites are formed.

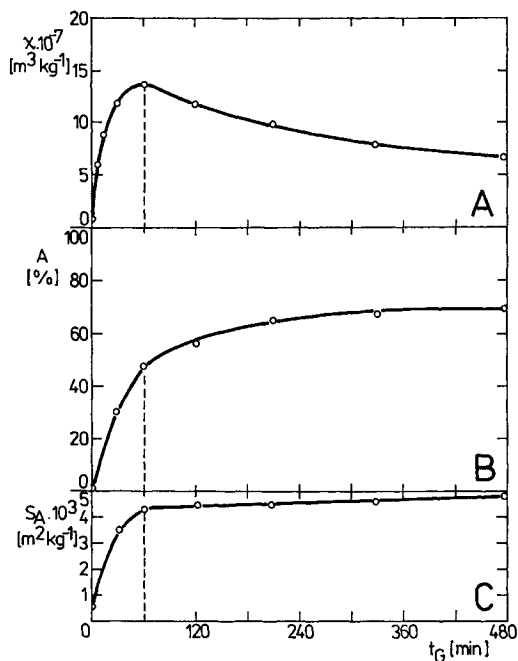


Fig. 5.3 Variations of specific surface,  $S_A$  (A), amorphization,  $A$  (B), and volume magnetic susceptibility,  $\chi$  (C) with the time of mechanical activation,  $t_G$ .

In order to elucidate the influence of mechanical activation on the oxidative decomposition of chalcopyrite, the chalcopyrite-pyrite mixture was subjected to mechanical activation for different times. Figure 5.3 shows the changes in physical properties of the mixture during the course of grinding. The specific surface area increases for the first hour and then stabilizes due to equilibrium between particle breakage and aggregation. During grinding, a quasi-generation of amorphous chalcopyrite takes place, while the structure of pyrite does not change. The transformations of the surface and the structure are accompanied by changes in the volume magnetic susceptibility of the mineral mixture. The 5- or even 15-fold increase in magnetic susceptibility suggests that the magnetically ordered phase is transformed into a non-ordered phase, and the substance passes from an antiferromagnetic into a paramagnetic state.

The maximum mass increase  $\Delta m$ , corresponding to the amount of  $CuSO_4$  in the products and the temperature of the first exothermic reaction (Fig. 5.4) were selected to estimate the effect of mechanical activation on the oxidative decomposition. A comparison of Figs 5.2, 5.3 and 5.4 shows that the investigated quantities exhibit characteristic extremes for the time of grinding at which the volume magnetic susceptibility attains its maximum and the highest concentration of paramagnetic centres is to be observed.

### ***Pyrite $FeS_2$***

The oxidative decomposition of pyrite following its mechanical activation was thoroughly studied [5.12-5.16]. The authors have declared the view that the mechanical activation produces significant change in physico-chemical properties of this mineral which affects the

surface as well as the bulk structure. The observed differences are caused by the applied regime of grinding [5.12]. However, we can state that magnetite  $\text{Fe}_3\text{O}_4$  occurs among grinding products irrespective of dry or wet grinding. The presence of pyrrhotite  $\text{FeS}$  as a product of partial desulfurization was observed in small amounts only in the case of dry grinding of the mineral. As to new phases, Kulebakin mentions the presence of  $\text{FeSO}_4 \cdot \text{H}_2\text{O}$  and  $4\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{Fe}_2\text{O}_3 \cdot 27\text{H}_2\text{O}$  [5.12].

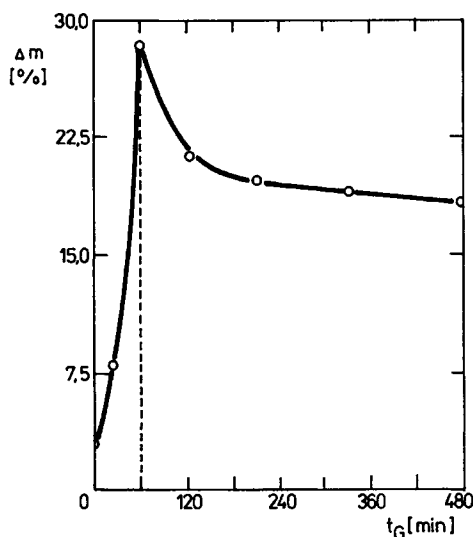


Fig. 5.4 Variation of maximum mass increase,  $\Delta m$  in TG curves with time of mechanical activation,  $t_G$ .

The DTA and TG records of pyrite samples are given in Figures 5.5-5.6. The DTA record of a non-activated sample (Fig. 5.5, curve 1) is analogous to the published one [5.17]. The value of mass loss  $\Delta m = 29.3\%$  calculated from TG record (Fig. 5.6, curve 1) corresponds the transformation of pyrite taking place in the temperature interval 500-600°C according to the following reaction



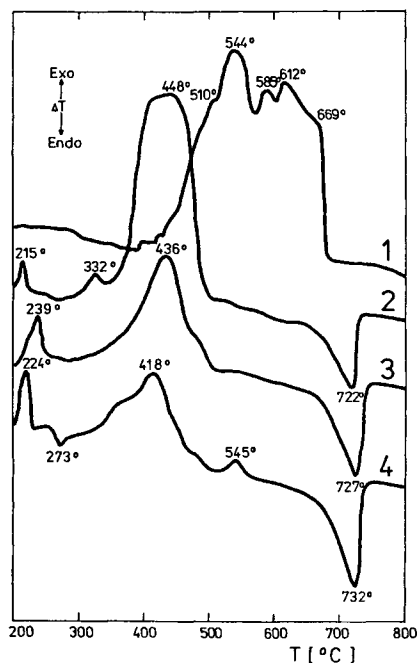


Fig. 5.5 DTA curves of  $\text{FeS}_2$ . Time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, 4 - 30 min [5.18].

The DTA records of mechanically activated  $\text{FeS}_2$  samples (Fig. 5.5, curves 2-4) are significantly different. Besides the 100-130°C decreases in the peak temperature of DTA effects, we can observe new effects in the region 650-750°C. According to literature data [5.19] some products of mechanochemical oxidation of pyrite are formed on the surface of the mineral in the course of its mechanical activation. The investigation of samples by XPS method showed that the surface of the pyrite activated for ten or more minutes was covered by a layer of  $\text{Fe}_2(\text{SO}_4)_3$  [5.20].

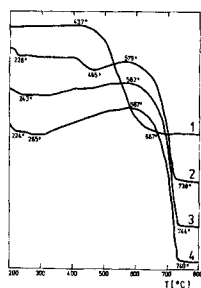


Fig. 5.6 TG curves of  $\text{FeS}_2$ , time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, 4 - 30 min [5.18].

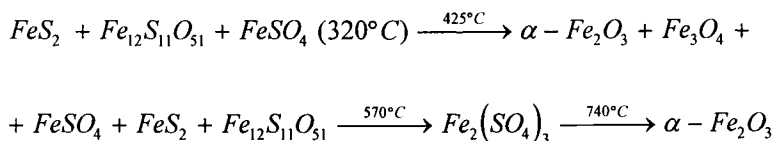
In the absence of data showing the presence of pyritic iron or sulfur on the surface, we can conclude that ferric sulfate forms a compact layer on the surface of the mineral. The endothermic effects with apex temperatures of 722-732°C (Fig. 5.6, curves 2-4) are to be attributed to decomposition the mentioned ferric sulfate. In the case of the pyrite mechanically

activated for 30 min, the decomposition of sulfate is accompanied by the mass loss  $\Delta m = 44\%$  which is in good agreement with the theoretical value of 47.4 %. The effects in the temperature region 190-250°C correspond to gradual decomposition of the hydrated sulfates formed by reaction with water during exposure to air.

The values of activation energy of the oxidation of pyrite are given as a function of the time of mechanical activation in Fig. 5.7. The disordering of structure and the liberalization of chemical bonds in mechanically activated solids usually brings about an increase in the rate of decomposition and a decrease in apparent activation energy [5.3]. In this case, the effect of disordering of the pyrite structure overlapped the formation of the surface layer of sulfate. This compact layer hinders the transport of oxygen to the pyrite surface below, thus the rate controlling step is diffusion through the surface layer. The activation energy of oxidation increases up to  $t_G = 10$  min. At higher times of mechanical activation the surface of pyrite is already covered with a compact layer of sulfate and thus the activation energy of the thermal oxidative decomposition is practically independent of the time of activation.

Kulebakin [5.12] has proposed the following mechanism of the oxidizing decomposition.

Mechanically activated  $\text{FeS}_2$  (air, 7 min)



The effect of long-term storage of pyrite has been studied by Žižajev [5.21]. The different relaxation processes (e.g. recrystallization, diffusion) as well as the chemical reactions proceed after finishing the act of mechanical activation. It was estimated that the storage of mechanically activated sulfides may even lead to their complete decomposition.

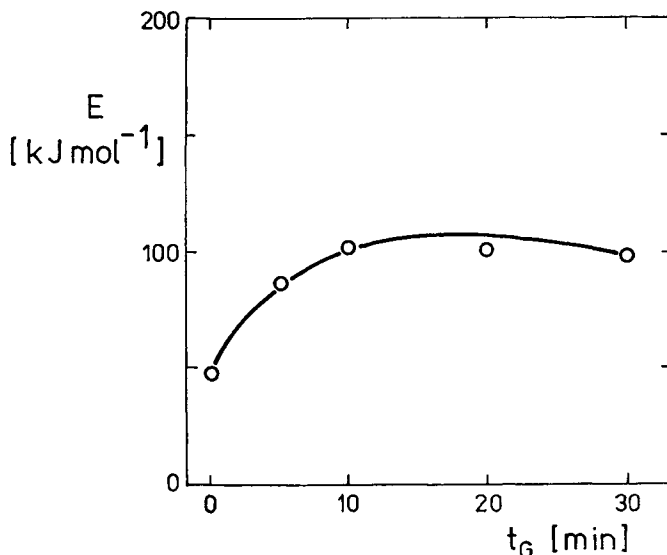


Fig. 5.7 Activation energy,  $E$  of  $\text{FeS}_2$  oxidation vs. time of mechanical activation,  $t_G$  [5.18].

## Arsenopyrite FeAsS

The oxidation of non-activated FeAsS takes place in the region 440-650°C [5.22]. The solid products of decomposition are maghemite  $\gamma\text{-Fe}_2\text{O}_3$  and hematite  $\alpha\text{-Fe}_2\text{O}_3$ .

Korneva [5.23-5.24] investigated arsenopyrite mechanically activated in a planetary mill under different regimes (dry-wet grinding, iron-agate balls) with the intention to prepare an activated product with constant specific surface area. The study of diffraction patterns of the activated products has shown that the structure is most disordered during dry grinding by using iron balls. Infrared spectroscopy showed that the band at  $\approx 435\text{ cm}^{-1}$  corresponding to the stretching vibration of the As-S bond, is reduced indicating weakening of this bond. A similar weakening was also observed for the band at  $370\text{ cm}^{-1}$  corresponding to stretching vibration of the Fe-As bond. The study of the products of oxidative decomposition obtained at 460, 530 and 600°C has shown that some X-ray amorphous phases characterized in infrared spectra by the bands corresponding to the  $\text{SO}_4^{2-}$  and  $\text{AsO}_4^{3-}$  are present together with non-decomposed FeAsS and  $\gamma\text{-Fe}_2\text{O}_3$ . The authors of papers [5.23-5.24] suppose the presence of iron arsenites. If temperatures 730-780°C are used, the bands corresponding to sulfates do not appear, indicating their degradation. The supposed arsenites are transformed into arsenates at temperatures above 900°C. Qualitative X-ray analysis revealed the presence of a compound  $\text{Fe}_3\text{AsO}_7$  ( $\text{Fe}_2\text{O}_3\cdot\text{FeAsO}_4$ ) together with hematite  $\alpha\text{-Fe}_2\text{O}_3$ . If the products obtained at 900°C did not originate in mechanical activation involving FeAsS grinding in air with iron balls but grinding with agate balls, the presence of  $\text{Fe}_4\text{As}_2\text{O}_{11}$  was recorded besides  $\text{Fe}_3\text{AsO}_7$  and  $\alpha\text{-Fe}_2\text{O}_3$ .

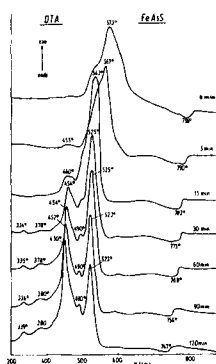


Fig. 5.8 DTA curves of FeAsS (time of mechanical activation denoted on the curves).

The results of thermoanalytical study of the oxidative decomposition of arsenopyrite from Pezinok in Slovakia are presented in Figs 5.8 and 5.9. The non-activated sample shows a break at 450°C on the DTA record (Fig. 5.8) and a considerable exothermic effect at 573°C with a bend between these two temperatures. On the basis of X-ray diffraction analyses of the samples oxidized at the temperatures corresponding to the extremes on DTA records we can conclude that the temperature of 573°C corresponds to FeAsS oxidation and the temperature of 798°C corresponds to the decomposition of accessory ankerite  $\text{Ca}(\text{Mg,Fe})(\text{CO}_3)_2$  in agreement with the literature [5.25-5.26]. Arsenopyrite begins to decompose non-oxidatively at temperatures of about 500°C and arsenic escapes for a great part. A portion of arsenic is likely to be bonded to calcium in calcium arsenate. The presence of other arsenates, e.g.  $\text{Fe}_3\text{AsO}_7$  [5.23-5.24] or unidentified  $\text{Fe}_x\text{As}_y\text{O}_z$  [5.14] has also been mentioned in literature. Iron preferentially forms maghemite  $\gamma\text{-Fe}_2\text{O}_3$  which is transformed into hematite  $\alpha\text{-Fe}_2\text{O}_3$  at

higher temperatures. A more exact identification is not possible by XRD due to overlap of the peaks from different phases and amorphization due to grinding.

We can observe considerable structural effect and a significant shift in positions of the exothermic process in the case of activated samples (plots 1-6). The difference between the peak temperature for a non-activated sample and the sample activated for 120 min of this effect amounts to 50°C [5.27].

In analogy to the calorimetric effects presented in Fig. 5.8 the thermogravimetric records in Fig. 5.9 demonstrate that considerable changes in weight of the FeAsS samples are produced by mechanical activation. These effects are accompanied by a decrease in initial and final temperatures of the decomposition of arsenopyrite.

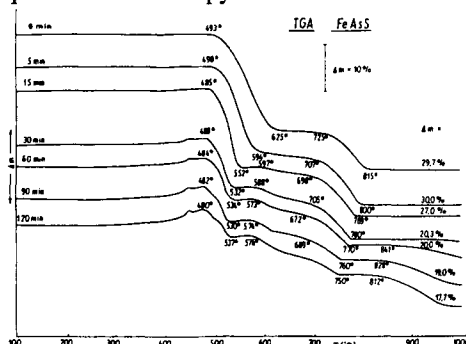


Fig. 5.9 TG curves of FeAsS (time of mechanical activation denoted on the curves).

The chemical analysis of the products of oxidative decomposition has shown that the content of arsenic in the solid-phase products is dependent on the time of mechanical activation and increases up to a certain time  $t_M$ . In Fig. 5.10B this fact is expressed by the ratio As/Fe in the solid phase. This effect is a function of temperature and is limited by the time for the first 60 minutes. After grinding for longer than 60 min, there is no further reduction in the peak temperature of the main exothermic reaction (Fig. 5.8) and the content of arsenic in the solid phase decreases (Fig. 5.10B). The observed effect is to be interpreted in harmony with the changes in surface-structural quantities which manifests itself in mechanically activated arsenopyrite (Fig. 5.10A). It is characteristic of shorter time of grinding that the specific surface  $S_A$  and the degree of disorder  $F$  in arsenopyrite structure increase. At a higher degree of disorder the character of formation of new surface does not change, but the mineral undergoes considerable amorphization. The retardation of formation of bulk defects is evidently a determining factor because the reactivity decreases in this region [5.28].

### Galena PbS

The decomposition of PbS follows a complicated mechanism because  $PbSO_4$ ,  $nPbO \cdot PbSO_4$  ( $n = 1, 2, 4$ ),  $5PbSO_4 \cdot PbO$  and metallic Pb arise in addition to PbO as products or intermediates of oxidation [5.29-5.32].

The DTA record of non-activated PbS (Fig. 5.11, curve 1) indicates exothermic effects at 460°C and 660°C and an endotherm at 850°C. The exotherm at 460°C is due to slight oxidation of PbS resulting in a slight increase in mass on the TG curve (Fig. 5.12, curve 2). The process at 660°C corresponds to a set of overlapping oxidation reactions giving rise to anglesite or oxysulfates. On the TG curve we can observe the increase in mass beginning at 500°C and a maximum ( $\alpha = 4.5\%$ ) at 800°C. According to [5.32] the position of this maximum corresponds to the following equation

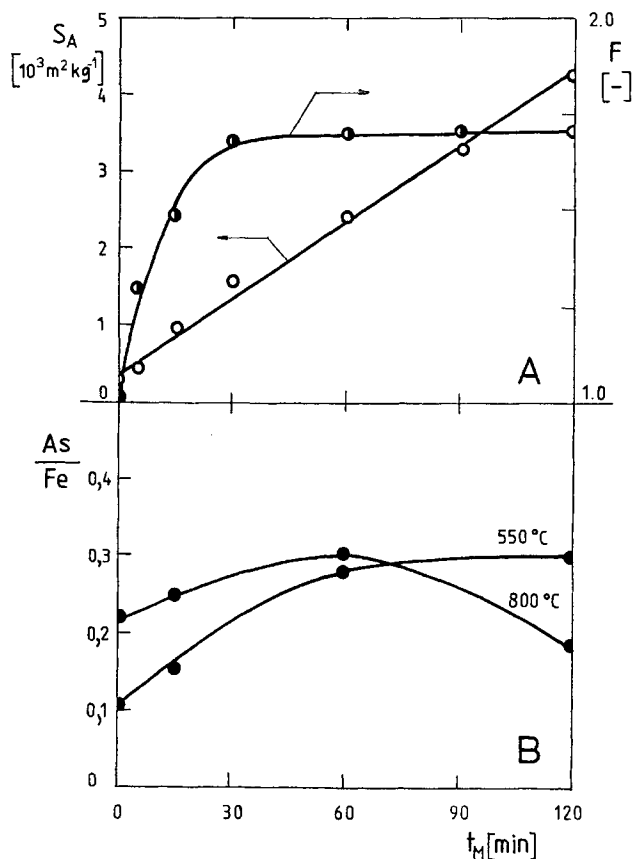
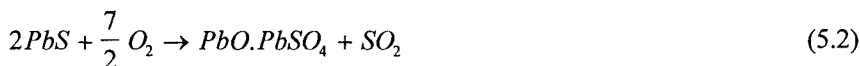


Fig. 5.10 A- Specific surface area,  $S_A$  and degree of FeAsS disorder,  $F$  vs. time of mechanical activation,  $t_M$ ,  
 B- As/Fe ratio for oxidative decomposition of FeAsS vs. time of mechanical activation,  $t_M$ .

By heating over 800°C the mass of sample begins to decrease and oxides prevail over sulfates in the product. Margulis has reported that the eutectic  $PbO + 2PbO.SO_4$  melt originates in this region [5.33].

Mechanical activation shifts the peak temperature of the exotherm at 660°C to lower temperature (Fig. 5.11, curves 2,3). The corresponding TG curves in Fig. 5.12 also show a shift in onset temperature of the processes accompanied by a mass increase.

A steeper rise of the TG curve of non-activated sample with temperature, when compared with the curve of activated sample, confirms the more rapid course of the first stage of oxidation  $PbS \rightarrow PbSO_4$ . The particle size effect together with the shift of rate controlling step from kinetic to diffusion as well as unfavourable conditions of the flow of a gaseous product may be taken into consideration when explaining these results [5.12].

The XRD traces taken at temperatures corresponding to completion of exothermic reactions show  $\text{PbSO}_4$  starts to appear as early as at  $380^\circ\text{C}$  for a sample activated for 10 min. For samples oxidised at  $760^\circ\text{C}$ , the peaks for  $\text{PbSO}_4$  and  $\text{PbO}\cdot\text{PbSO}_4$  appear while the samples ignited at  $1000^\circ\text{C}$  contain not only  $\text{PbSO}_4$  and  $\text{PbO}\cdot\text{PbSO}_4$  but also  $\text{PbO}$ .

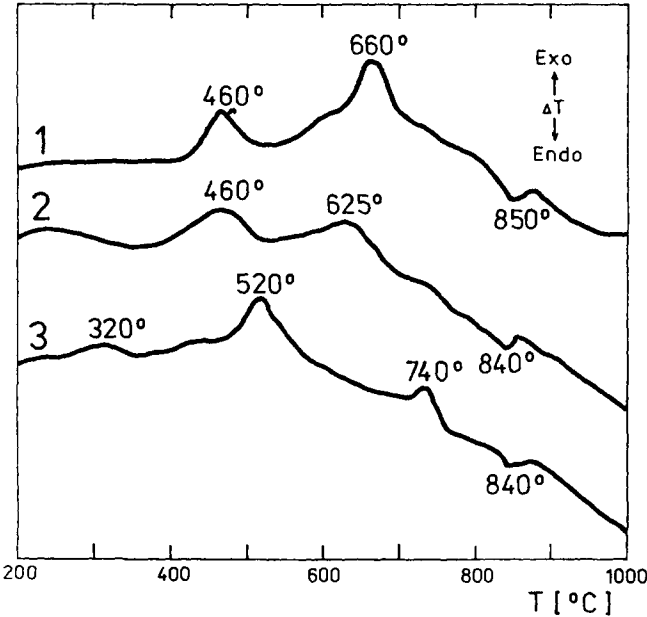


Fig. 5.11 DTA curves of  $\text{PbS}$ . Time of mechanical activation: 1 - 0 min, 2 - 10 min, 3 - 30 min [5.18].

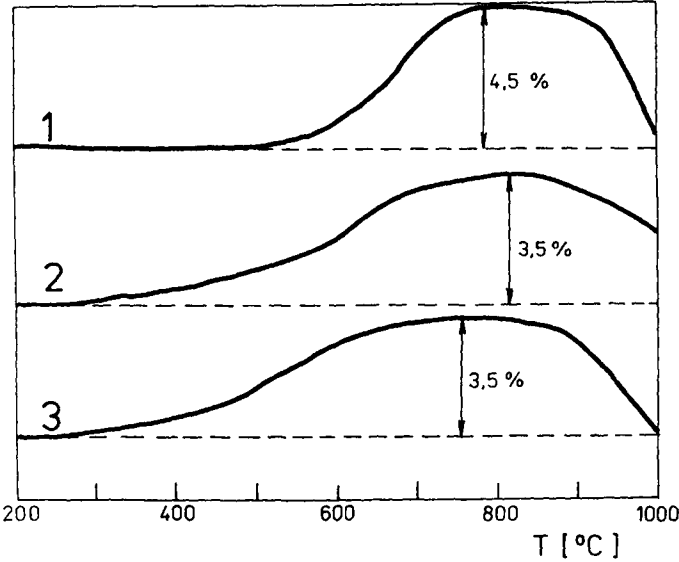


Fig. 5.12 TG curves of  $\text{PbS}$ . Time of mechanical activation: 1 - 0 min, 2 - 10 min, 3 - 30 min.

## Sphalerite ZnS

Sphalerite is a frequently studied mineral. The interest in this sulfide derives from the metallurgical industry in which it is exploited as the main source of zinc and several associated metals (cadmium and manganese). Non-traditional application of sphalerite include the exploitation of its luminescence properties and memory effect in electronics [5.34-5.35].

The thermal analysis of sphalerite has been predominantly applied to studying the influence of the amount and granularity of the sample, the atmosphere, type of inert, heating rate and other quantities on the parameters of the DTA effects [5.25-5.26,5.36-5.37]. Kopp and Kerr investigated the effect of substituting isomorphous iron for zinc in the sphalerite lattice on the course of the DTA effects [5.38]. A linear increase in the lattice constant of sphalerite and, thus, a disordering of its crystal structure occurs when the iron content increases from 0.1 to 13 %. At the same time, the temperature of the DTA effects decreases.

The oxidation of sphalerite was investigated by differential thermal analysis with typical curves shown in Fig. 5.13. The oxidative decomposition of sphalerite proceeds in three typical stages. The first and second stages ( $T = 400\text{-}750^\circ\text{C}$ ) are characterised by exothermic processes and by the fact that the exotherms depend on the time of mechanical activation and are shifted to lower values. The third stage ( $T > 800^\circ\text{C}$ ) is endothermic and does not exhibit any dependence on the time of mechanical activation. These results are consistent with the literature [5.39]. The exothermic reaction



takes place in the region  $350\text{-}800^\circ\text{C}$ . This reaction is accompanied by exothermic formation of sulfate which is dependent on the presence of  $\text{SO}_2$



At temperatures above  $800^\circ\text{C}$ , the solid products of reactions (2) and (3) may enter into exothermic reaction to give the oxysulfate  $\text{ZnO} \cdot \text{ZnSO}_4$  [5.40].

Owing to the presence of Fe and  $\text{SiO}_2$  in the original sample [5.41], the formation of zinc ferrite, zinc silicate or magnetite cannot be ruled out.

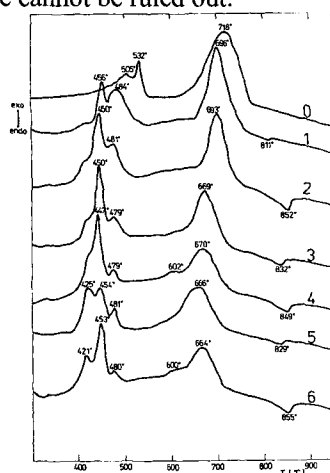


Fig. 5.13 DTA curves of ZnS. Time of mechanical activation: 0 - 0 min, 1 - 5 min, 2 - 10 min, 3 - 20 min, 4 - 30 min, 5 - 45 min, 6 - 60 min [5.42].

The limiting temperatures  $T_{DTA}$  of the individual exotherms in the course of the oxidation of sphalerite are plotted as a function of activation time in Fig. 5.14. In comparison with a non-activated sample, the values of  $T_{DTA}$  decrease with increasing time of mechanical activation. This decrease is most significant for the exotherm at the lowest temperature (421-456°C).

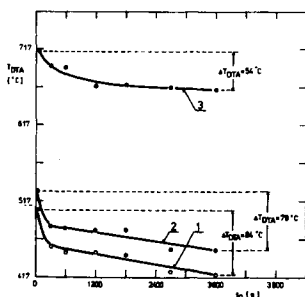


Fig. 5.14 Variation of limiting temperatures,  $T_{DTA}$  of individual exotherms of sphalerite with time of mechanical activation,  $t_G$ : 1 - exotherm I (421-456°C), 2 - exotherm II (453-484°C), 3 - exotherm III (664-694°C) [5.42].

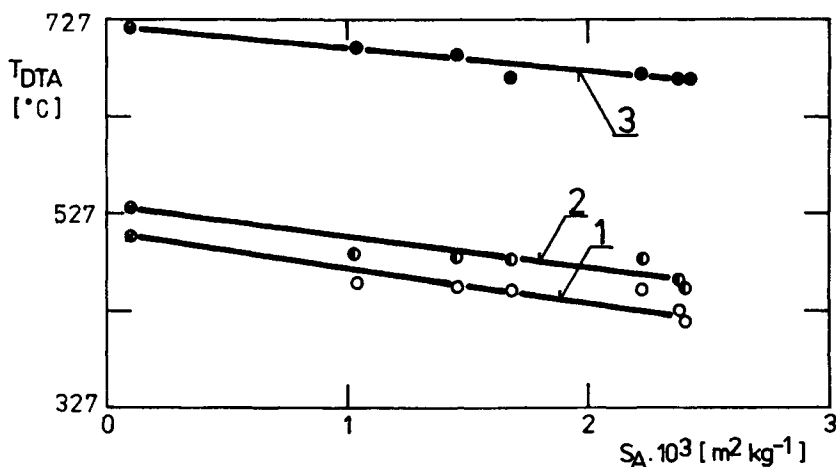


Fig. 5.15 Dependence of limiting temperatures,  $T_{DTA}$  of individual exotherms of sphalerite on specific surface,  $S_A$ : 1 - exotherm I (421-456°C), 2 - exotherm II (453-484°C), 3 - exotherm III (664-696°C) [5.42].

The difference between the values of the limiting temperatures,  $\Delta T_{DTA}$ , expressed by the relation

$$\Delta T_{DTA} = T_{DTA}^* - T_{DTA}^0 \quad (5.5)$$

where  $*$  denotes the mechanically activated sample and  $^0$  the non-activated sample, is equal to 84°C for the first exotherm. For the subsequent exotherms occurring at higher temperatures, the values of  $\Delta T_{DTA}$  are lower (79°C and 54°C, for II and III respectively).

The proportion of different oxidation products formed, including oxides, sulfates, oxysulfates and others, varies with temperature. These products change significantly the quality of the surface and a high-temperature sintering of the sphalerite may also occur.

Because of structural changes, the probability of annealing the defects formed by mechanical activation increases with the temperature.

The values of  $T_{DTA}$  for both quantities (surface area and structural ordering) are plotted in Figs. 5.15 and 5.16. The decrease in  $T_{DTA}$  values with increasing surface area and decreasing degree of structure ordering were observed for all three exotherms. Clearly, the exothermic decomposition of sphalerite in an oxidising environment is sensitive to both these quantities.

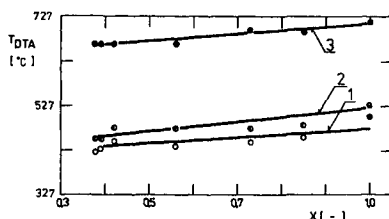


Fig. 5.16 Dependence of limiting temperatures,  $T_{DTA}$  of individual exotherms of sphalerite on content of crystalline phase, X: 1 - exotherm I (421-456°C), 2 - exotherm II (453-484°C), 3 - exotherm III (664-696°C) [5.42].

If we want to determine which of the quantities, specific surface  $S_A$  or content of crystalline phase X, is more important in enhancing the reactivity, we must divide the reaction rate by the specific surface area of the samples [5.43-5.44].

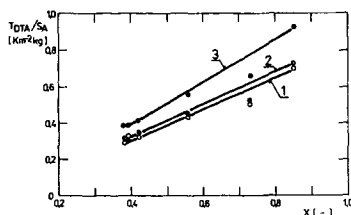


Fig. 5.17 Dependence of  $T_{DTA}/S_A$  on content of crystalline phase, X for individual exotherms of sphalerite: 1 - exotherm I (421-456°C), 2 - exotherm II (453-486°C), 3 - exotherm III (664-696°C) [5.42].

Figure 5.17 shows the variation of  $T_{DTA}/S_A$  with the content of crystalline phase X of mechanically activated sphalerite plotted for the three exotherms. The relationship between  $T_{DTA}/S_A$  and X is clearly linear and can be expressed by the following equation

$$\frac{T_{DTA}}{S_A} = a + bX \quad (5.6)$$

for which the values of the parameters a and b, as well as the corresponding correlation coefficients of linear regression r, are given in Table 5.2. The relations presented show the sensitivity of the thermal oxidation decomposition of sphalerite to structural disordering produced by mechanical activation. The increase in parameter b for exotherms I-III indicates the influence of the annealing of the structural disorder of sphalerite at increasing temperatures.

Table 5.2 Values of parameters a and b and correlation coefficients r of linear regression  $T_{DTA}/S_A = a + bX$  for exotherms I, II and III

| Exotherm        | Parameters |      | Correlation coefficient |
|-----------------|------------|------|-------------------------|
|                 | a          | b    | r                       |
| I (421-456°C)   | -0.02      | 0.79 | 0.974                   |
| II (453-484°C)  | -0.01      | 0.82 | 0.975                   |
| III (664-696°C) | -0.02      | 1.05 | 0.975                   |

## 5.2. Decomposition in an inert atmosphere (pyrolysis)

### *Chalcopyrite CuFeS<sub>2</sub>*

The thermal decomposition of CuFeS<sub>2</sub> in an inert atmosphere proceeds in accord with literature [5.45-5.46] through bornite as an intermediate



While only bornite was positively identified among the newly arisen phases at 500°C in agreement with equations (5.7) and (5.8), it appeared that besides a greater content of bornite the presence of troilite FeS (JCPDS 11-151) and djurleite Cu<sub>1.93</sub>S (JCPDS 23-959) was recorded for the temperature of 700°C. The presence of talnakhite Cu<sub>17.6</sub>Fe<sub>17.6</sub>S<sub>32</sub> (JCPDS 11-515) was also indentified on diffraction patterns.

The series of CuFeS<sub>2</sub> samples were prepared by grinding in different media (air, methanol) in order to alter the physico-chemical properties of the samples and their reactivity in the thermal decomposition [5.47].

The changes in specific surface area S<sub>A</sub> and S<sub>G</sub> (Figs. 5.18A and 5.18B) which result from dry grinding are more substantial than those which result from grinding in methanol. After 20 min of dry grinding the specific surface area, S<sub>A</sub>, increased from an initial value of 0.35 m<sup>2</sup>g<sup>-1</sup> to a maximum value of 4.0 m<sup>2</sup>g<sup>-1</sup>. At this value, a constant value of S<sub>A</sub> and a decrease in S<sub>G</sub> values indicate that intensive particle agglomeration has occurred. In the methanol grinding process the critical value of S<sub>A</sub> is not reached in the observed time interval; apparently no significant agglomeration of particles takes place.

The degree of structural disorder F (Fig. 5.18C), which gives integral information on the changes in lattice strain and in crystallite size, increases 3.7 times with the grinding time in air, but in methanol there was a 20 % decrease.

The values of magnetic susceptibility are influenced by the grinding environment in the same way: the measured values of the specific magnetic susceptibility, χ when grinding in methanol do not change significantly (Fig. 5.18D), whereas during dry grinding a 12-fold increase in χ occurs.

Low-temperature α-chalcopyrite has antiferromagnetic properties, i.e. it has a magnetically ordered structure. From the literature data [5.48] it is known that magnetic susceptibility of antiferromagnetic and ferromagnetic substances is independent of particle size.

The experimentally determined specific surface area dependence of the samples studied (Fig. 5.19) suggests that during grinding in methanol the antiferromagnetic properties of chalcopyrite are unchanged. However, an increase in the specific magnetic susceptibility of dry-ground samples within a narrow range of  $S_A$  is mainly due to the magnetic order-disorder transformation of chalcopyrite which has been described in earlier papers [5.49-5.50]. The increase may also be partly due to enrichment of the surface layer by paramagnetic iron oxide, but conclusive evidence is lacking.

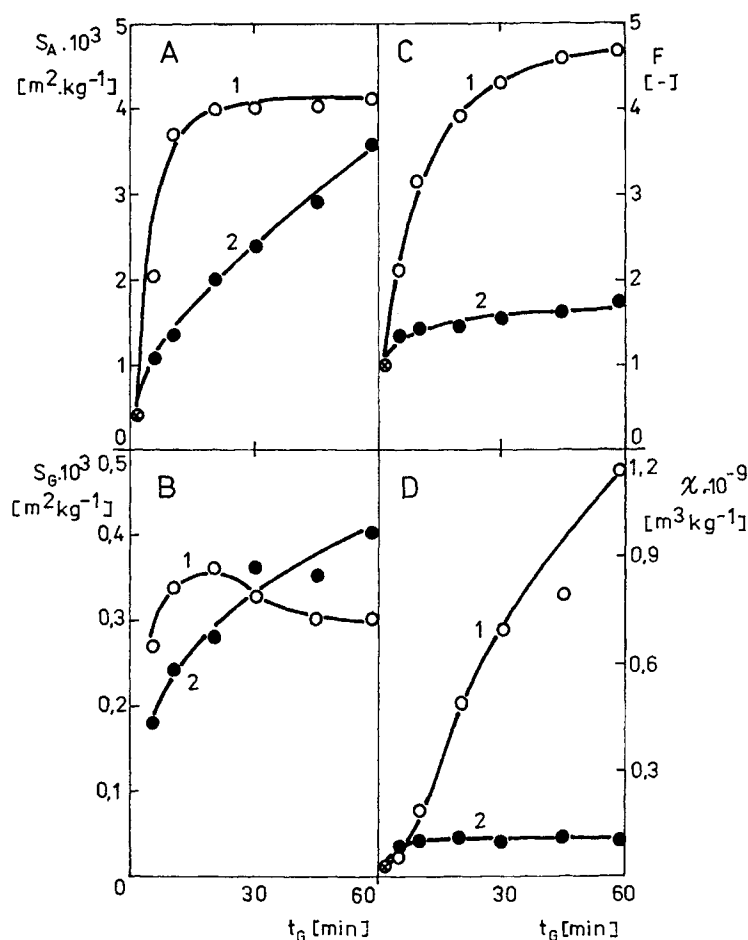


Fig. 5.18 Influence of grinding time,  $t_G$  of  $\text{CuFeS}_2$  and grinding environment on the specific surface area determined by the BET method,  $S_A$  (A), calculated from the dispersion analysis data,  $S_G$  (B), on the structural disorder,  $F$  (C) and on the specific magnetic susceptibility,  $\chi$  (D). 1 - dry grinding, 2 - grinding in methanol [5.47].

Figure 5.20 shows the changes in the rate constant of the non-oxidative thermal decomposition reaction of chalcopyrite with the changes in  $S_A$  and  $F$  during grinding.

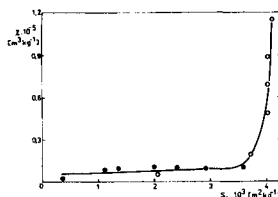


Fig. 5.19 Specific magnetic susceptibility,  $\chi$  vs. specific surface area,  $S_A$  of  $\text{CuFeS}_2$  ground in methanol (●) and in air (○); [5.47].

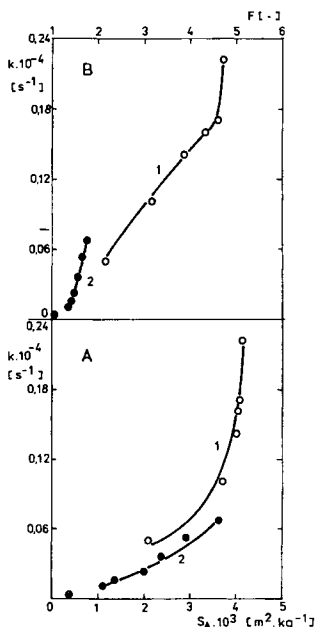


Fig. 5.20 Rate constant,  $k$  vs. specific surface area,  $S_A$  (A) and structural disorder,  $F$  (B) for chalcopyrite samples ground in air (○) and in methanol (●), ⊗ as-received sample [5.47].

It is evident that the rate of thermal decomposition reaction changes with both of these variables. The determining influence of  $S_A$  and  $F$  may be expressed by an empirical „surface-structural“ coefficient in the form of the product  $S_AF$  by means of the following relationship (see Fig. 5.21)

$$k = a + bS_AF \quad (5.9)$$

For the samples investigated  $a = 2.57 \times 10^{-3}$  and  $b = 9.04 \times 10^{-3}$ , and the correlation coefficient value  $r = 0.9955$ .

Thermal decomposition of chalcopyrite is a heterogeneous reaction, the rate of which increases with the surface area of the sample. The mechanochemical effect due to structural and/or compositional changes should therefore be considered as an excess reactivity adding to the effect of the increase in specific surface area [5.43-5.44]. The excess specific reactivity for such cases may be expressed as the ratio of the rate constant to the specific area of the activated powder,  $k/S_A$ .

In dry-ground powders, a linear increase in the excess reactivity with increasing specific magnetic susceptibility was found (see Fig. 5.22). The values of  $k/S_A$  determined for powder ground in methanol oscillate, however, around that measured for the as-received sample.

The results obtained are in good agreement with the literature data [5.49-5.50]. Plastic strain leading to crystallographic shear in the sulfur sublattice and to a change in cation distribution between octa- and tetra- positions may, therefore be considered as the source of the excess changes both in magnetic properties and in reactivity of mechanically activated chalcopyrite.

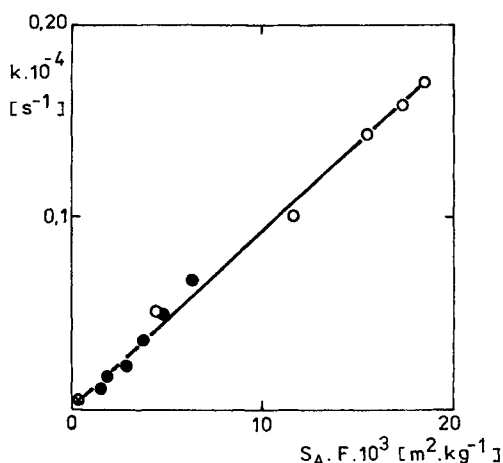


Fig. 5.21 Rate constant,  $k$  vs. „surface-structural“ coefficient,  $S_A F$  for  $\text{CuFeS}_2$  ground in air (○) and in methanol (●), ⊗, as-received sample [5.47].

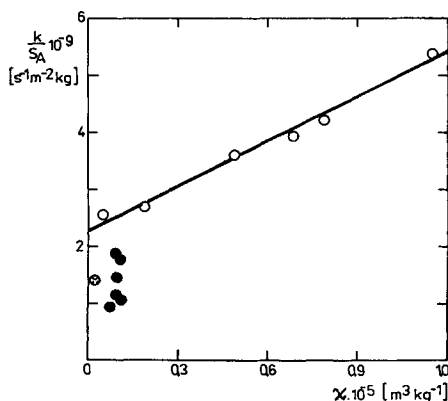


Fig. 5.22 Excess reactivity,  $k/S_A$  vs. magnetic susceptibility,  $\chi$  for  $\text{CuFeS}_2$ : ⊗, as-received sample; ○, dry-ground samples; ●, methanol-ground samples [5.47].

### **Bornite $\text{Cu}_5\text{FeS}_4$**

The thermal decomposition of bornite was performed in argon atmosphere and studied in the temperature region 406-664°C. The values of the degree of conversion of  $\text{Cu}_5\text{FeS}_4$  obtained at 664°C are given as a function of reaction time in Fig. 5.23 for non-activated sample as well as for samples activated 10-30 min. It results from this relationship that the decomposition of non-activated sample is the slowest and the differences in decomposition

rates of activated samples are small. This may be explained by the decrease in the reaction surface area of  $\text{Cu}_5\text{FeS}_4$  with the time of mechanical activation.

Arrhenius plots for the thermal decomposition of  $\text{Cu}_5\text{FeS}_4$  are presented in Fig. 5.24 and the corresponding values of apparent activation energy are listed in Tab. 5.3. In the low temperature region (406-492°C) the decomposition is sensitive to the temperature change and the values of activation energy indicate that the rate determining step of the whole process is chemical reaction [5.51]. The apparent activation energies of this decomposition measured in the region of higher temperatures (492-664°C) imply that the rate determining step is probably diffusion. The break of the Arrhenius plot in Fig. 5.24 indicates a change in decomposition mechanism involving a transition from chemical reaction to diffusion. The mechanical activation makes this change appear at lower temperatures when compared with non-activated sample.

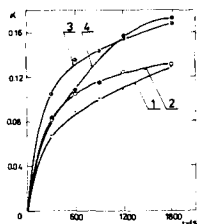


Fig. 5.23 Conversion degree,  $\alpha$  of  $\text{Cu}_5\text{FeS}_4$  vs. reaction time,  $t_T$ . Temperature 664°C, time of mechanical activation: 1 - 0 min, 2 - 10 min, 3 - 20 min, 4 - 30 min.

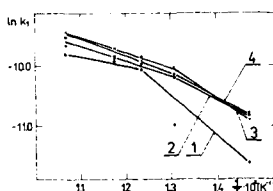


Fig. 5.24 Arrhenius plot for thermal decomposition of  $\text{Cu}_5\text{FeS}_4$ . Temperature 406-664°C, time of mechanical activation: 1 - 0 min, 2 - 10 min, 3 - 20 min, 4 - 30 min.

Table 5.3 Apparent activation energy,  $E$  of thermal decomposition of  $\text{Cu}_5\text{FeS}_4$

| Mechanical activation<br>(min) | Temperature<br>(°C) | $E$<br>( $\text{kJmol}^{-1}$ ) |
|--------------------------------|---------------------|--------------------------------|
| 0                              | 406-492             | 57                             |
|                                | 492-664             | 23                             |
| 10                             | 406-492             | 32                             |
|                                | 492-664             | 17                             |
| 20                             | 406-492             | 46                             |
|                                | 492-664             | 20                             |
| 30                             | 406-492             | 34                             |
|                                | 492-664             | 20                             |

### Arsenopyrite $\text{FeAsS}$

Arsenopyrite is a mineral which does not have any great practical importance when it occurs in the pure form. Provided it occurs as an admixture in the concentrates of non-ferrous metals,

the presence of arsenic brings up problems in the course of extraction of these metals as well as environmental problems associated with disposal. The importance of this mineral increases if it occurs in association with gold, which is becoming increasingly important. The extraction of gold usually proceeds in the sequence: flotation → oxidative roasting → cyanidation. The most problematic step is oxidative roasting because the volatile arsenic oxides are toxic and improper conditions cause entrainment of gold with flue dust.

Mechanical activation makes it possible

- to increase the retention of arsenic in the solid phase and thus to limit its transition into volatile toxic form,
- to reduce the temperature of oxidative decomposition, leading to lesser entrainment of gold in the flue dust and a greater metal content in the product for cyanidation [5.14, 5.27, 5.52].

Mechanical activation reduces the unfavourable effects of roasting but does not eliminate it from the technological scheme. An alternative solution consists in the application of non-traditional methods of arsenic extraction. From the view-point of thermal analysis the method of roasting in inert medium is interesting [5.53-5.54].

The thermal decomposition of arsenopyrite in inert medium obeys the following equation



In agreement with this equation, we confirmed the formation of pyrrhotite by X-ray phase analysis and identified a black ring on the walls of the quartz reactor outside the reaction zone as elemental arsenic [5.55].

A detailed microscopic investigation of the phase transformations occurring in the course of arsenopyrite decomposition in inert atmosphere was performed by Čejchan [5.56]. According to this author, the arising pyrrhotite advances from the surface into the bulk of arsenopyrite and fills the cracks in its grains. Following this, a transformation of individual particles of the mineral into spongy aggregates of pyrrhotite can be observed. We assume that the properties of the solid-phase product limit the progress of reaction (5.10) and determine its mechanism in the region controlled by diffusion. The remainders of arsenopyrite disappear at 700°C and the pyrrhotite sponge entirely fills the particles.

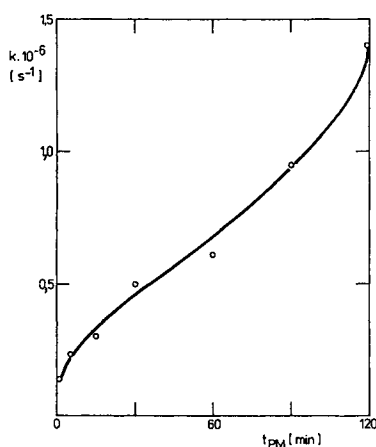


Fig. 5.25 Rate constant,  $k$  of  $FeAsS$  decomposition as a function of the time of mechanical activation,  $t_{PM}$ . Reaction temperature 552°C [5.55].

In Fig. 5.25 the values of the rate constant of decomposition are plotted against the grinding time  $t_{PM}$ . The mechanical activation accelerates the decomposition by almost one order of magnitude. The values of the apparent activation energy  $E$  of the decomposition of FeAsS, as calculated from the Arrhenius equation, for the temperature interval  $T = 366-750^\circ\text{C}$  are represented as a function of grinding time in Fig. 5.26. The values are typical of heterogeneous processes, the rate determining step of which is diffusion across the layer of a solid product [5.51]. Owing to the labilization of the bonds of mechanically activated samples, the value  $E$  decreases with increasing grinding time. At the same time, we observe a decrease in the response of  $E$  to grinding time which may be the consequence of an increased tendency of ground particles to recombine.

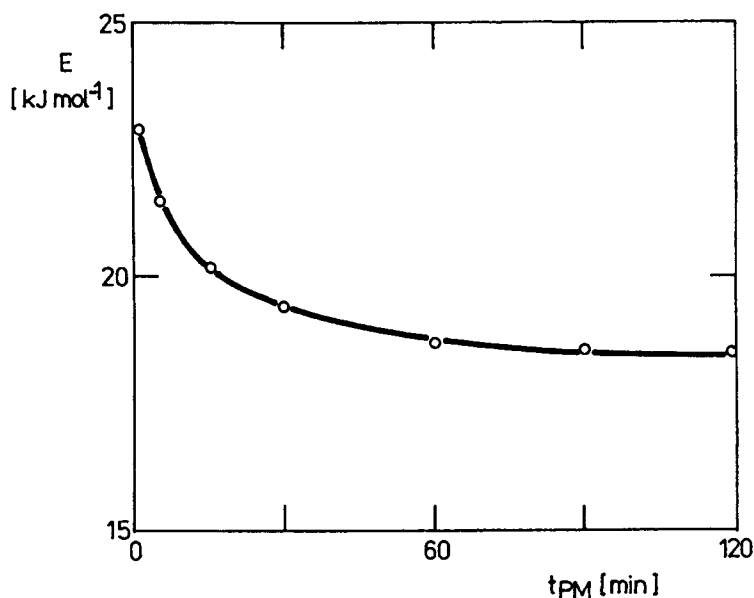


Fig. 5.26 Apparent activation energy,  $E$  of FeAsS decomposition as a function of the time of mechanical activation,  $t_{PM}$ . Reaction temperature  $366-750^\circ\text{C}$  [5.55].

The process of mechanical activation of arsenopyrite is accompanied by changes in its solid state properties. In Fig. 5.27 the values of the specific surface area  $S_A$  as well as of the transmittance  $T$ , obtained by evaluating the infrared spectra, are represented as a function of the time of mechanical activation. While the quantity  $S_A$  is a measure of formation of new surface area, the quantity  $T$  can be used as a measure of structure disorder of the mineral. It has been discussed in the literature that infrared spectroscopy can be used for characterizing the degree of crystallinity of different minerals. For pyrite, the relationship between grinding time and the transmittance of pyrite at  $340\text{ cm}^{-1}$  and  $411\text{ cm}^{-1}$  was presented [5.57]. The course of the change in  $S_A$  and  $T$  in Fig. 5.27 indicates an increase in surface and structure disorder of arsenopyrite due to mechanical activation.

The relationship between surface-structure changes and reactivity of mechanically activated samples of arsenopyrite is represented in Fig. 5.28. This relationship is linear in the

investigated region and can be described, with a high degree of correlation ( $r = 0.996$ ), by the following empirical equation

$$k = \left( 0.111 + 0.103 \frac{S_A}{T} \right) \cdot 10^6 \quad (5.11)$$

In connection with our preceding studies in which we found structure sensitivity of the reactions of chalcopyrite and sphalerite of the solid-liquid [5.58] or solid-gas [5.41] type we can also document on the basis of equation (5.11) the structure sensitivity of reaction (5.10) which is a case of heterogeneous reactions of the type  $\text{solid}_1 \rightarrow \text{solid}_2 + \text{gas}$ .

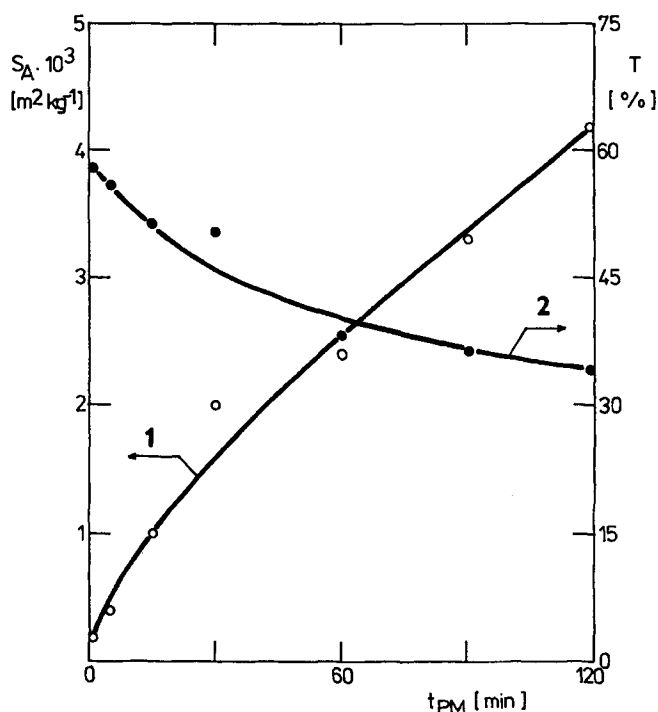


Fig. 5.27 Variation of specific surface,  $S_A$  (curve 1) and transmittance,  $T$  (curve 2) of FeAsS with the time of mechanical activation,  $t_{PM}$  [5.55].

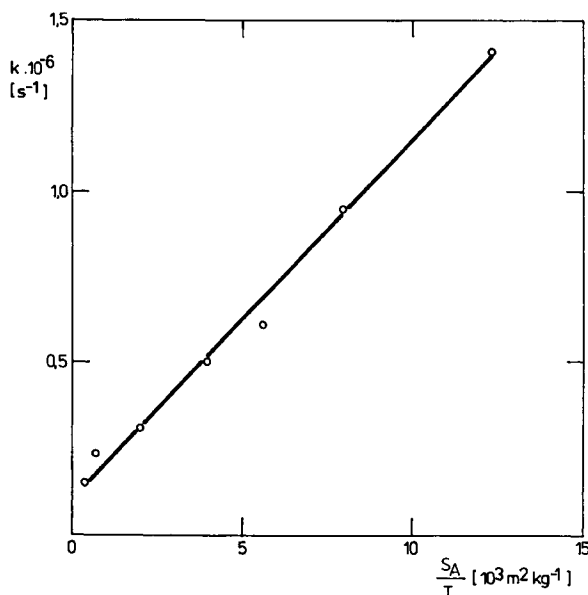


Fig. 5.28 Variation of the rate constant of FeAsS decomposition,  $k$  as a function of  $S_A/T$  [5.55].

### Pyrite $\text{FeS}_2$

Decomposition of pyrite  $\text{FeS}_2$  in an inert medium to give elemental sulfur can be expressed by the following scheme



Reaction (5.12) was frequently studied [5.59] and is used for the so-called high-temperature pyrotrinitization of pyrite [5.60]. It is assumed that species  $\text{Fe}_7\text{S}_8$  is an intermediate that participates in formation of the solid  $\text{FeS}$  [5.61].

Reaction (5.12) is an heterogeneous reaction of the type  $\text{solid}_1 \rightarrow \text{solid}_2 + \text{gas}$ . It is a characteristic of these reactions that they involve decay and rearrangement of the structural domains of the crystal [5.62]. The temperature applied in this process plays an important role because it initiates the breakage of bonds in the crystal and the transition of atoms and molecules into the gaseous state.

The extent of transformation of  $\text{FeS}_2$  by heating in argon are plotted against the reaction time for temperatures of 475°C and 561°C in Figs. 5.29 and 5.30 respectively. The samples were mechanically activated for 5, 10, 15, 20 and 30 min. The plots exhibit a parabolic character and the maximum decomposition rate appears in the initial reaction stage. The experimental results were processed and the plots of the calculated rate constants,  $k_1$ , in Arrhenius coordinates are represented for the temperatures of 475-561°C in Fig. 5.31. The calculated values of apparent activation energy,  $E$ , and pre-exponential factor,  $A$ , obtained for individual mechanically activated samples are listed in Table 5.4. The relationship between logarithm of  $A$  and the value of  $E$  exhibits a compensation effect (Fig. 5.32).

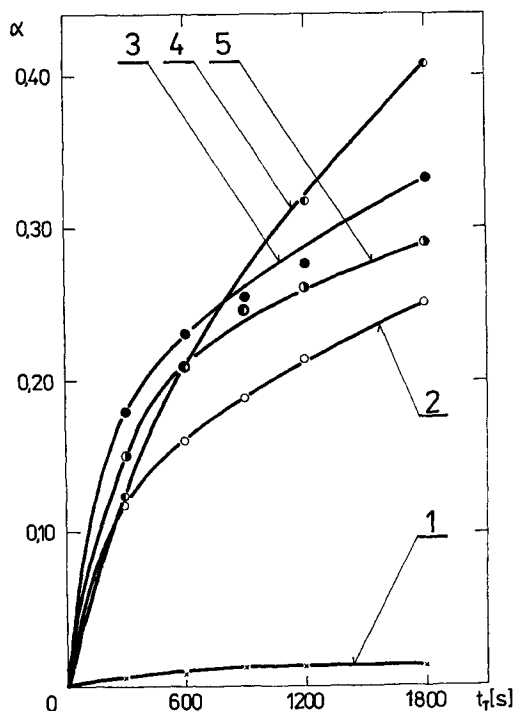


Fig. 5.29 Variation of the degree of  $\text{FeS}_2$  conversion,  $\alpha$  with reaction time,  $t_T$ . Temperature  $475^\circ\text{C}$ , time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 15 min, 4 - 20 min, 5 - 30 min [5.63].

The products of thermal decomposition of pyrite were investigated by X-ray diffraction and electron microscopy. We identified the presence of pyrrhotite (4C)  $\text{Fe}_{1-x}\text{S}$  (JCPDS 22-1120) and pyrrhotite  $\text{Fe}_9\text{S}_8$  (JCPDS 15-37) in the sample mechanically activated for 30 min and treated at the temperatures of  $501^\circ\text{C}$  and  $561^\circ\text{C}$  for 30 min. Photomicrographs of the non-activated sample and the sample subjected to 30 min mechanical activation are presented in Fig. 5.33. After mechanical activation the surface of  $\text{FeS}_2$  is more disordered (compare Fig. 5.33A and 5.33C) and the thermal treatment brings about disintegration. A higher portion of fine particles is characteristic for a mechanically activated sample.

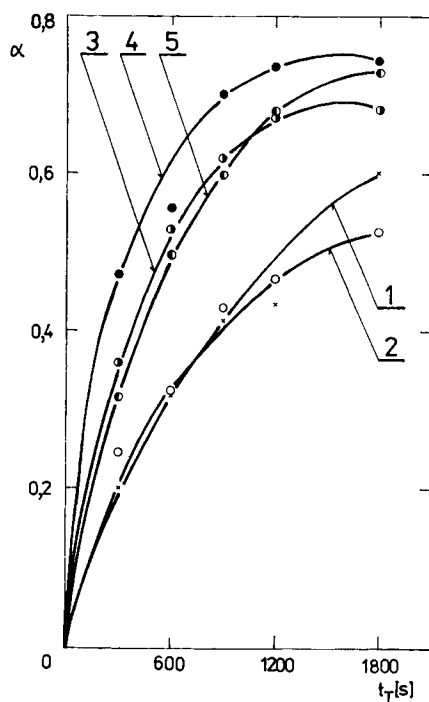


Fig. 5.30 Variation of the degree of  $\text{FeS}_2$  conversion,  $\alpha$  with reaction time,  $t_T$ . Temperature  $561^\circ\text{C}$ , time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 15 min, 4 - 20 min, 5 - 30 min [5.63].

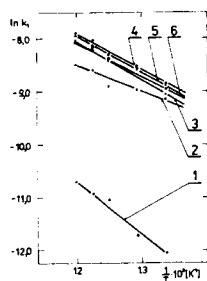


Fig. 5.31 Arrhenius plot for thermal decomposition of  $\text{FeS}_2$ , temperature =  $475\text{--}561^\circ\text{C}$ . Time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 15 min, 4 - 20 min, 5 - 30 min [5.63].

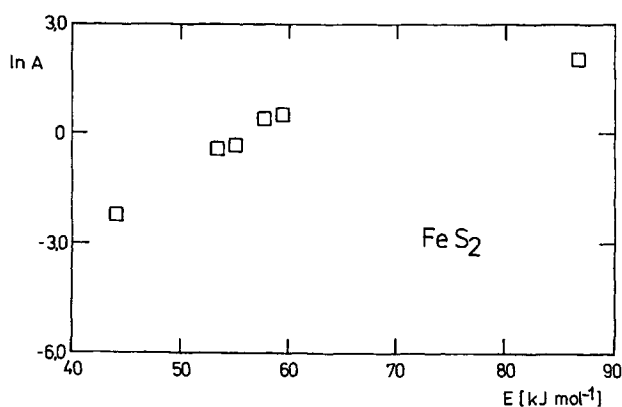


Fig. 5.32 The compensation effect in the reaction  $\text{FeS}_2 \rightarrow \text{FeS} + \text{S}$  [5.63].

Table 5.4 Values of specific surface,  $S_G$ , microstrains,  $\epsilon$ , and Arrhenius parameters (apparent activation energy,  $E$ , and pre-exponential factor,  $A$ ) of reaction (5.12)

| Time of mechanical<br>activation<br>(min) | $S_G \times 10^{-3}$<br>( $\text{m}^2 \text{kg}^{-1}$ ) | $\epsilon$<br>(‰) | $E$<br>( $\text{kJmol}^{-1}$ ) | $A$<br>( $\text{s}^{-1}$ ) |
|-------------------------------------------|---------------------------------------------------------|-------------------|--------------------------------|----------------------------|
| 0                                         | 0.02                                                    | 1.1               | 87                             | 6.512                      |
| 5                                         | 0.26                                                    | 2.8               | 44                             | 0.113                      |
| 10                                        | 0.30                                                    | 3.2               | 59                             | 1.649                      |
| 15                                        | 0.31                                                    | 4.1               | 58                             | 1.507                      |
| 20                                        | 0.27                                                    | 4.3               | 55                             | 0.977                      |
| 30                                        | 0.28                                                    | 4.4               | 53                             | 0.710                      |

Reaction (5.12) is a topochemical reaction in which the decomposition proceeds so that the interface preserves the position parallel to the crystal plane from which it arises [5.62]. The contour lines of the original crystal can be observed at an appropriate magnification by investigating the decomposition of  $\text{FeS}_2$  as well (Fig. 5.33B).

If we compare Fig. 5.29 with Fig. 5.30 we can see that the degree of conversion of reaction (5.12) increases with increasing mechanical disordering of pyrite. It is known that the rate of reaction in the solid phase in the initial stage is determined by the number of contacts between the reacting particles and the magnitude of their area [5.64]. It was Senna [5.43] who drew attention to the problem of adequate evaluation of the surface of mechanically activated particles, as the ultrafine particles formed by mechanical activation of sulphides in air may recombine, giving rise to the so-called agglomerates [5.15]. For appraising the surface area of the particles prone to agglomerate formation it is convenient to use the granulometric surface  $S_G$  which sensitively indicates the effect of grain recombination.

If we refer the rate constant to the initial surface area of the reacting particles, we can judge the structure sensitivity of a given reaction. The specific rate constant of thermal decomposition of pyrite  $k_1/S_G$  as a function of its structural disorder as characterized by

microstrains  $\varepsilon$  is plotted in Fig 5.34. It results from these curves that reaction (5.12) investigated in the interval 475-561°C belongs to the structure-sensitive types. The structure sensitivity is at its maximum in the region  $\varepsilon \leq 3.2\%$ , where the effect of agglomeration does not yet manifest itself and the values of  $S_G$  increase (see Table 5.4). For greater microstrains in the  $\text{FeS}_2$  lattice, the structure sensitivity decreases. Owing to the formation of agglomerates in these samples, the contact surface of particles decreases just in those places where the concentration of different types of disorder is maximum. The application of the thermal processing usually brings about an increase in mechanical strength of the aggregate. The formation of elemental sulfur as gaseous product of reaction (5.12) is thus inhibited and the overall rate of reaction is controlled by sulfur diffusion through the layer of solid  $\text{FeS}$ .

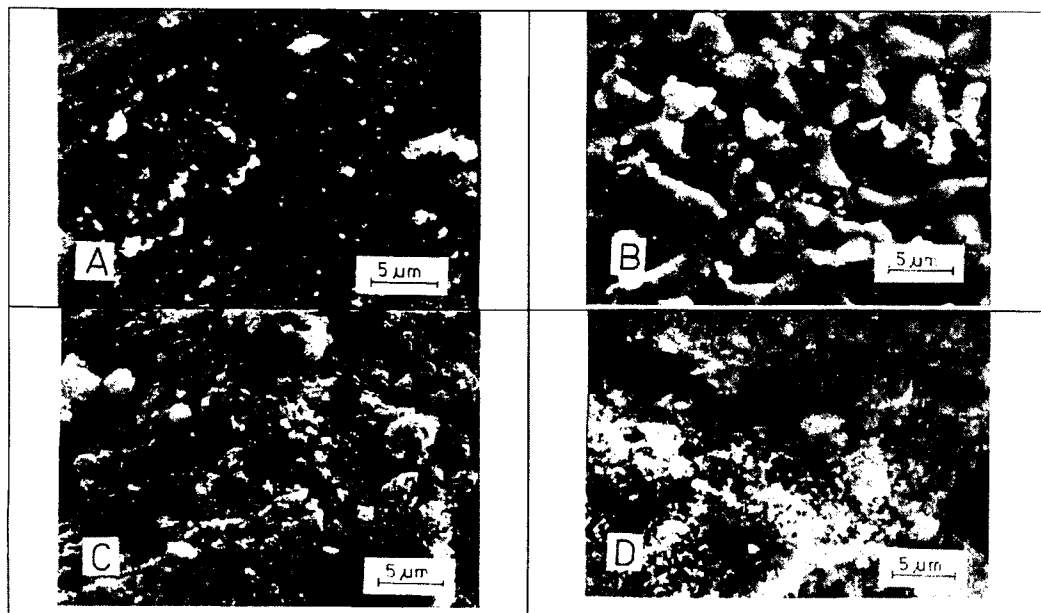


Fig. 5.33 Scanning electron microphotographs of  $\text{FeS}_2$ . A,B - non-activated sample, C,D - mechanical activation for 30 min, A, C - without heating, B, D - after heating at 561°C in argon for 30 min [5.63].

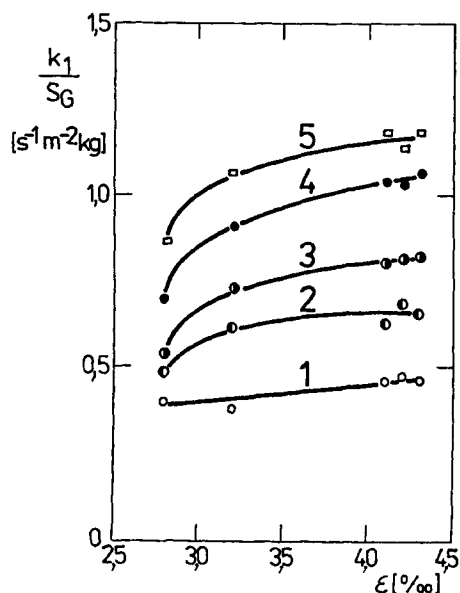
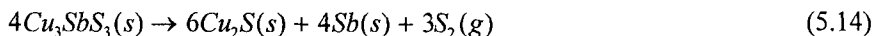
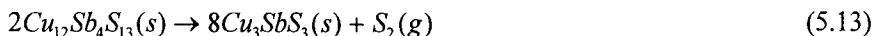


Fig. 5.34 Variation of the ratio,  $k_1/S_G$  with microstrains,  $\varepsilon$  of mechanically activated  $\text{FeS}_2$ . Temperature of decomposition : 1 - 475°C, 2 - 501°C, 3 - 527°C, 4 - 544°C, 5 - 561°C [5.63].

#### ***Tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$***

The thermal decomposition of tetrahedrite has been investigated by Imriš et al. [5.66-5.68] and Ibragimov and Isakova [5.69-5.70]. Because a great number of other elements occur in the mineral, e.g. Hg, Fe, Zn, Ag, Cd, Co, Cr, Mo, Ni, Pb, Sn and Bi, a description of the decomposition is rather complicated. In an inert medium at temperatures 550-880°C, it may be expressed by the simplified equations



The heating of tetrahedrite in an inert medium may also involve the escape of gaseous  $\text{SbS}$  and  $\text{Hg}$  and the disintegration of the mineral in two phases. Chalcopyrite  $\text{CuFeS}_2$  and fematinitite  $\text{Cu}_3\text{SbS}_4$  has been identified in the decomposition at 500°C and a melt of sulfides, as well as fematinitite, has been identified at 630°C.

The thermal decomposition of tetrahedrite was investigated in a dynamic reactor with a static layer of the solid phase (Fig. 5.35).

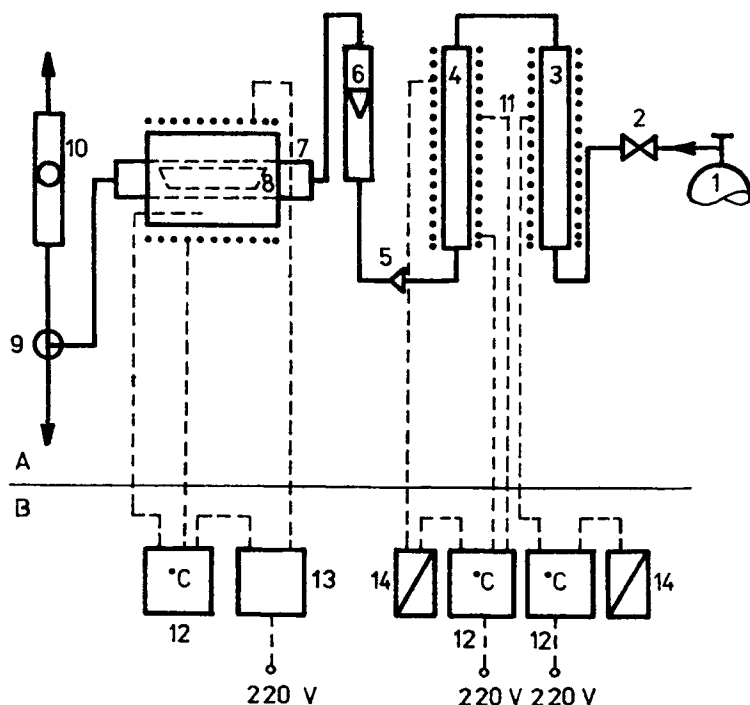


Fig. 5.35 Diagram of the apparatus: 1 - pressure gas vessel with argon, 2 - reducing valve, 3,4 - purifiers, 5 - needle valve, 6 - rotameter, 7 - dynamic reactor, 8 - sample, 9 - distributor, 10 - rotameter, 11 - thermocouples, 12 - temperature controller, 13 - regulating transformer, 14 - contactor [5.71].

The dependence of the tetrahedrite conversion degree  $\alpha$  is represented in Figs. 5.36 and 5.37 for different experiments. We can observe that the conversion degree increases with temperature and the graphs describing this process exhibit a parabolic character. The  $\alpha$  values for mechanically activated samples are greater than for non-activated samples. The plot of  $\alpha$  versus  $t_T$  for all activated samples at 492°C is presented in Fig. 5.38. Provided it is valid that the grinding time  $t_G \leq 10$  min, considerable differences in the values of  $\alpha$  appear between individual samples, beyond this time the differences are small because of the effect of agglomeration.

X-ray phase analysis was performed with a non-activated sample as well as with a sample mechanically activated for 30 min. Bornite  $\text{Cu}_5\text{FeS}_4$  (JCPDS 14-323) and digenite  $\text{Cu}_{1.765}\text{S}$  (JCPDS 23-960) were identified in the decomposition products obtained at 500, 620 and 840°C. Only small differences in the quantitative proportions of these decomposition products were observed for both samples. These results are consistent with the investigations of Ibragimov and Isakova [5.69-5.70].

The temperature dependence of the decomposition of tetrahedrite in the region 492-699°C is represented in the Arrhenius plots for separate mechanically activated samples in Fig. 5.39. These plots do not show any break in slope, which would indicate a change in reaction mechanism. The corresponding apparent activation energies are listed in Table 5.5. Their low

values and small sensitivity to mechanical disordering of the mineral structure indicate that diffusion is the rate-determining step in the decomposition of tetrahedrite in the region 492-699°C in argon atmosphere.

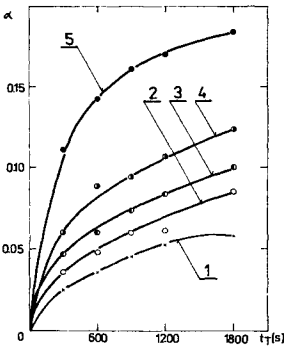


Fig. 5.36 The influence of the reaction time,  $t_T$  on the conversion degree,  $\alpha$  of non-activated  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  for different temperatures: 1 - 492°C, 2 - 535°C, 3 - 595°C, 4 - 647°C, 5 - 699°C [5.71].

Table 5.5 The apparent activation energy,  $E$  of mechanically activated samples of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  [5.71]

| Grinding time<br>$t_G$ (min) | Temperature<br>$T$ (°C) | $E$<br>(kJmol <sup>-1</sup> ) |
|------------------------------|-------------------------|-------------------------------|
| 0                            | 492-699                 | 30                            |
| 5                            | 492-699                 | 26                            |
| 10                           | 492-699                 | 19                            |
| 15                           | 492-699                 | 22                            |
| 20                           | 492-699                 | 18                            |

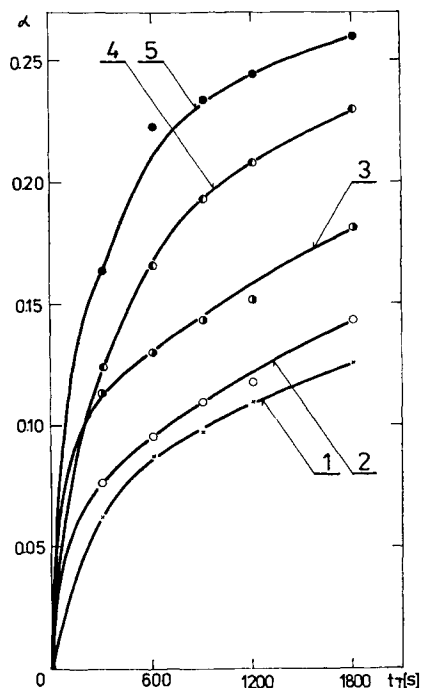


Fig. 5.37 The influence of the reaction time,  $t_T$  on the conversion degree,  $\alpha$  of non-activated  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  for different temperatures: 1 - 492°C, 2 - 535°C, 3 - 595°C, 4 - 647°C, 5 - 699°C [5.71].

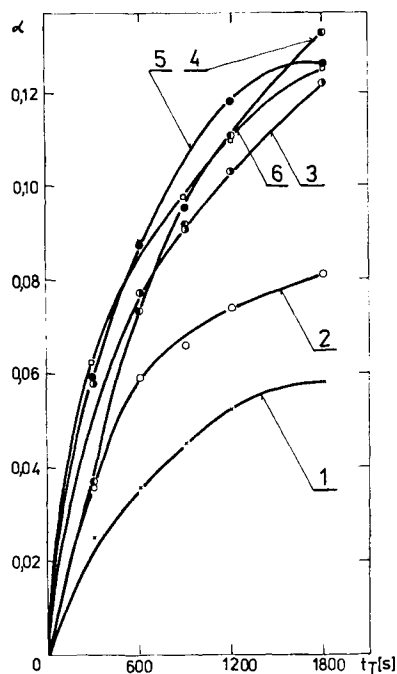


Fig. 5.38 The influence of the reaction time,  $t_T$  on the degree of conversion,  $\alpha$  of  $\text{Cu}_{14}\text{Sb}_4\text{S}_{13}$ . Time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, 4 - 15 min, 5 - 20 min, 6 - 30 min [5.71].

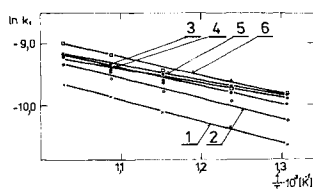


Fig. 5.39 The influence of the grinding time,  $t_G$  of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  on the Arrhenius plot,  $T = 492\text{--}699^\circ\text{C}$ . Time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, 4 - 15 min, 5 - 20 min, 6 - 30 min [5.71].

### 5.3. Reductive decomposition

The need to promote new and innovative energy technologies in extraction metallurgy stimulates the search for the methods of direct reduction of sulfides of non-ferrous metals for obtaining pure metals. The use of different reducing agents, e.g. hydrogen, carbon monoxide, methane and carbon has been investigated [5.72-5.76]. The application of hydrogen to reduction of simple sulfides gives rise not only to elemental metal but also to hydrogen sulfide the decomposition of which yields sulfur and hydrogen which may be recycled into the primary process.

#### *Cinnabar HgS*

At temperature exceeding  $340^\circ\text{C}$  the reaction between cinnabar and hydrogen [5.77] takes place according to the following equation

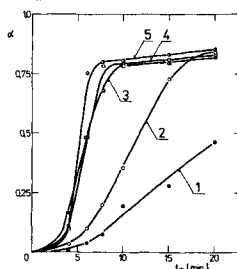


Fig. 5.40 The influence of the reaction time,  $t_T$  on the conversion degree,  $\alpha$  of non-activated  $\text{HgS}$ . Reaction temperatures: 1 -  $363^\circ\text{C}$ , 2 -  $406^\circ\text{C}$ , 3 -  $470^\circ\text{C}$ , 4 -  $449^\circ\text{C}$ , 5 -  $562^\circ\text{C}$ .

The reductive decomposition of  $\text{HgS}$  was studied in the temperature range  $363\text{--}562^\circ\text{C}$  for a non-activated sample as well as for a sample mechanically activated for 15 min. The dependence of the degree of conversion  $\alpha$  on the time of thermal decomposition  $t_T$  for different experiments is given in Figs 5.40 and 5.41. While we can observe that the rate of decomposition increases in the whole interval of the values of  $t_T$ , although a gradual retardation of the decomposition is apparent at higher temperatures and the decomposition is limited by the degree of conversion  $\alpha = 0.8\text{--}0.9$ . If we compare the above figures with each other, we can see that the mechanical activation probably does not change the mechanism of

decomposition and accelerates the decomposition rate only slightly. The influence of mechanical activation decreases with increasing temperature.

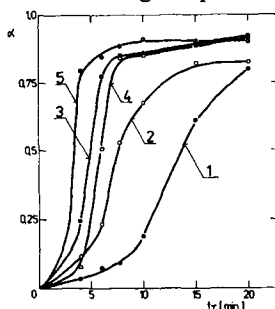


Fig. 5.41 The influence of the reaction time,  $t_T$  on the conversion degree,  $\alpha$  of mechanically activated HgS for 15 min. Reaction temperatures: 1 - 363°C, 2 - 406°C, 3 - 470°C, 4 - 449°C, 5 - 562°C.

The Arrhenius plots in Fig. 5.42 give evidence of a change in reaction mechanism at  $T = 471^\circ\text{C}$  ( $1/T = 1.345 \times 10^{-3} \text{ K}$ ) which is manifested by the change slope for the non-activated samples and mechanically activated for 5 and 15 minutes. The change in mechanism can be related with the process of dissociative sublimation which begins just at this temperature [5.78]. At temperatures above  $471^\circ\text{C}$  the process involving simultaneous dissociative sublimation and reductive decomposition of cinnabar proceeds. The elemental sulfur formed in the first process immediately reacts with the flowing hydrogen to give hydrogen sulfide owing to which the reaction surface is set free and the overall process is accelerated. For the activated samples the values of apparent activation energy in the temperature region  $471\text{--}492^\circ\text{C}$  are equal to  $155\text{--}162 \text{ kJmol}^{-1}$  which points out that the chemical reaction is the rate determining step of the whole process.

### ***Stibnite $\text{Sb}_2\text{S}_3$***

The reaction of  $\text{Sb}_2\text{S}_3$  with hydrogen obeys the following equation



According to the temperature used [5.77] stibnite can turn into volatile and partially decomposed forms



The investigation of the decomposition products of  $\text{Sb}_2\text{S}_3$  in paper [5.79] has shown that gaseous  $\text{SbS}$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{Sb}_2\text{S}_2$ ,  $\text{S}_2$ ,  $\text{Sb}_3\text{S}_2$ ,  $\text{Sb}_3\text{S}_3$ ,  $\text{Sb}_3\text{S}_4$ ,  $\text{Sb}_4\text{S}_4$  and  $\text{Sb}_4\text{S}_5$  occur among the products of reactions (5.17) and (5.18).

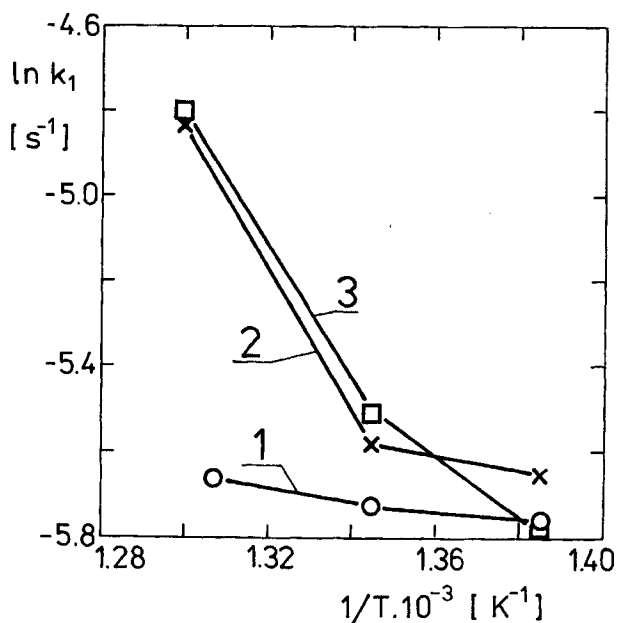


Fig. 5.42 The influence of mechanical activation of HgS on Arrhenius plot,  $T = 449-492^{\circ}\text{C}$ . Time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 15 min.

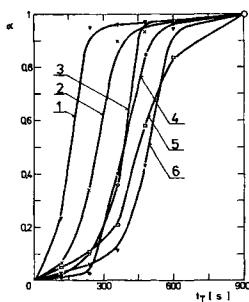


Fig. 5.43 The influence of the reaction time  $t_T$  on the conversion degree,  $\alpha$  of non-activated  $\text{Sb}_2\text{S}_3$ . Reaction temperatures: 1 -  $681^{\circ}\text{C}$ , 2 -  $656^{\circ}\text{C}$ , 3 -  $630^{\circ}\text{C}$ , 4 -  $604^{\circ}\text{C}$ , 5 -  $578^{\circ}\text{C}$ , 6 -  $552^{\circ}\text{C}$ .

A study of the decomposition of  $\text{Sb}_2\text{S}_3$  in a hydrogen atmosphere are illustrated by the kinetic relationships represented in Figs 5.43 and 5.44. These figures show that the conversion reaches the value  $\alpha = 1$  under given experimental conditions and the temporal course is dependent on temperature.

X-ray phase analysis applied to a sample mechanically activated for 15 min and thermally processed at  $578^{\circ}\text{C}$ ,  $604^{\circ}\text{C}$  and  $655^{\circ}\text{C}$  for 5 min indicated the presence of monoclinic sulfur (JCPDS 13-141) and metallic antimony (JCPDS 5-562). The photomicrograph of the same sample processed at  $655^{\circ}\text{C}$  is given in Fig. 5.45B. The microstructure of the mineral comprises a considerable number of micropores while the reaction surface is not blocked.

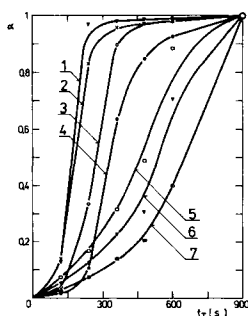


Fig. 5.44 The influence of the reaction time,  $t_T$  on the conversion degree,  $\alpha$  of  $\text{Sb}_2\text{S}_3$  mechanically activated for 15 min. Reaction temperatures: 1 - 681°C, 2 - 656°C, 3 - 630°C, 4 - 604°C, 5 - 578°C, 6 - 552°C, 7 - 527°C.

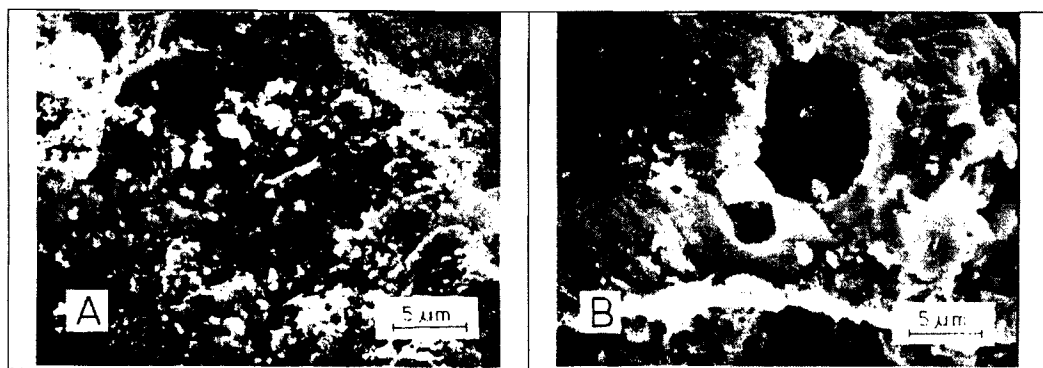


Fig. 5.45 Scanning electron micrographs of  $\text{Sb}_2\text{S}_3$ . Mechanical activation 15 min, A - sample without thermal treatment, B - temperature 655°C.

The character of the Arrhenius plots in Fig. 5.46 indicates that no change in reaction mechanism takes place in the investigated temperature region. Mechanical activation brings about a decrease in apparent activation energy from  $130 \text{ kJmol}^{-1}$  for non-activated sample to  $58 \text{ kJmol}^{-1}$  for a sample activated for 15 min. Both values indicate that the surface chemical reaction of the particles of  $\text{Sb}_2\text{S}_3$  is the rate determining step. The value of  $130 \text{ kJmol}^{-1}$  is in very good agreement with the value of  $121 \text{ kJmol}^{-1}$  found by Chupeng [5.80] for equal reaction of non-activated  $\text{Sb}_2\text{S}_3$  in the temperature region 450-520°C.

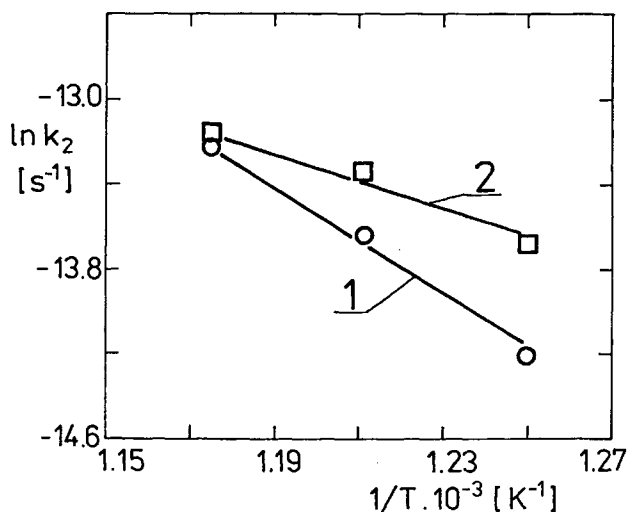


Fig. 5.46 The influence of mechanical activation of  $\text{Sb}_2\text{S}_3$  on Arrhenius plot,  $T = 527\text{-}578^\circ\text{C}$ . Time of mechanical activation: 1 - 0 min, 2 - 15 min.

### Galena $\text{PbS}$

In the eighties several papers dealing with the kinetics of reduction of galena with hydrogen appeared [5.76, 5.81-5.84]. It was found by thermogravimetric investigations that mass loss from galena heated in following hydrogen occurs at temperatures over  $500^\circ\text{C}$  [5.76, 5.84]. At temperatures over  $750^\circ\text{C}$  the reduced lead vaporizes. An isothermal study [5.82] in the region  $675\text{-}825^\circ\text{C}$  showed that the maximum rate of reduction took place at the commencement and was independent of temperature, the reaction rate slowed with increasing reduction time. The stoichiometry of the process in this region can be expressed by the following equations



The degree of conversion of galena due to the reaction with hydrogen was studied for a non-activated sample and a sample mechanically activated for 15 min in Figs. 5.47 and 5.48. The reduction was investigated in the temperature interval  $664\text{-}775^\circ\text{C}$ . Differences between the above mentioned samples occurred only in the temperature range between  $664^\circ\text{C}$  and  $707^\circ\text{C}$ . In agreement with eqn. (5.19), the surface of reacting particles was subjected to fusion at higher temperatures. In all cases, however, we can observe the maximum rate in the initial stage of reaction and the retardation at higher reaction time.

The Arrhenius plots for the reduction of galena by hydrogen are represented in Fig. 5.49. Their character indicates that no change in mechanism due to temperature or structure disordering of mechanically activated sample takes place in the investigated temperature interval  $707\text{-}775^\circ\text{C}$ . The equal calculated values of apparent activation energy for the

reference sample ( $42 \text{ kJmol}^{-1}$ ) and for the sample mechanically activated for 15 min indicate that chemical reaction is the rate determining step of PbS reduction.

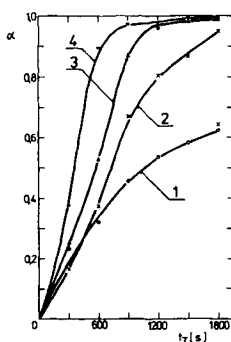


Fig. 5.47 The influence of the reaction time,  $t_T$  on the conversion degree,  $\alpha$  of non-activated PbS. Reaction temperatures: 1 -  $406^\circ\text{C}$ , 2 -  $707^\circ\text{C}$ , 3 -  $750^\circ\text{C}$ , 4 -  $775^\circ\text{C}$ .

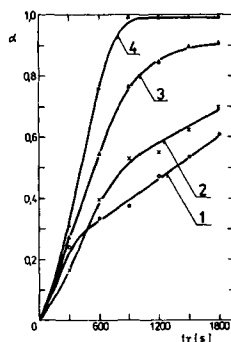


Fig. 5.48 The influence of the reaction time,  $t_T$  on the conversion degree,  $\alpha$  of PbS mechanically activated for 15 min. Reaction temperatures: 1 -  $406^\circ\text{C}$ , 2 -  $707^\circ\text{C}$ , 3 -  $750^\circ\text{C}$ , 4 -  $775^\circ\text{C}$ .

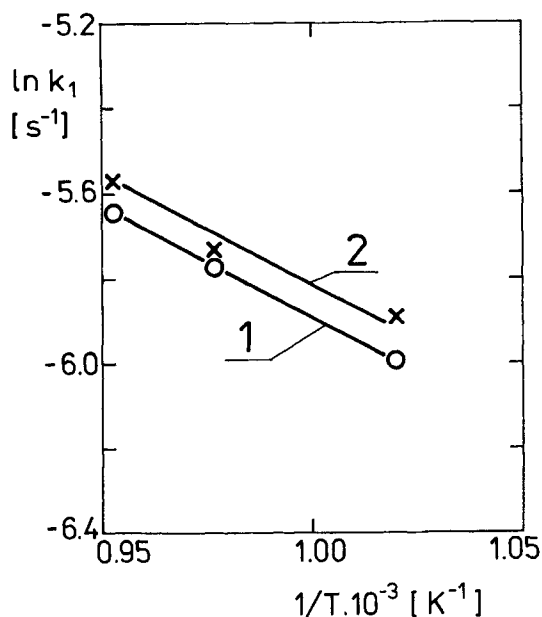


Fig. 5.49 The influence of mechanical activation of PbS on Arrhenius plot,  $T = 707\text{--}775^\circ\text{C}$ . Time of mechanical activation: 1 - 0 min, 2 - 15 min.

### Sphalerite ZnS

In comparison with galena the reducibility of sphalerite is worse [5.76]. Jovanović has alleged that the degree of reduction of ZnS reaches the value  $\alpha = 0.35$  for the temperature of  $797^\circ\text{C}$  [5.84]. The process is complicated by the fact that zinc is evaporated in the hydrogen flow at high temperatures. At the same time hydrogen sulfide originating in the reaction of hydrogen with the sulfur atoms of sphalerite leaves the surface. At the temperatures between  $900^\circ\text{C}$  and  $950^\circ\text{C}$  hydrogen sulfide can react with zinc vapour to form secondary ZnS [5.76, 5.85].

Owing to the complicated mechanism, a temperature range of  $400^\circ\text{C}$ – $750^\circ\text{C}$  was chosen for studying the influence of mechanical activation on the rate of reduction of sphalerite because zinc does not vaporize in this temperature interval and the reaction can be described by the equation



In Fig. 5.50 the dependence of the degree of conversion  $\alpha$  on reaction time  $t_r$  is given for the sphalerite samples mechanically activated for 5–30 min in a planetary mill. For all samples, we can observe the parabolic course of reduction with the maximum rate at the commencement. Elemental zinc (JCPDS 4-831) and sulfur (JCPDS 8-247) were detected by X-ray phase analysis of the sample mechanically activated for 15 min and subsequently reduced by hydrogen for 20 min at  $664^\circ\text{C}$  and  $750^\circ\text{C}$ . The presence of elemental sulfur in reaction products may be a result of hydrogen sulfide decomposition. In paper [5.76] it is alleged that reverse reaction of zinc with hydrogen sulfide takes place in the cooler part of reaction tube which could lead to explanation of the retardation of the process.

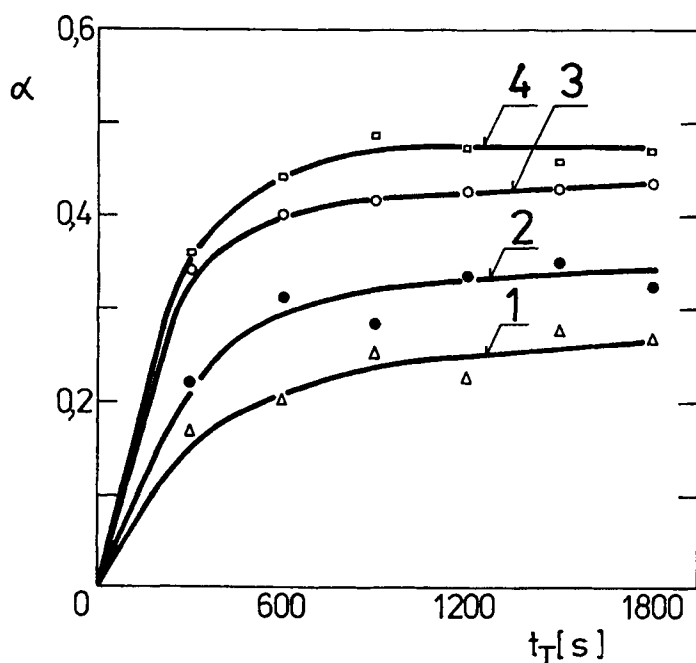


Fig. 5.50 The influence of the reaction time,  $t_T$  on the conversion degree,  $\alpha$  of mechanically activated ZnS. Time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, 4 - 30 min. Reaction temperature 664°C.

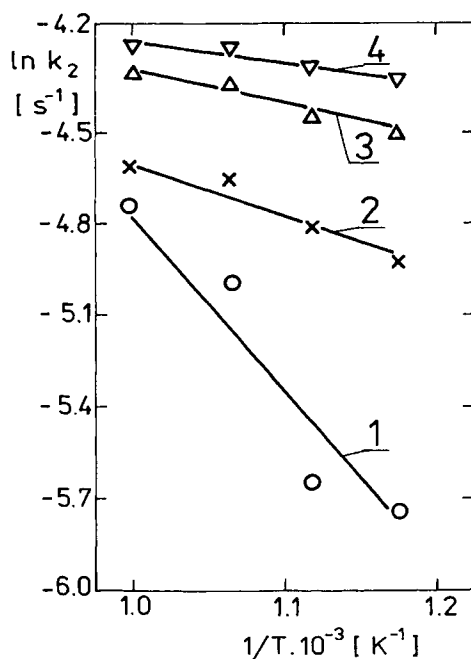


Fig. 5.51 The influence of mechanical activation of ZnS on Arrhenius plot,  $T = 578-750^\circ\text{C}$ . Time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, 4 - 30 min.

The values of apparent activation energy calculated from the plots in Fig. 5.51 are 49, 12, 7 and 4  $\text{kJmol}^{-1}$  for non-activated sample and samples activated for 5, 10 and 30 min, respectively. The disordering of sphalerite by grinding brings about a reduction in the values of activation energy. These values show that the diffusion regime, probably involving the secondary ZnS originating from the above-mentioned recombination of Zn and  $\text{H}_2\text{S}$  determines the rate of reaction (5.21).

The relationship between the reactivity of mechanically activated sphalerite expressed by the apparent rate constant of thermal decomposition  $k_{\text{GB}}$  and the changes in surface structural properties  $S_A/X$  (Fig. 5.52B) or in hyperfine structure  $S_A / A_{\text{Mn}^{2+}}$  (Fig. 5.52A) were studied in [5.41]. A small response of reactivity to significant changes in the properties of sphalerite is characteristic of the initial region where mechanical activation time was less than 15 min. At longer times, the structure of sphalerite is so altered that further, rather small, changes in structure bring about a rapid increase in reactivity. It is probable that the new phase identified by the EPR method contributes to this enhanced reactivity. This information demonstrates the structure sensitivity of reaction (5.21).

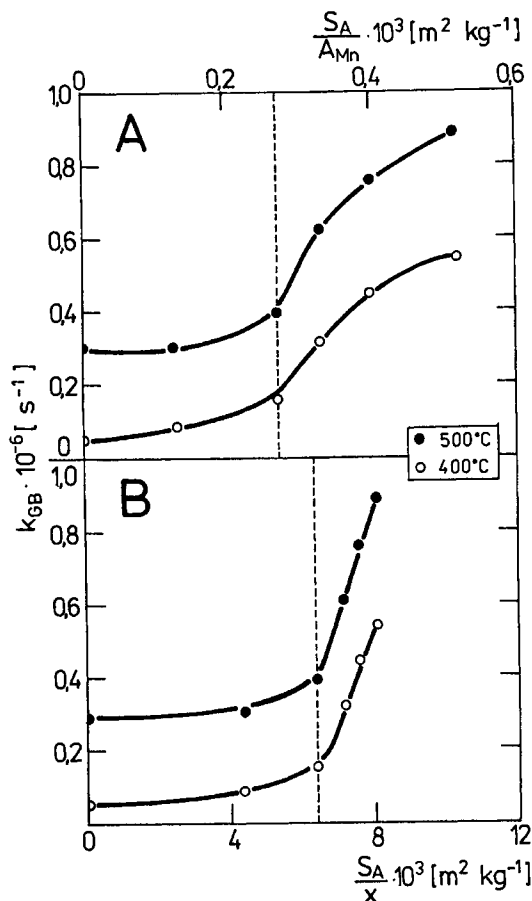


Fig. 5.52 Reactivity of mechanically activated ZnS: A,  $k_{\text{GB}}$  vs.  $S_A/A_{\text{Mn}}$ ; B,  $k_{\text{GB}}$  vs.  $S_A/X$  ( $k_{\text{GB}}$  - apparent rate constant,  $S_A$  - specific surface area,  $A_{\text{Mn}}$  - amplitude of the resonance line of  $\text{Mn}^{2+}$ ,  $X$  - content of crystalline phase) [5.41].

## 5.4. Solid state exchange reactions

It is also possible to prepare the elemental metals or their oxides by solid-state reaction of sulfides [5.86] according to the reactions



In reaction (5.22) the reduction of the metal sulfide MeS is performed with a reducing element R (R = Cu, Al, Mn, Si, Fe), while reaction (5.23) represents a displacement reaction.

The concept of direct reduction of ores to metals by mechanical activation was introduced by Molčanov and Jusupov [5.19]. The authors named the process mechanometallurgy. By dry grinding of cinnabar HgS in a planetary mill equipped with copper vials and balls it was possible to obtain elemental mercury according to the following reaction



By the authors the reduction also proceeds in the course of mechanical activation of cinnabar by grinding in water using iron balls



Matteazzi and LeCaër [5.86] have studied the reduction reactions of selected sulfides with the different metals. The experiments were performed by grinding of sulfide-metal mixtures in a vibratory mill under nitrogen atmosphere for 24 hours. The reactions under study are summarized in Table 5.6.

Table 5.6 The solid reductive decomposition reactions and identified products [5.86]

| Simplified reaction scheme                                      | Identified products                                                                                          |
|-----------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------|
| 3FeS + 2Al → 3Fe + Al <sub>2</sub> O <sub>3</sub>               | α-Fe, Fe-Al alloy, Al <sub>2</sub> S <sub>3</sub> , FeAl <sub>2</sub> O <sub>4</sub>                         |
| FeS + Mn → Fe + MnS                                             | α-Fe, MnS, MnS <sub>2</sub> , γ-(Fe-Mn) alloy                                                                |
| 2FeS + Si → 2Fe + SiS <sub>2</sub>                              | SiS <sub>2</sub> , FeSi, α-FeSi <sub>2</sub> , Fe-Si solid solution, Fe <sub>1-x</sub> Si <sub>x</sub> alloy |
| 3Cu <sub>2</sub> S + 2Al → 6Cu + Al <sub>2</sub> S <sub>3</sub> | Cu, γ-Al <sub>2</sub> S <sub>3</sub> , Cu-Al <sub>2</sub> S <sub>3</sub>                                     |
| Cu <sub>2</sub> S + Fe → 2Cu + FeS                              | Cu, FeS, Cu <sub>5</sub> FeS <sub>4</sub> , Fe <sub>1-x</sub> O, Fe <sub>1-x</sub> Cu <sub>x</sub> alloy     |
| 3CoS + 2Al → 3Co + Al <sub>2</sub> S <sub>3</sub>               | Co, Al <sub>2</sub> S <sub>3</sub> , Co <sub>2</sub> Al <sub>5</sub>                                         |
| 3PbS + 2Al → 3Pb + Al <sub>2</sub> S <sub>3</sub>               | Pb, Al <sub>2</sub> S <sub>3</sub>                                                                           |
| 3ZnS + 2Al → 3Zn + Al <sub>2</sub> S <sub>3</sub>               | Zn, Al <sub>2</sub> S <sub>3</sub>                                                                           |

The reduction of metal sulfides by room temperature vibratory grinding with a suitable reducing agent has been shown to be feasible. Metals, alloys, intermetallic compounds and sulfide nanocomposites were obtained with crystallite sizes in the range 10-30 nm [5.86].

The concept of direct reduction was also applied for ternary sulfides. Baláž et al. accomplished the activation of chalcopyrite  $\text{CuFeS}_2$  by intensive grinding in the presence of copper, iron and sulfur. Among the products of solid reductive decomposition of chalcopyrite the  $\text{CuS}$ ,  $\text{Cu}_5\text{FeS}_4$ ,  $\text{Cu}_{17.6}\text{Fe}_{17.7}\text{S}_{32}$  and  $\text{Cu}_7\text{S}_4$  were unambiguously identified [5.87].

The different displacement reactions were studied with the aim of performing reductions which normally require high temperature during low temperature grinding without the application of external heat [5.86, 5.88-5.95]. The different substances and reducing agents were applied under the influence of mechanical activation.

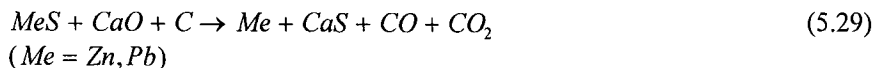
Among displacement reagents calcium oxide is frequently used. In reaction (5.23) this reagent forms  $\text{CaS}$  which can be transformed to a more inert phase, such as  $\text{CaSO}_4$  without the evolving of  $\text{SO}_2$ .

Sulfides of iron, tungsten and molybdenum may be changed to corresponding oxides [5.88] by the following simplified reactions



The possibility of the application of  $\text{CaO}$  for gold bearing pyrite decomposition via mechanochemical route will be described in Chapter 8.3.

The combined effect of reduction element and the displacement reagent was studied by Avvakumov [5.15]. The rate of the reaction



doubles after mechanical activation with a concomitant decrease in the temperature of commencement of the reaction of 100-150°C.

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## **Chapter 6 CHEMICAL LEACHING OF MECHANICALLY ACTIVATED MINERALS**

- 6.1. Acid oxidizing leaching**
- 6.2. Acid non-oxidizing leaching**
- 6.3. Alkaline leaching**
- 6.4. Leaching of sulfides containing gold and silver**
- 6.5. Electrochemical aspects of leaching of mechanically activated sulfides**
- 6.6. References**

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The traditional scheme of metals extraction from minerals involves some processes of mechanical character ameliorating the accessibility of the valuable component by the leaching agent. Leaching represents the key stage in the extraction scheme and its course may be affected by selection and choice of the method leaching and/or by convenient pretreatment of the solid phase. Thermal and mechanical activation belongs among the most important pretreatment methods which influence solid phase leachability.

The thermal activation of sulfidic ores aims at transforming the poorly soluble minerals into more soluble forms. That enables better selectivity in transfer of usable metal into solution, nevertheless it appears that some new problems concerning exploitation of the sulfur emissions arise. In the past three decades enhanced public awareness and governmental pressure have focussed on the problem of sulfur oxide pollution. Sulfidic minerals account for a large fraction of the sulfur oxides. The special problem of the minerals is the presence of small amounts of As, Hg, Te, Se which may be emitted together with sulfur in form of oxides by the thermal activation.

The mechanical activation of minerals makes it possible to reduce their decomposition temperature or causes such a degree of disordering that the thermal activation may be omitted entirely. In this process, the complex influence of surface and bulk properties occurs. The mineral activation leads to a positive influence on the leaching reaction kinetics, to an increase in the measured surface area and to further phenomena, especially the potential mitigation of environmental pollutants which is becoming increasingly important with time.

At present, it is not known whether the kinetics of heterogeneous reactions are determined by the contact area, the structure of the mineral, or both. The required modification of the structure can be achieved by mechanical activation of the mineral, typically by intensive grinding. The breaking of bonds in the crystalline lattice of the mineral brings about a decrease ( $\Delta E^*$ ) in activation energy and an increase in the rate of leaching [6.1]

$$\Delta E^* = E - E^* \quad (6.1)$$

where  $E$  is the apparent activation energy of the non-disordered mineral and  $E^*$  is the apparent activation energy of the disordered mineral.

The relationship between the rate of leaching and temperature is usually described by the Arrhenius equation

$$k = Z \exp (-E / RT) \quad (6.2)$$

where  $k$ ,  $Z$ ,  $R$  and  $T$  stand for the rate constant of leaching for the non-disordered mineral, pre-exponential factor, gas constant and reaction temperature, respectively.

For the disordered mineral we can write

$$k = Z \exp (-E^* / RT) \quad (6.3)$$

and after substituting for  $E^*$  from (6.1) we obtain

$$k^* = k \exp (\Delta E^* / RT) \quad (6.4)$$

From (6.1) it is clear that  $\exp (\Delta E^*/RT) > 1$  and thus it follows from eq. (6.4) that  $k^* > k$ , i.e., the rate of leaching of a disordered mineral is greater than that of an ordered mineral.

It was Senna who analysed the effect of surface area and the structural disordering on the leachability of mechanically activated minerals [6.2]. In order to solve the problem – whether surface area or structural parameters are predominant for the reactivity, the rate constant is divided by the proper surface area and plot against the applied energy by activation (Fig. 6.1).

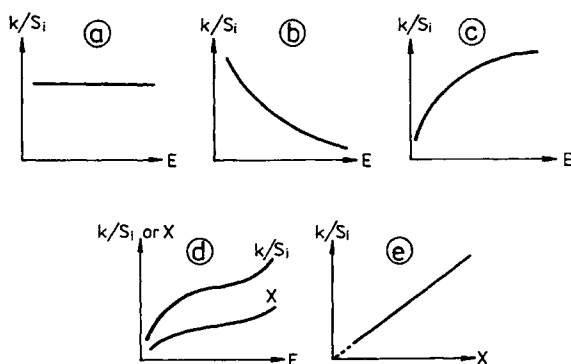


Fig. 6.1 The schematic diagrams representing the mutual dependence of physico-chemical characteristics and reactivity of mechanically activated solids:  $k$  - the rate constant of leaching,  $S_i$  - surface area,  $X$  - structural imperfections,  $E$  - applied energy [6.2].

If the rate constant of leaching divided by the surface area remains constant with respect to the applied energy, as shown in Figure 6.1a, then the measured surface area may be the effective surface area and at the same time, the reaction rate is insensitive to structural changes.

If, on the other hand, the value  $k/S_i$  decreases with applied energy, as shown in Figure 6.1b, then the surface area is probably not the effective surface area.

In the third case where  $k/S_i$  increases with increasing applied energy, as shown in Figure 6.1c, the surface area  $S_i$  may be again the effective surface area, with an overlapping effect of the structural imperfection, as a result of mechanical activation.

Alternatively, when  $k/S_i$  and  $X$  vary parallel to each other with  $E$ , as shown in Figure 6.1d, or the value  $k/S_i$  is proportional to  $X$ , as shown in Figure 6.1e, it seems more appropriate to accept the chosen  $S_i$  as an effective surface area.

### 6.1. Acid oxidizing leaching

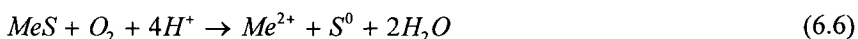
Though some simple sulfides of non-ferrous metals are partially soluble in inorganic acids, the efficient leaching requires the presence of oxidizing agents [6.3-6.4]. Amongst these agents,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{FeCl}_3$ ,  $\text{CuCl}_2$ ,  $\text{HCl} + \text{O}_2$ ,  $\text{H}_2\text{SO}_4 + \text{O}_2$ ,  $\text{NH}_3 + \text{O}_2$  are most frequently used. Others, such as ozone, peroxides ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2\text{SO}_5$ ) and compounds with high oxidation state of metals ( $\text{K}_2\text{Cr}_2\text{O}_7$ ) have also been tested [6.5-6.9].

In Table 6.1 the values of the standard redox potentials  $E^0$  of common oxidizing agents are listed.

Table 6.1 Standard redox potentials [6.10]

| Redox couple                                       |                                          | E° (V) |
|----------------------------------------------------|------------------------------------------|--------|
| $\text{Cr}^{3+} + \text{e}$                        | $= \text{Cr}^{2+}$                       | - 0.41 |
| $\text{Cu}^{2+} + \text{e}$                        | $= \text{Cu}^{+}$                        | 0.17   |
| $\text{Fe}^{3+} + \text{e}$                        | $= \text{Fe}^{2+}$                       | 0.77   |
| $\text{MnO}_2 + 4\text{H}^{+} + 2\text{e}$         | $= \text{Mn}^{2+} + 2\text{H}_2\text{O}$ | 1.24   |
| $\text{ClO}_4^{-} + 8\text{H}^{+} + 8\text{e}$     | $= \text{Cl}^{-} + 4\text{H}_2\text{O}$  | 1.35   |
| $\text{ClO}_3^{-} + 6\text{H}^{+} + 6\text{e}$     | $= \text{Cl}^{-} + 3\text{H}_2\text{O}$  | 1.45   |
| $\text{ClO}^{-} + 2\text{H}^{+} + 2\text{e}$       | $= \text{Cl}^{-} + \text{H}_2\text{O}$   | 1.50   |
| $\text{Mn}^{3+} + \text{e}$                        | $= \text{Mn}^{2+}$                       | 1.51   |
| $\text{H}_2\text{O}_2 + 2\text{H}^{+} + 2\text{e}$ | $= 2\text{H}_2\text{O}$                  | 1.77   |

The leaching of sulfides (MeS) in the presence of oxidizing agents can be described by the following equations



The form of arising sulfur product depends on pH and temperature:

- at  $\text{pH} < 2$  and  $T < 160^{\circ}\text{C}$  elemental sulfur arises,
- at  $\text{pH} > 2$  sulfates with possible formation of polythionates can be observed and
- at  $T > 100^{\circ}\text{C}$  there is a tendency to complete oxidation of sulfur to sulfates and to formation of basic hydroxysulfates by hydrolysis.

### Chalcopyrite $\text{CuFeS}_2$

Chalcopyrite belongs to the group of the most exploited sulfidic copper minerals. Its refractory character often requires an activation pretreatment step [6.11]. The activation techniques were summarized by Dutrizac and can be divided into three general categories: changing the chalcopyrite to other sulfides by adding or removing Cu, Fe or S, catalyzing the reaction with traces of Ag, and promoting the rate of leaching by fine grinding and/or induced lattice strain [6.12]. The techniques are summarized in Table 6.2.

Table 6.2 Activation methods for  $\text{CuFeS}_2$  [6.12]

| Method                                                 | References |
|--------------------------------------------------------|------------|
| Activation with sulfur                                 | 6.13-6.14  |
| Activation with covellite                              | 6.15       |
| Activation with copper                                 | 6.16       |
| Activation with iron                                   | 6.17-6.18  |
| Activation with carbon                                 | 6.19       |
| Activation by sulfur removal with $\text{H}_2$         | 6.20       |
| Activation by sulfur removal in vacuum or in inert gas | 6.21       |
| Activation by silver catalysis in solution             | 6.22-6.23  |
| Mechanical activation                                  | 6.24-6.25  |

Hydrometallurgical treatment of chalcopyrite most frequently takes place by oxidizing leaching [6.11] with low cost ferric sulfate frequently used, which gives the possibility of regenerating the leaching agent e.g. by aeration [6.3]. The reaction of chalcopyrite with ferric sulfate in acid medium is governed by the following equation



The attractiveness of the study of the reaction (6.7) is documented by a number of publications [6.26-6.30]. However, these papers are not consistent in proposing the rate determining step. Different views about this subject can be divided into three classes according to which the rate determining stage is represented by

- diffusion processes at the chalcopyrite-ferric sulfate interface (diffusion of electrons or ions of copper or iron through a layer of sulfur or intermediate sulfide phases arising during the course of the reaction),
- the rate of proper chemical reaction and
- diffusion processes within the bulk chalcopyrite.

The present knowledge of the mechanism of the reaction of chalcopyrite with ferric sulfate enables us to elucidate some phenomena, but it does not allow us to give a consistent interpretation of experimental observations. The material presented in these papers was obtained by studying the influence of temperature, concentration, accompanying ions, stirring intensity, and grain size on kinetics of the reaction. The possibility of affecting the reactivity of chalcopyrite by pretreatment is not taken into consideration in these studies.

The intensification of the oxidative leaching of chalcopyrite by mechanical activation has been studied since 1973. Even the first communication [6.31] showed the favourable effect of vibration grinding on the rate of leaching. Later it was revealed that a similar effect could be achieved by grinding in an attritors or turbomills [6.32-6.33, 6.25].

However, there has been disagreement over the factors influencing the leaching rate of chalcopyrite. Beckstead and co-workers [6.32] claimed that the leaching behaviour of activated  $\text{CuFeS}_2$  was the same as that of a sample activated and then thermally treated to remove the structural disorder caused during milling (Fig. 6.2).

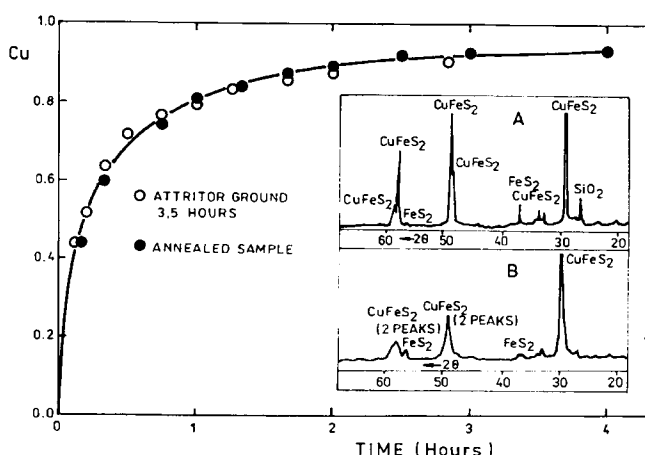


Fig. 6.2 Copper extraction,  $\epsilon_{\text{Cu}}$  vs. time of activation for attritor-ground  $\text{CuFeS}_2$  and strain-relieved attritor-ground  $\text{CuFeS}_2$ , leaching agent:  $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$  [6.32].

The thermal treatment of the disordered chalcopyrite was performed in an evacuated sealed capsule at 600°C for 120 minutes. However, at this temperature there is a phase transformation from  $\alpha$ -CuFeS<sub>2</sub> to  $\beta$ -CuFeS<sub>2</sub> (see Chapter 4). Ferreira and Burkin [6.34] report that the  $\beta$ -form reacts with ferric sulfate more rapidly than the  $\alpha$ -form (Fig. 6.3).

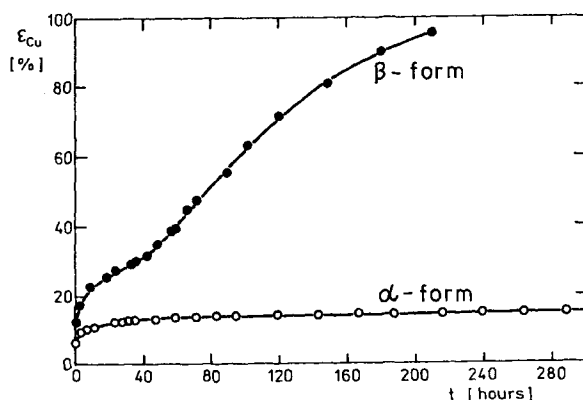


Fig. 6.3 Comparison of copper recovery,  $\epsilon_{Cu}$  for leaching of  $\alpha$ - and  $\beta$ -chalcopyrite,  $t$  - leaching time [6.34].

In Fig. 6.4 physico-chemical changes of CuFeS<sub>2</sub> activated in two different type of mills are illustrated. From this Figure is evident, that the products of grinding in the attritor and vibration mill differ in specific structural deterioration. According to the published data, these differences are due to the differences in grinding environment and ball dimensions [6.35]. It is known that grinding in aqueous environment and/or the use of small mill balls is more favourable for new surfaces formation whereas dry grinding and/or the use of larger mill balls favour amorphisation.

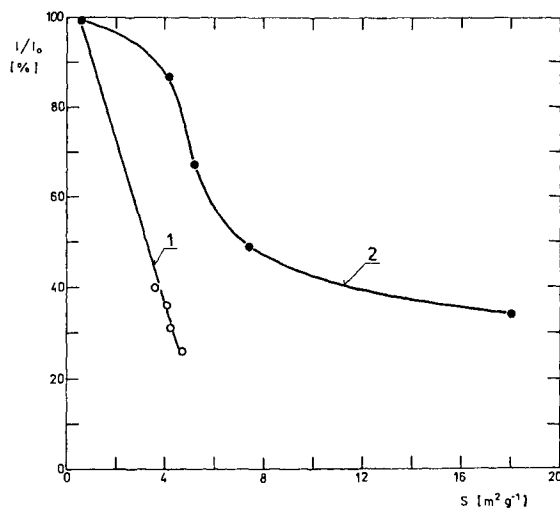


Fig. 6.4 The relative intensity,  $I/I_0$  of (112) diffraction line of CuFeS<sub>2</sub> vs. specific surface area,  $S$  for samples mechanically activated in a vibration mill (1) or in an attritor (2).

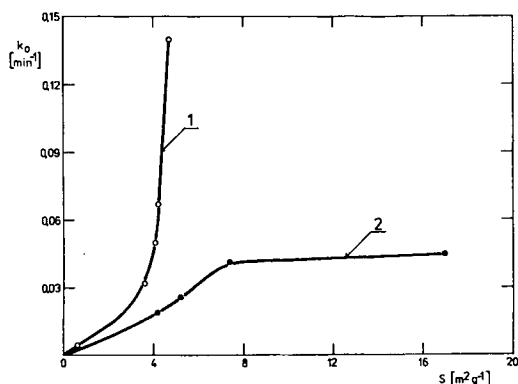


Fig. 6.5 The initial reaction rate,  $k_0$  vs. specific surface area,  $S$  for  $\text{CuFeS}_2$  mechanically activated in vibration mill (1) and attritor (2).

The effect of mechanical activation on chalcopyrite reactivity was determined by studying the initial reaction rate of reaction (6.7). From these results, shown in Fig. 6.5, it follows that for samples ground in the attritor an 11-fold increase in the initial reaction rate was accompanied by an increase in the specific surface area from 0.59 to 17  $\text{m}^2\text{g}^{-1}$  (i.e. 28-fold). In case of samples ground in vibration mill a greater than 30-fold increase of  $k_0$  was achieved despite an eightfold specific surface area increase, i.e. from 0.59 to 4.7  $\text{m}^2\text{g}^{-1}$  only.

When comparing Fig. 6.4 and 6.5 one can observe that the specific reactivity of the studied samples changes in accordance with their specific amorphisation. In case of samples activated in the attritor the initial reaction rate increases in accordance with the amorphisation over the whole range of specific surface area. In case of samples activated in the vibration mill the increase in initial reaction rate is, however, greater than that expected from the degree of amorphisation. Samples with  $k_0 > 0.06 \text{ min}^{-1}$  show an unusual trend, the origin of which could be related to phase transformation of  $\text{CuFeS}_2$ .

The influence of conditions of the mechanical activation on quantities characterizing the structure of chalcopyrite (specific surface  $S$  and content of crystalline phase  $X$ ) and on kinetics of the reaction of chalcopyrite with ferric sulfate (initial rate constant  $k_0$ ) was studied in paper [6.24] in conformity with the so-called complete plan of experiments  $2^3$  [6.36]. The results are summarized in Table 6.3 and Fig. 6.6.

Table 6.3 Complete plan of experiments  $2^3$

| Experi-<br>ment | Mechanical activation        |                                               |                         | Structural parameters                |            |                                        | Kinetics<br>$k_0 \cdot 10^{-4}$<br>( $\text{s}^{-1}$ ) |
|-----------------|------------------------------|-----------------------------------------------|-------------------------|--------------------------------------|------------|----------------------------------------|--------------------------------------------------------|
|                 | Amplitude<br>of mill<br>(mm) | Revolutions<br>of mill<br>( $\text{s}^{-1}$ ) | Grinding<br>time<br>(h) | $S$<br>( $\text{m}^2\text{g}^{-1}$ ) | $X$<br>(%) | $S/X$<br>( $\text{m}^2\text{g}^{-1}$ ) |                                                        |
| 1               | 2.4                          | 13.2                                          | 0.5                     | 2.09                                 | 87.10      | 2.40                                   | 3.71                                                   |
| 2               | 2.4                          | 18.5                                          | 0.5                     | 3.69                                 | 80.97      | 4.56                                   | 7.14                                                   |
| 3               | 4.4                          | 13.2                                          | 0.5                     | 3.21                                 | 84.29      | 3.81                                   | 6.97                                                   |
| 4               | 4.4                          | 18.5                                          | 0.5                     | 4.14                                 | 67.50      | 6.13                                   | 8.63                                                   |
| 5               | 2.4                          | 13.2                                          | 2                       | 3.19                                 | 77.35      | 4.12                                   | 6.03                                                   |
| 6               | 2.4                          | 18.5                                          | 2                       | 3.51                                 | 59.00      | 5.95                                   | 11.63                                                  |
| 7               | 4.4                          | 13.2                                          | 2                       | 3.59                                 | 52.51      | 6.84                                   | 9.18                                                   |
| 8               | 4.4                          | 18.5                                          | 2                       | 5.29                                 | 46.42      | 11.40                                  | 15.72                                                  |

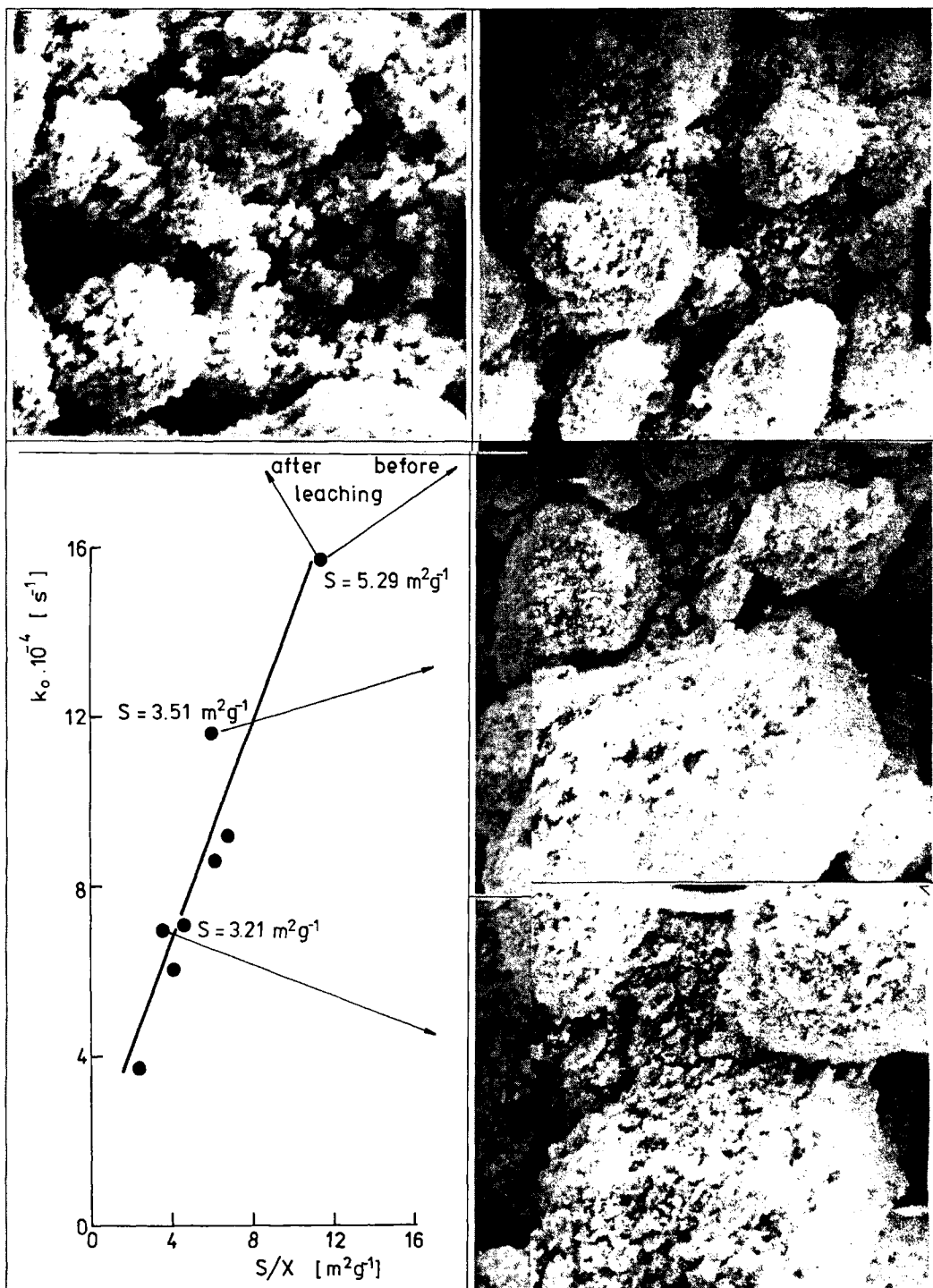


Fig. 6.6 Structural sensitivity of reaction (6.7): influence of the ratio of specific surface to volume disordering of  $\text{CuFeS}_2$ ,  $S/X$  on initial rate constant  $k_0$  [6.24].

It follows from the dependence of the initial rate constant  $k_0$  on the degree of structural disordering of chalcopryrite, as expressed by the ratio  $S/X$ , that there is a linear relationship between  $k_0$  and  $S/X$  which may be expressed by the following equation

$$k_0 = (1.387 + 1.281 S / X) \cdot 10^{-4} \quad (6.8)$$

(coefficient of simple correlation is 0.948).

The validity of the linear relationship (6.8) between the initial rate constant of leaching  $k_0$  and the ratio  $S/X$  indicates the equal influence of surface increase and structural disorder on the reaction rate of chalcopryrite leaching and provides evidence for the structural sensitivity of reaction (6.7).

The temperature sensitivity of the reaction of chalcopryrite with ferric sulfate was studied in the temperature interval 60-95°C by the use of two mechanically activated samples characterized by disordering  $S/X = 5.95 \text{ m}^2\text{g}^{-1}$  and  $11.40 \text{ m}^2\text{g}^{-1}$  as well as of a non-activated sample ( $S/X = 0.004 \text{ m}^2\text{g}^{-1}$ ). The dependence of the initial rate constant plotted in the Arrhenius coordinates is represented in Fig. 6.7.

It is known from the literature on mechanical activation that the rate of chemical reaction may be favourably affected by disordering of the structure provided that the rate of chemical reaction is the rate determining step [6.37]. The typical activation energies of such an elementary step may be in the range 40 to 290  $\text{kJ mol}^{-1}$  according to the type of reaction and the strength of bonds in the solid reactant [6.38]. Not only is the amount of energy accumulated by defects important, but the type of defects involving this energy is also of great importance from the point of view of kinetics [6.39]. Different chemical processes are sensitive to the types of defects present. For the reaction taking place at the solid-liquid interface, such as leaching of chalcopryrite, the contact area as well as the defect concentration in the bulk surface is decisive. The experimentally determined structural sensitivity of the reaction is in good agreement with the above-mentioned information.

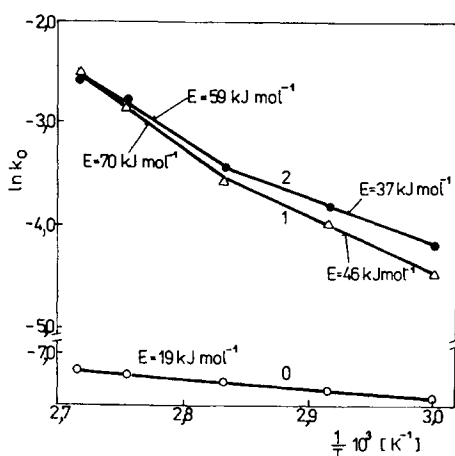


Fig. 6.7 Arrhenius plot for reaction (6.7):  $S/X = 0.004 \text{ m}^2\text{g}^{-1}$  (0),  $S/X = 5.95 \text{ m}^2\text{g}^{-1}$  (1),  $S/X = 11.40 \text{ m}^2\text{g}^{-1}$  (2) [6.24].

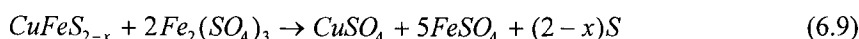
The break in the Arrhenius plot (Fig. 6.7) indicates that the rate controlling step changes with temperature. The rate of a reaction controlled by diffusion is less sensitive to temperature than the rate of a process controlled by chemical reaction. The apparent activation energies of diffusion are usually between 0 and 30 kJ mol<sup>-1</sup> and the activation energy determined for the non-activated sample is within this range.

No general rules are valid for the structural sensitivity of the processes controlled by internal diffusion. If the rate determining step is the transfer through the solid product layer, e.g. elemental sulfur, the overall rate may be enhanced only by changing the identity or porosity of the reaction product. However, if the rate determining step is self-diffusion within the bulk sulfide the overall rate may be enhanced by structural defects, as in the case of chemical reaction.

Unlike the non-activated sample, the plot of the activation energies for the mechanically activated samples indicate a change in the rate determining step. This change may be explained by the notion that reaction rate of a non-activated sample is controlled by diffusion. The acceleration of self-diffusion by the effect of mechanical activation causes the chemical reaction to gradually take on the character of the rate determining step. This proposal is corroborated by the values of apparent activation energy calculated for mechanically activated samples and their differences in the region of lower ( $T < 80^\circ\text{C}$ ) and higher temperatures ( $T > 80^\circ\text{C}$ ).

Gock [6.40] has analysed reaction (6.7) by studying the reactivity and surface properties of chalcopyrite activated by grinding in a vibration mill. By analysing for copper and iron in solution he concluded that

- the first step is the dissolution of surface layers formed by mechanochemical surface reaction by vibration grinding,
- the active sites which are characterized by the presence of  $\text{CuFeS}_{2-x}$  ( $\beta\text{-CuFeS}_2$ ) are leached out in the following step



- the leaching of chalcopyrite by reaction (6.7) is proceeded by the previous two stages.
- Murr and Hiskey [6.8] leached chalcopyrite using the strong oxidation agent  $\text{K}_2\text{Cr}_2\text{O}_7$

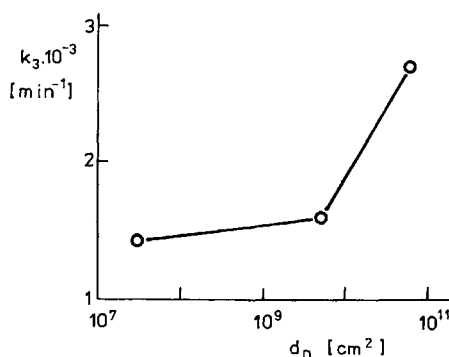
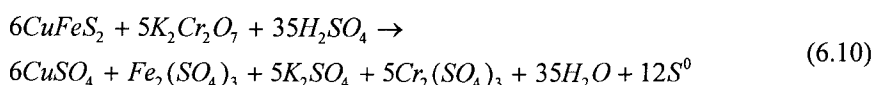


Fig. 6.8 Reaction rate constant,  $k_s$  vs. dislocation density,  $d_D$  for  $\text{CuFeS}_2$  samples [6.8].

The samples of  $\text{CuFeS}_2$  were shock loaded and then examined in the transmission electron microscope. The mechanically activated samples contained roughly  $10^3$  and  $10^4$  times more dislocations than the natural, unshocked materials. In Fig. 6.8 the direct effect of dislocation density on the  $\text{CuFeS}_2$  leaching rate is clear. The influence of crystal defects can be partly masked by variations in surface chemisorption as well as variations in the nature of the sulfur reaction product layer.

Ferric chloride leaching of mechanically activated chalcopyrite was studied by Maurice and Hawk who used two types of mills. The increase of surface area was determined for both autogeneous grinding in a tumbling mill and in a shaker mill, but the resultant defect density was only determined for the shaker mill [6.41].

The mechanical activation of chalcopyrite in the presence of copper, iron and sulfur was presented in paper [6.42]. The leachability of the products after mechanical activation is shown in Fig. 6.9. Clearly, large differences between activated samples and non-activated  $\text{CuFeS}_2$  can be detected. The reactive formation of phases during grinding which have better leachability than chalcopyrite may well be responsible for the enhanced leachability of copper.

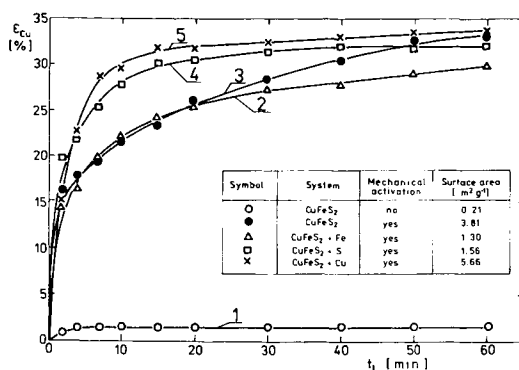


Fig. 6.9 Influence of the leaching time,  $t_L$  on the copper recovery,  $\epsilon_{\text{Cu}}$  for different systems: 1 - non-activated  $\text{CuFeS}_2$ , 2 - mechanically activated mixture ( $\text{CuFeS}_2 + \text{Fe}$ ), 3 - mechanically activated  $\text{CuFeS}_2$ , 4 - mechanically activated mixture ( $\text{CuFeS}_2 + \text{S}$ ), 5 - mechanically activated mixture ( $\text{CuFeS}_2 + \text{Cu}$ ) [6.42].

### Pentlandite $(\text{Fe}, \text{Ni})_9\text{S}_8$

Pentlandite  $(\text{Fe}, \text{Ni})_9\text{S}_8$  is one of the most commercially important nickel minerals and different approaches have been examined to improve nickel extraction. Among these approaches was mechanical activation with a subsequent autoclave leaching under oxygen pressure [6.43-6.44].

The different oxidative leaching media were tested for hydrometallurgical treatment of pentlandite - ferric chloride [6.45-6.46], ferric sulfate [6.47] and hydrogen peroxide [6.48]. A review of different methods of nickel extraction from sulfidic ores is given by Boateng and Phillips [6.49].

The reactivity of pentlandite concentrate mechanically activated in an attritor has been tested for ferric sulfate leaching in paper [6.50]. The main components were estimated as pentlandite  $(\text{Fe}, \text{Ni})_9\text{S}_8$ , chalcopyrite  $\text{CuFeS}_2$ , pyrrhotite  $\text{FeS}$  and pyrite  $\text{FeS}_2$ . Owing to mechanical activation considerable amorphization of these phases and an increase in specific surface area were found (Table 6.4).

Table 6.4 Relative intensity of  $(\text{Fe,Ni})_9\text{S}_8$  XRD peak,  $I_R$  and specific surface area,  $S$  of mechanically activated pentlandite concentrate [6.50]

| Grinding time<br>(min) | $I_R$<br>(%) | $S$<br>( $\text{m}^2\text{g}^{-1}$ ) |
|------------------------|--------------|--------------------------------------|
| 0                      | 100          | 0.34                                 |
| 10                     | 59           | 2.77                                 |
| 30                     | 48           | 5.49                                 |
| 60                     | 13           | 5.08                                 |

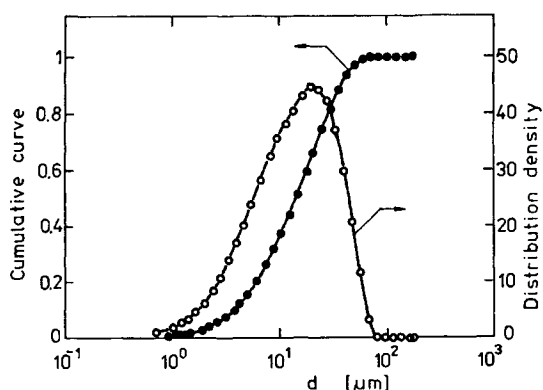


Fig. 6.10 Particle size distribution of pentlandite concentrate, as received sample [6.50].

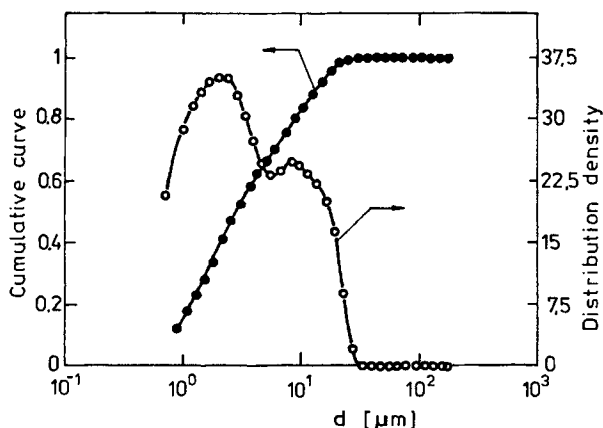


Fig. 6.11 Particle size distribution of pentlandite concentrate, time of mechanical activation 60 min [6.50].

The increase in specific surface is accompanied by changes in particle size distribution. The maximum of the monomodal distribution curve was observed at  $20\ \mu\text{m}$  for the as-received sample (Fig. 6.10). The size distribution curve changes and becomes bimodal when the time of grinding is extended to 60 min (Fig. 6.11). The first maximum, corresponding to particle size of  $2\ \mu\text{m}$ , can be attributed to particles formed by fragmentation during mechanical activation, whereas the second maximum at  $9\ \mu\text{m}$  corresponds to aggregates formed of

ultrafine particles [6.50]. The general course of disintegration due to grinding is characterized by the average size of particles which manifests itself as an integral characteristic which is calculated from granulometric analysis (Fig. 6.12). It results from this figure that the average size of particles decreases exponentially from 18  $\mu\text{m}$  to 5.3  $\mu\text{m}$  after 60 min grinding.

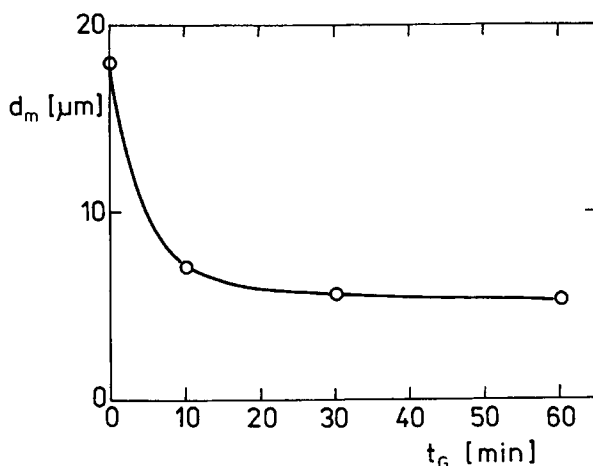


Fig. 6.12 Mean particle diameter,  $d_m$  vs. time of mechanical activation,  $t_G$  of pentlandite concentrate [6.50].

The plots giving the recovery of nickel, copper and cobalt from differently activated samples of pentlandite concentrate are presented in Figs 6.13-6.15.

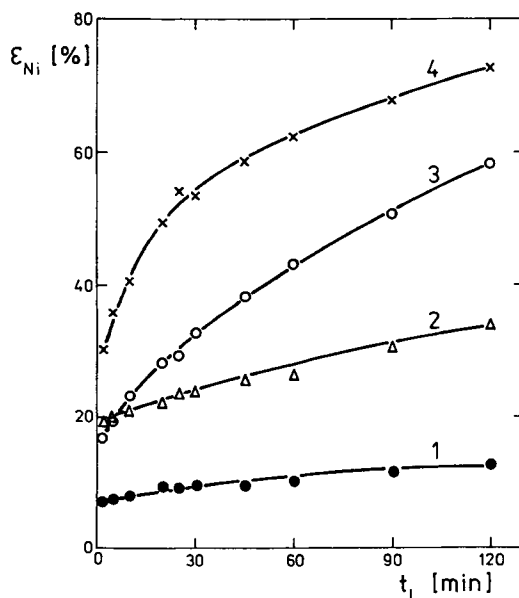


Fig. 6.13 Recovery of nickel into leach,  $\epsilon_{Ni}$  with the time of chemical leaching,  $t_L$  for pentlandite concentrate activated in different times: 1 - as received sample, 2 - 10 min, 3 - 30 min, 4 - 60 min [6.50].

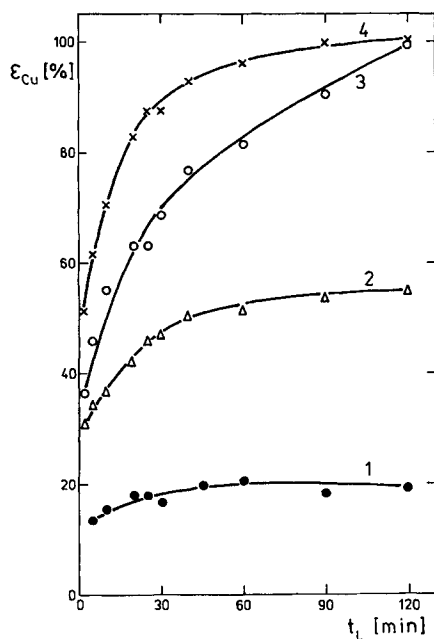


Fig. 6.14 Recovery of copper into leach,  $\varepsilon_{Cu}$  with the time of chemical leaching,  $t_L$  for pentlandite concentrate activated in different times: 1 - as received sample, 2 - 10 min, 3 - 30 min, 4 - 60 min [6.50].

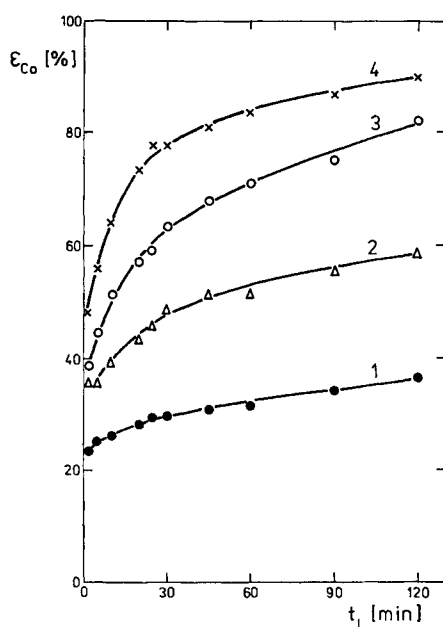


Fig. 6.15 Recovery of cobalt into leach,  $\varepsilon_{Co}$  with the time of chemical leaching,  $t_L$  for pentlandite concentrate activated in different times: 1 - as received sample, 2 - 10 min, 3 - 30 min, 4 - 60 min [6.50].

Clearly, mechanical activation accelerates the extraction of nickel, copper and cobalt into the leach solution and a recovery of 73-100 % can be achieved after 120 minutes' leaching. The recovery of individual metals from the as received sample under identical experimental conditions did not exceed 37 %.

### Galena PbS

To use of chloride medium to extract lead from sulfidic ores is not a recent idea [6.51-6.52]. The leaching of galena with ferric chloride follows the equation



The reaction produces elemental sulfur in solid state which is a great merit of this process when compared with the classical pyrometallurgical method which forms gaseous  $\text{SO}_2$  [6.53].

The interest in technological application of this reaction has stimulated a great number of theoretical studies aiming at elucidation of the mechanism of leaching. The results of these investigations are summarized by Kobayashi [6.53].

The studies aiming to correlate the solid state properties of galena with the  $E_h$ -pH diagram of the Pb-S- $\text{H}_2\text{O}$  system [6.54] or with the course of flotation and hydrometallurgical processes [6.55-6.56] may also be regarded as contributions to the behaviour of galena in aqueous media.

Galena is a typical semiconductor and its properties are dependent on defectiveness of its structure and the presence of impurities. One of the methods of influencing the defectiveness of the structure of a mineral consists of irradiation with gamma rays [6.57]. Another, more practical way is mechanical activation through intensive grinding.

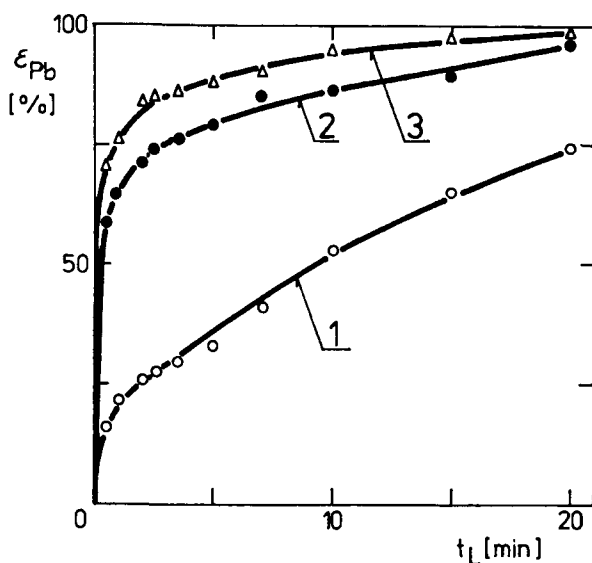


Fig. 6.16 Lead recovery,  $\epsilon_{Pb}$  vs. time of leaching,  $t_L$  for mechanically activated PbS, time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, leaching agent:  $\text{FeCl}_3 + \text{HCl}$  [6.58].

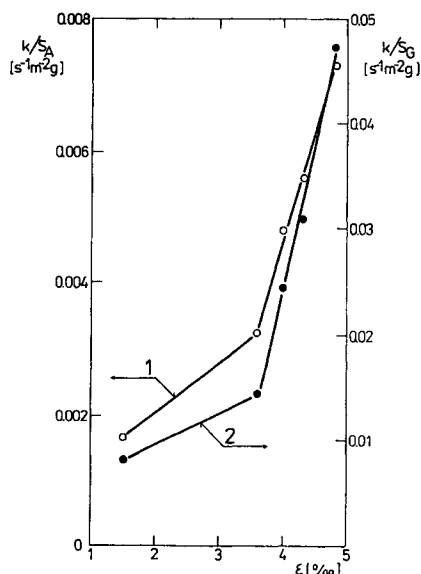


Fig. 6.17 Specific rate constant,  $k/S_A$  (1) and specific rate constant,  $k/S_G$  (2) vs. microstrains,  $\epsilon$  for leaching of mechanically activated PbS, ( $S_A$  – adsorption surface area,  $S_G$  – granulometric surface area), time of mechanical activation: 10 min, leaching agent:  $FeCl_3 + HCl$  [6.58].

The leaching curves for galena mechanically activated for 5 or 10 min in a planetary mill as well as for a non-activated sample are presented in Fig. 6.16. In Fig. 6.17 the specific rate constant for leaching,  $k/S_A$  is presented and shows a dependence on PbS structural disordering as defined by the microstrain,  $\epsilon$ . The broken line at  $\epsilon = 3.6$  ‰ reflects differences in the specific surface area of samples under study [6.58].

The temperature sensitivity of reaction (6.11) was measured for two concentrations of  $FeCl_3$ : 0.05 M and 0.6 M. The rate constants obtained (Fig. 6.18) show that both temperature and mechanical activation accelerate the leaching. The calculated values of experimental activation energy (in  $kJ\ mol^{-1}$ ) are presented in Fig. 6.19 and in dilute (0.05 M)  $FeCl_3$  solution the Arrhenius plot is linear over the temperature range 30–60°C. The values of activation energy correspond to those typical of reactions controlled by either diffusion or surface chemical control [6.59] suggesting that a mixed kinetic model probably applies in this case. At higher concentrations of  $FeCl_3$  (0.6 M) the different values of activation energy were calculated. While for  $T = 30$ –60°C these values are typical of diffusion control, for higher temperatures - mainly for mechanically activated samples - the rate controlling step is shifted to surface chemical control.

According to the literature, there is no unequivocal opinion on the character of the solid products of reaction (6.11). Elemental sulfur and lead (II) chloride are both regarded as a rate-limiting product, but in the case of  $PbCl_2$  the retardation effect is attributed to its low solubility at higher concentrations. The techniques of scanning electron microscopy, energy-dispersive X-ray spectroscopy, X-ray diffraction and others have frequently been applied to analysis of reaction products [6.60–6.61]. The method of X-ray photoelectron spectroscopy (XPS) has been used only rarely [6.62–6.63].

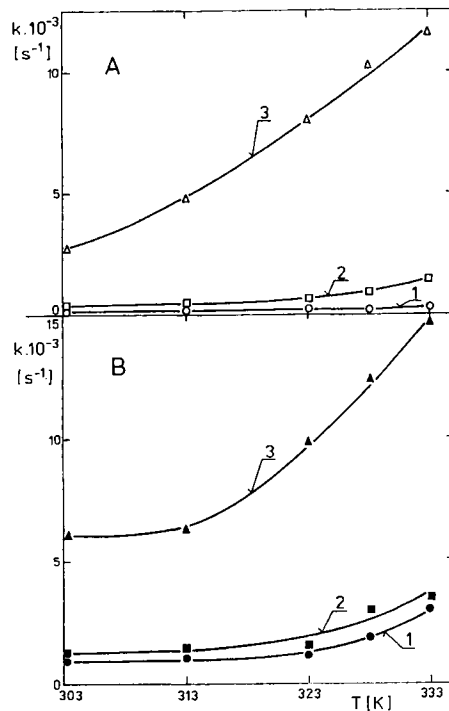


Fig. 6.18 Rate constant of leaching,  $k$  vs. temperature,  $T$  for PbS. Concentration of  $\text{FeCl}_3$ : A - 0.05 M, B - 0.6 M, time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 30 min [6.58].

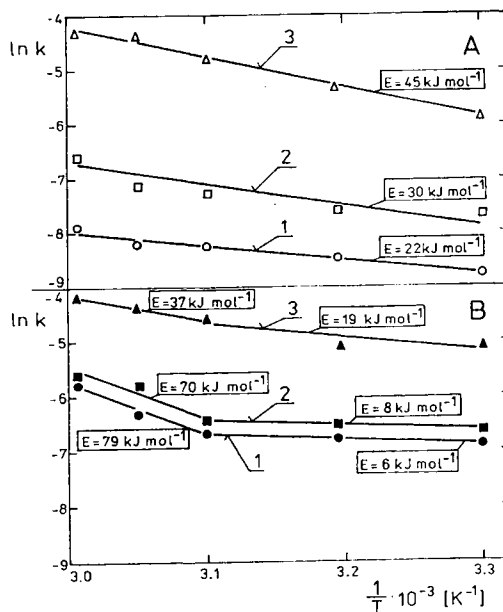


Fig. 6.19 Arrhenius plot of PbS leaching in  $\text{FeCl}_3$  solutions. Temperature: 30-60°C, concentration of  $\text{FeCl}_3$ : A - 0.05 M, B - 0.6 M, time of mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 30 min [6.58].

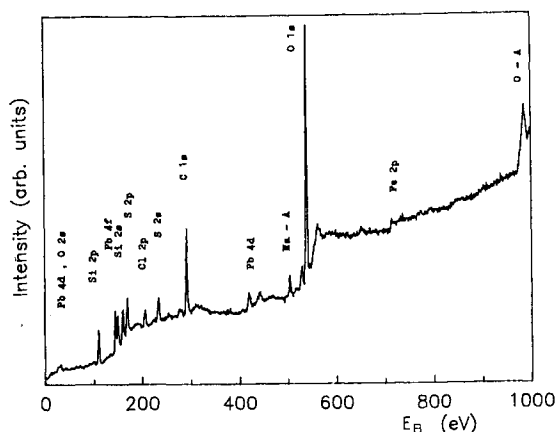


Fig. 6.20 XPS survey spectrum of PbS after leaching in chloride solution (0.05 M  $\text{FeCl}_3$  + 0.5 M  $\text{HCl}$  + 4 M  $\text{NaCl}$ ), temperature  $60^\circ\text{C}$  [6.64].

The survey XPS spectrum is shown in Fig. 6.20. Besides the basic elements (lead and sulfur) the presence of silicon originating from the quartz admixture in the galena sample can be observed. Furthermore, carbon was also present, but this is usually present on the surface of all minerals. The iron, chlorine and sodium come from the leaching agent used. The O(1s) line of oxygen is a superposition of the signals of this element present in quartz and in the products of mechanochemical oxidation of galena arising during the course of sample preparation. The XPS spectra were measured in the high-resolution regime and the Pb(4f) and S(2p) lines were analysed in more detail. As different values of  $E_B$  had been published in the literature, these values were measured for standard PbO,  $\text{PbO}_2$ , PbS and  $\text{PbSO}_4$ . These measured values of  $E_B$  were used to interpret the XPS spectra of galena [6.64].

The results are summarized in Tables 6.5-6.7. Leaching in ferric and sodium chlorides resulted in enrichment of the surface layer of galena with these elements (Table 6.7). Before leaching no silicon was observed in the surface of sample, but after leaching it was readily detected. Its absence in the non-leached sample may be due to a considerable quantity of  $\text{PbSO}_4$  (Table 6.5) arising during treatment of the sample by mechanical activation. We assume that  $\text{PbSO}_4$  forms a compact layer on the surface of galena, which prevented our identification of the admixed silicon present in the form of quartz. In the course of leaching  $\text{PbSO}_4$  was washed out from the surface of PbS (Table 6.5) and the silicon could also be detected.

In accordance with equation (6.11)  $\text{PbCl}_2$  (Table 6.5) and elemental sulfur (Table 6.6) can unambiguously be identified as reaction products of leaching. A considerable amount of PbO is also present and its occurrence may be due to it being an intermediate of the decomposition of  $\text{PbSO}_4$  [6.65].

Table 6.5 Values of binding energies,  $E_B$  and concentration of individual lead compounds, c in the PbS surface [6.64]

| Compound        | Before leaching |          | After leaching |          |
|-----------------|-----------------|----------|----------------|----------|
|                 | $E_B$ (eV)      | c (at %) | $E_B$ (eV)     | c (at %) |
| PbS             | 137.7           | 72       | -              | 0        |
| $\text{PbSO}_4$ | 139.4           | 28       | -              | 0        |
| $\text{PbCl}_2$ | -               | 0        | 139.2          | 37       |
| PbO             | -               | 0        | 138.0          | 63       |

Table 6.6 Values of binding energies,  $E_B$  and concentration of individual sulfur compounds,  $c$  in the PbS surface [6.64]

| Form of sulfur | Before leaching |            | After leaching |            |
|----------------|-----------------|------------|----------------|------------|
|                | $E_B$ (eV)      | $c$ (at %) | $E_B$ (eV)     | $c$ (at %) |
| $S^{2-}$       | 161.3           | 74         | -              | 0          |
| $S^0$          | -               | 0          | 163.2          | 100        |
| $S^{6+}$       | 168.4           | 26         | -              | 0          |

Table 6.7 Atomic ratio Me/Pb in the surface of PbS [6.64]

| Me | Before Leaching | After leaching and argon sputtering for |       |        |
|----|-----------------|-----------------------------------------|-------|--------|
|    |                 | 0 min                                   | 5 min | 20 min |
| Pb | 1.0             | 1.0                                     | 1.0   | 1.0    |
| S  | 0.8             | 6.3                                     | 6.7   | 4.2    |
| Si | 0.0             | 12.3                                    | 11.0  | 8.7    |
| O  | 1.5             | 31.4                                    | 17.0  | 19.0   |
| C  | 1.9             | 29.7                                    | 11.0  | 5.7    |
| Fe | 0.0             | 0.2                                     | 0.0   | 0.0    |
| Na | 0.0             | 1.9                                     | 2.1   | 2.1    |
| Cl | 0.0             | 2.5                                     | 1.7   | 1.1    |

In order to compare the composition of the surface with the composition of layers occurring deeper in the bulk of the leached galena, the samples were bombarded in the preparation chamber of the spectrometer with argon ions accelerated in an ion gun to an energy of 4.5 keV. The ion sputtering continued for 5 or 20 min. On the basis of calibration relationships valid for the ion gun used, it may be assumed that the treatment lasting 5 min resulted in removal of a layer about 30 nm thick from the surface, whereas the treatment lasting 20 min caused removal of a layer about 100 nm thick (because of the surface topography these values are approximately orientational). The results are given in Table 6.7. Except for sodium, ion sputtering produced a decrease in the relative concentration of all measured elements. The Na/Pb concentration ratio in the surface remained stable even after 20 min sputtering, which can be explained by a great migration ability of sodium. After the ion sputtering was finished, this element migrated from the regions unaffected by ions. The decrease in relative concentration of Cl, Fe, S and O gives evidence that the products of equation (6.11) viz.  $PbCl_2$ ,  $FeCl_2$  and S, or  $PbO$  originally present in the surface layers are removed by argon-ion sputtering. If we regard the atomic concentration ratio Me/Pb for 20 min sputtering as characteristic of the bulk composition of the sample and compare it with the corresponding value obtained for 5 min sputtering we can observe that sulfur is sputtered off at a rate equal to that of chlorine. The atomic masses of both of these elements are similar, and if we suppose that they are bound in the reaction products by equally strong bonds, then a similar sputtering rate may be expected for them. The values  $4.2/6.7 = 0.6$  for sulfur and  $1.1/1.7 = 0.6$  for chlorine are consistent with this view.

The selection of a leaching agent suitable for sphalerite has been given considerable attention with results having been summarized in many publications [6.66 - 6.71]. Although various acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HCl}$ ,  $\text{HNO}_3$ ,  $\text{HClO}_4$ ), bases ( $\text{NH}_4\text{OH}$ ) and salt solutions have been tested, ferric sulfate and chloride solutions predominate among the possible oxidative leaching agents. Strong oxidizing agents allow leaching at atmospheric pressure, whereas the use of acids frequently necessitates the application of autoclave leaching in the presence of oxygen [6.72 - 6.73].

The preparation of sphalerite for hydrometallurgical operations can be performed by various methods. Exner and co-workers [6.72] found that activation of the mineral by irradiation with ultraviolet rays raised the recovery of zinc in a subsequent high-pressure leaching. The authors pointed out the importance of the solid state properties of sphalerite for the progress of the leaching. Mechanical activation, which produces changes in the physico-chemical properties of the solid phase, may also be applied to the pretreatment of sphalerite. More recently, several papers have appeared which have documented the positive influence of mechanical activation on the rate of leaching of sphalerite [6.74 - 6.78]. Such leaching makes it possible to obtain sufficient yields of zinc in short time intervals at atmospheric pressure. However, the importance of the solid-state properties of the mineral is a problem requiring deeper understanding.

In paper [6.79] an attempt to study the correlation between the changes in surface and bulk properties of sphalerite due to mechanical activation with the rate of oxidative leaching of the mineral was made. Hydrogen peroxide was selected as a model strong oxidative lixiviant for the leaching. As Lotens and Wesker [6.80] stated in their study of oxidative leaching of sphalerite by this lixiviant, overall reactions of sulfides (where sulfur is formally present as  $\text{S}^{2-}$  in the crystal lattice) in accordance with the literature data can be represented as



with sulfate formation occurring to a lesser extent according to

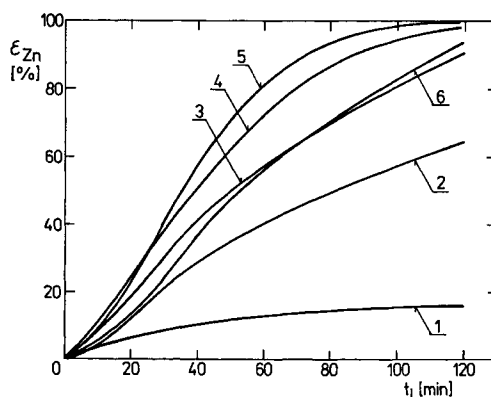
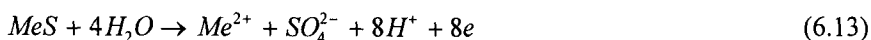


Fig. 6.21 The influence of time of leaching,  $t_L$  on the recovery of zinc,  $\epsilon_{Zn}$  from mechanically activated ZnS. Time of mechanical activation: 1 - 0 min, 2 - 7.5 min, 3 - 15 min, 4 - 60 min, 5 - 150 min, 6 - 240 min. Leaching agent:  $\text{H}_2\text{O}_2$  [6.79].

The dependence of the recovery of zinc into the leach solution on leaching time is represented in Fig. 6.21. From this relationship, 65-100 % of the zinc can be transferred into the solution in 120 min from the sphalerite ground for 7.5-60 min at laboratory temperature and atmospheric pressure if a 4 % solution of hydrogen peroxide is used. For an unground sample (Fig. 6.21, curve 1) the maximum value  $\epsilon_{Zn} = 17\%$  was attained.

Table 6.8 Recovery of zinc, iron and elemental sulfur to the leach solution of the sphalerite mechanically activated during  $t_G = 150$  min. Leaching agent:  $H_2O_2$  [6.79]

| Time of leaching<br>$t_L$ (min) | Recovery (%) |    |       |
|---------------------------------|--------------|----|-------|
|                                 | Zn           | Fe | S     |
| 20                              | 22.86        | 0  | 7.24  |
| 40                              | 57.86        | 0  | 21.45 |
| 60                              | 81.43        | 0  | 29.22 |
| 80                              | 94.29        | 0  | 39.41 |
| 120                             | 99.84        | 0  | 40.47 |

In Table 6.8 the results of chemical analyses of leach solution (Zn, Fe) and leach residue (S) for sphalerite mechanically activated for 150 min are summarized. During leaching in hydrogen peroxide no iron was detected in the solution. In accordance with eq. (6.12) the elemental sulfur in leach residues can be detected. Lotens and Wesker [6.80] found 54-60 % of elemental sulfur in their tests on leaching of sphalerite using  $H_2O_2$  as the oxidation agent.

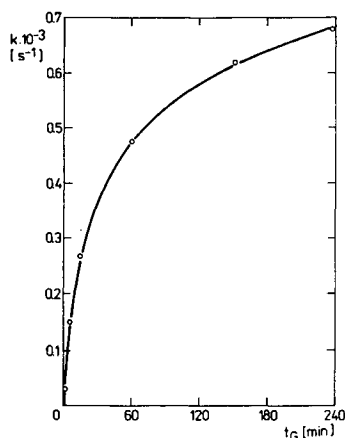


Fig. 6.22 The influence of time of mechanical activation,  $t_G$  on the rate constant of zinc leaching from  $ZnS$ ,  $k$ . Leaching agent:  $H_2O_2$  [6.79].

The recovery of zinc into the solution increases with grinding time. The leaching curves suggest that the rate of the process simultaneously increases as well. The dependence of the rate of leaching on grinding time is represented in Fig. 6.22. The rate constant is compared with the specific surface,  $S_A$ , of the ground samples of sphalerite in Fig. 6.23. One can conclude from this figure that the rate is a linear function of surface area from 0 to  $4\text{ m}^2\text{g}^{-1}$ . Such dependence is quite consistent with leaching theory. Nevertheless, rapid increase in the rate at  $S_A \geq 4\text{ m}^2\text{g}^{-1}$  is observed. There is practically no dependence on the surface area of the ground samples in this region. From the relationship between the rate constant of leaching,  $k$ ,

and specific surface,  $S_A$ , in this region, it follows that the structure of the solid phase also contributes to the leachability of the mechanically activated samples. In this case, disordering of the sphalerite structure, described above, could be important. The evidence for this structure sensitivity of the reaction of sphalerite with hydrogen peroxide is given in Fig. 6.23 where the dependence of the specific rate constant (i.e., related to surface area),  $k/S_A$  on the amorphization of sphalerite,  $A$ , which is a measure of the disorder of its structure, is plotted. However, if the rate constant divided by the effective surface area remained constant with respect to the applied energy during mechanical activation, the reaction rate would be insensitive to the structural imperfections [6.2].

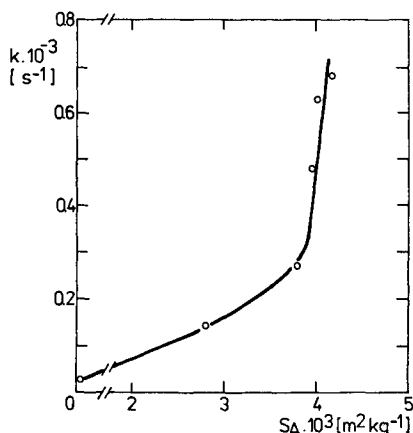


Fig. 6.23 The influence of surface area,  $S_A$  of mechanically activated ZnS on the rate constant of zinc leaching,  $k$ . Leaching agent:  $\text{H}_2\text{O}_2$  [6.79].

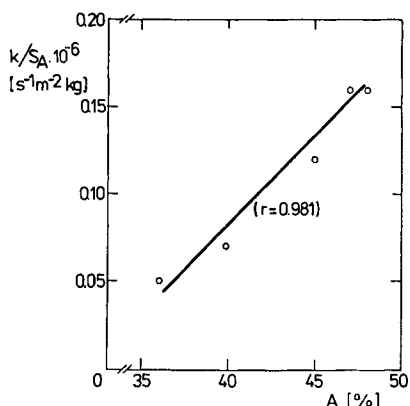


Fig. 6.24 The influence of amorphization,  $A$  on the ratio  $k/S_A$  for mechanically activated ZnS. Leaching agent:  $\text{H}_2\text{O}_2$  [6.79].

## 6.2. Acid non-oxidizing leaching

Among acid non-oxidizing leaching agents  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$  are frequently applied. The rate of leaching is usually low, especially in the case of  $\text{H}_2\text{SO}_4$ . A few sulfides, e.g. ZnS, NiS, CoS and FeS are soluble in dilute  $\text{H}_2\text{SO}_4$  solutions [6.4].

The acid non-oxidizing leaching of bivalent sulfides in  $H_2SO_4$  obeys the principal equation



The final products of reaction (6.14) are influenced by several factors, e.g. concentration of hydrogen ions or temperature. In some cases the formation of elemental sulfur can be observed.

### *Chalcopyrite $CuFeS_2$*

The first experiments with the leaching of mechanically activated  $CuFeS_2$  by means of sulfuric acid (in the absence of  $O_2$ ) were carried out by Gock [6.74]. He found that mechanical activation had a positive influence on the recovery of Cu and Fe into the solution. In the optimum experiment, the recovery of 42 % Fe and 21 % Cu was achieved after 120 minutes' leaching.

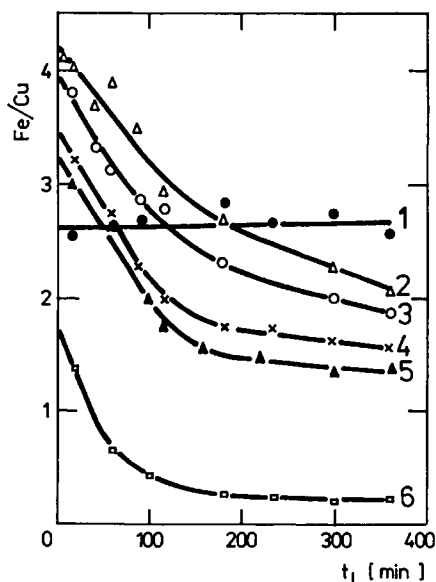


Fig. 6.25 Ratio Fe/Cu by leaching of mechanically activated  $CuFeS_2$ , time of vibration grinding: 1 - 0 min, 2 - 15 min, 3 - 30 min, 4 - 120 min, 5 - 150 min, 6 - 120 min and annealing by  $600^\circ C$ . Leaching agent: HCl [6.81].

Tkáčová et al. [6.81] investigated the leaching of a series of mechanically activated  $CuFeS_2$  samples in HCl. They found that the leaching proceeds very rapidly at the beginning and subsequently slows. The initial high rate of extraction might be due to dissolution of the surface layers formed by mechanochemical oxidation. Afterwards the leaching attacks the plastically deformed cores of the particles, the defectiveness of which increases with the time of mechanical activation. The dependence of the ratio Fe/Cu in leach on the time of mechanical activation is represented in Fig. 6.25. For mechanically activated samples we can observe that this ratio is inclined to approach unity indicating that the rate of transport of Fe and Cu into leach are comparable for long activation and leaching processes. After thermal

pretreatment of both non-activated and activated samples the dissolution of copper into solution prevails. This phenomenon is due to the formation of new phases at temperatures above 500°C and the translational shift in sublattice of chalcopyrite sulfur accompanied with passage of the Cu and Fe ions from tetrahedral to octahedral positions [6.82].

In paper [6.83] the  $H_2SO_4$  leaching of the  $CuFeS_2$  ground in a planetary mill is described and the results are represented in Fig. 6.26. As in the case of HCl application, the course of  $H_2SO_4$  leaching of chalcopyrite is affected by disordering of its structure.

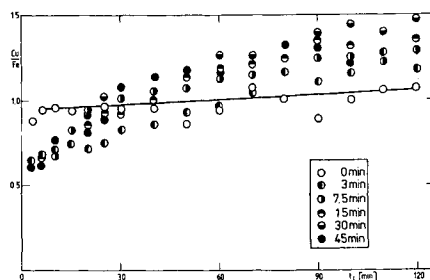


Fig. 6.26 Ratio Cu/Fe by leaching of mechanically activated  $CuFeS_2$ , time of planetary grinding 3 - 45 min. Leaching agent:  $H_2SO_4$  [6.83].

### Sphalerite ZnS

Li Ximing et al. studied sphalerite leaching in the acid medium of  $H_2SO_4$  [6.84 - 6.85]. The activation of mineral was performed in attrition mill. The observed effect of particle size diminution as well as solid state disordering led to the enhancement of zinc leaching rate. They also performed experiments aimed at annealing defects in the sphalerite by heating the mineral at 500°C in nitrogen atmosphere. The results of this was decreased reactivity in comparison with the non-activated mineral (Fig. 6.27).

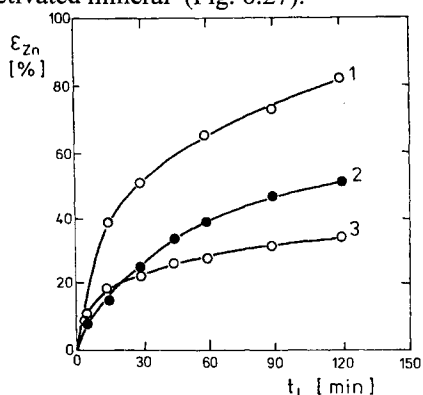


Fig. 6.27 The influence of leaching time,  $t_L$  on zinc recovery,  $\varepsilon_{Zn}$  for sphalerite, 1 - mechanically activated ZnS for 60 min, 2 - mechanically activated ZnS for 60 min and annealed, 3 - non-activated ZnS. Leaching agent:  $H_2SO_4$  [6.84].

Leaching of sphalerite by dilute  $H_2SO_4$  is governed by the equation



Iron can substitute for zinc in sphalerite structure and in  $\text{H}_2\text{SO}_4$  solubilizes along with zinc in form of sulfates.

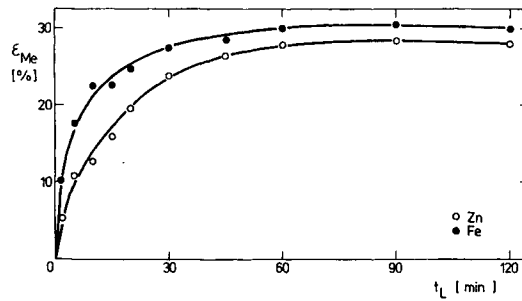


Fig. 6.28 The influence of leaching time,  $t_L$  on zinc and iron recovery,  $\epsilon_{Me}$  for non-activated ZnS. Leaching agent:  $\text{H}_2\text{SO}_4$  [6.83].

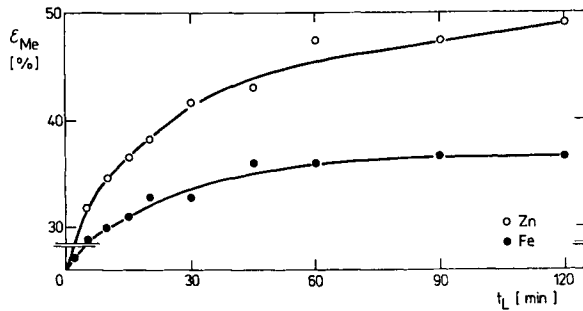


Fig. 6.29 The influence of leaching time,  $t_L$  on zinc and iron recovery,  $\epsilon_{Me}$  for ZnS mechanically activated for 5 min. Leaching agent:  $\text{H}_2\text{SO}_4$  [6.83].

In Fig. 6.28 - 6.29 the recoveries of both metals into solution for non-activated and 5 min activated sphalerite are plotted against leaching time. Mechanical activation accelerates the recoveries of both metals. From curves one can conclude that selectivity of leaching is also influenced. The selectivity defined as Zn/Fe ratio for different activated samples is plotted in Fig. 6.30.

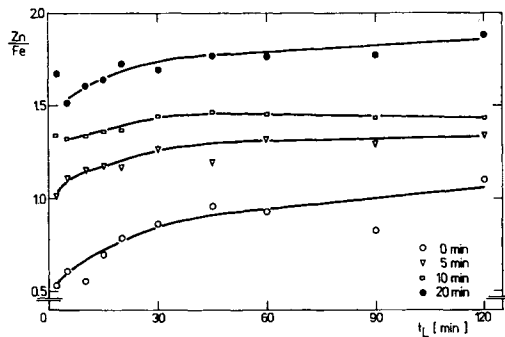


Fig. 6.30 The influence of leaching time,  $t_L$  on selectivity of leaching, Zn/Fe of mechanically activated ZnS. Time of mechanical activation: 5 - 20 min, leaching agent:  $\text{H}_2\text{SO}_4$  [6.83].

At present there are very few publications dealing with leaching of tetrahedrite in aqueous medium though as early as 1914, Nishihara published his results concerning the leachability of tetrahedrite ore [6.86]. He found that this mineral was relatively soluble in acidified ferric sulfate solution. The leaching of tetrahedrite was also studied in papers [6.87 - 6.92] in which acid oxidative leaching, bacterial leaching and pressure leaching were all applied.

The first trials to utilize mechanical activation for the intensification of acid non-oxidative leaching of tetrahedrite was described in papers [6.93 - 6.95]. In Fig. 6.31 the relationships between the rate constant of copper (1) and antimony (2) leaching in  $\text{H}_2\text{SO}_4$  medium vs. grinding time of tetrahedrite in a planetary mill are plotted. The rate of dissolution of copper is higher than that of antimony and may be due to the higher mobility of copper in the structure of tetrahedrite [6.96]. The effect of grinding is significant and increases up to  $t_{\text{PM}} = 10$  min after which time a decrease in the rate constant of leaching can be observed.

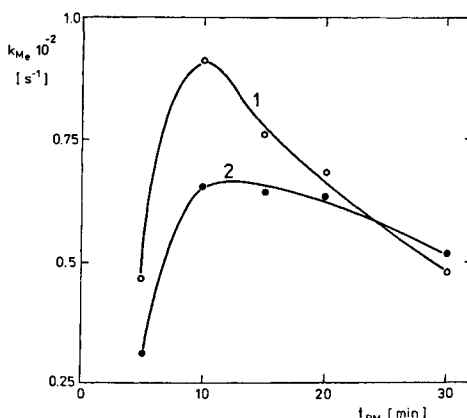


Fig. 6.31 The influence of time of mechanical activation,  $t_{\text{PM}}$  on the rate constant,  $k_{\text{Me}}$  of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  leaching, 1 - copper, 2 - antimony, leaching agent:  $\text{H}_2\text{SO}_4$  [6.94].

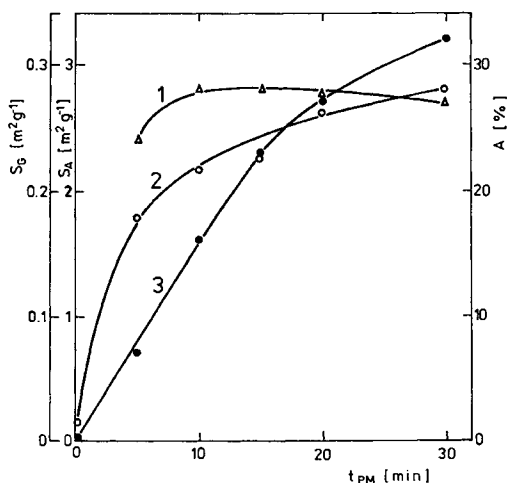


Fig. 6.32 The influence of time of mechanical activation,  $t_{\text{PM}}$  on physico-chemical changes of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , 1 - specific granulometric surface,  $S_G$ , 2 - specific adsorption surface,  $S_A$ , 3 - amorphization,  $A$  [6.94].

The values of granulometric surface area increase with grinding time up to 10 minutes (Fig. 6.32). At higher values of  $t_{PM}$  a stagnation and a decrease of  $S_G$  appears which is a symptom of particle aggregation and formation of agglomerates (see Chapter 3).

A comparison of Figs. 6.31 and 6.32 with each other shows that the course of leaching is significantly influenced by the surface changes caused by the mechanical activation of tetrahedrite. These changes are accompanied by a high degree amorphisation of the structure (Fig. 6.32, curve 3). The above effects arise immediately after a short grinding time owing to the low hardness and brittleness of  $Cu_{12}Sb_4S_{13}$  and confirm the considerations about the influence of mechanochemical effects on the course of leaching that have been presented in the preceeding paragraphs.

From the view-point of technological processes subsequent to leaching, the selectivity of the process, i.e. the solubilisation of useful components (Cu, Sb) compared to non-useful components (Fe), is important. The selectivity of leaching has been defined by the expression  $(\epsilon_{Cu} + \epsilon_{Sb})/\epsilon_{Fe}$  in this case. The dependence of this quantity on the time of mechanical activation is given in Fig. 6.33. Clearly, the selectivity of the process increases with leaching time. The influence of the mechanical activation is also significant with selectivity increasing up to 10 min grinding, beyond which grinding time become insignificant, probably due to agglomeration effects.

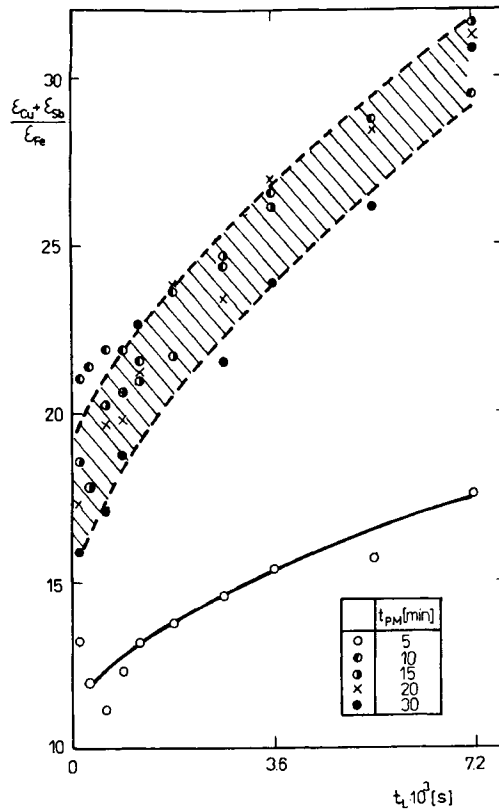
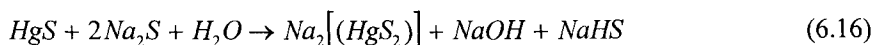


Fig. 6.33 The influence of time of leaching,  $t_L$  on selectivity of leaching of  $Cu_{12}Sb_4S_{13}$ ,  $(\epsilon_{Cu} + \epsilon_{Sb})/\epsilon_{Fe}$  mechanically activated for time  $t_{PM}$  [6.93].

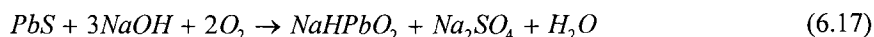
### 6.3. Alkaline leaching

Alkaline reagents, especially the strong bases such as hydroxides and sulfides of alkali and alkaline earth metals, can react with sulfides in two ways [6.97 - 6.98]

- by simple leaching of soluble sulfides



- by oxidation with oxygen or another oxidizing agent



in which sodium plumbite is  $\text{NaHPbO}_2$  soluble.

Treating sulfides by simple alkaline leaching is obviously limited to a very few minerals, such as those of Sb, As, Sn and Hg. The leach solutions invariably contain hydro- and polysulfides and oxidized sulfur compounds such as thionates and thiosulfates, particularly if they are in contact with air.

#### ***Stibnite $\text{Sb}_2\text{S}_3$***

The sulfides of alkaline metals can react with stibnite to give soluble complex salts [6.97, 6.99 - 6.100]



or



The salts are inclined to hydrolyze and  $\text{SH}^-$  ions are produced. If the pH value of the solution decreases, hydrogen sulfide is set free and the sulfide is taken into solution. Therefore, a weakly alkaline medium (e.g. NaOH) is necessary for preserving the solubility of these complex compounds.

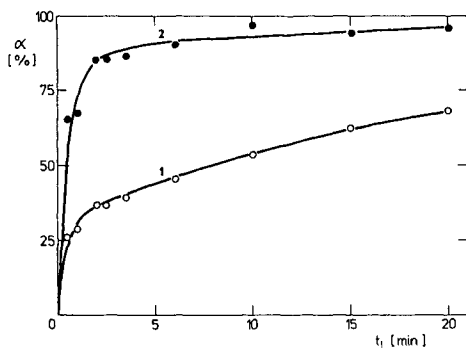


Fig. 6.34 Influence of leaching time,  $t_L$  on the recovery of antimony,  $\alpha$ : 1 – non-activated  $\text{Sb}_2\text{S}_3$ , 2 -  $\text{Sb}_2\text{S}_3$  activated for 20 min, leaching agent:  $\text{Na}_2\text{S} + \text{NaOH}$  [6.101].

In Fig. 6.34 the recovery of antimony into solution at 20°C is plotted against leaching time. If we compare non-activated sample (curve 1) with the sample mechanically activated for 20 min (curve 2), we observe that the mechanical activation positively affects the recovery of antimony and the rate of leaching. After 20 min leaching, 96 % of the antimony is solubilized from the activated stibnite whereas only 68 % was solubilized from untreated stibnite. Furthermore, the rate of leaching, as characterized by the ratio of the rate constants of the activated sample and standard, increased about ten fold.

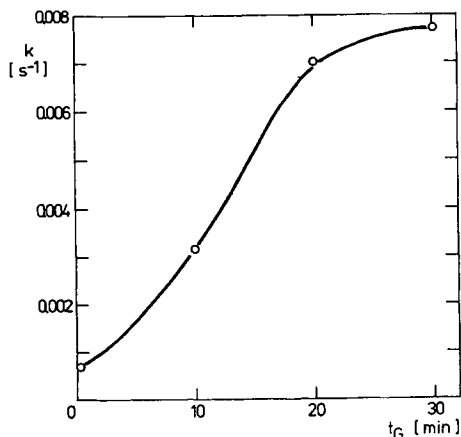


Fig. 6.35 Influence of the time of mechanical activation,  $t_G$  on the rate constant of antimony leaching,  $k$  for  $Sb_2S_3$ , leaching agent:  $Na_2S+NaOH$  [6.101].

The dependence of the leaching rate constant on the time of mechanical activation is represented in Fig. 6.35 and shows that activation accelerates leaching for all grinding times. The sigmoid form of the relationship with rapid increase in values  $k$  at the beginning and retardation at higher time of grinding indicates a dependence on the change in solid state properties of mechanically activated samples.

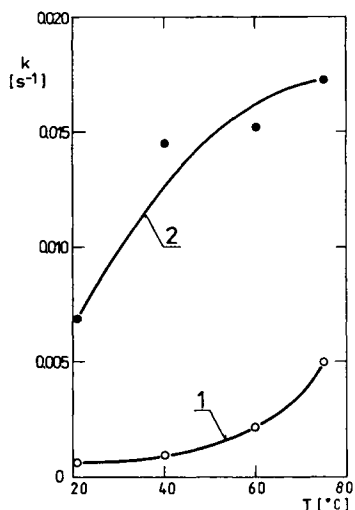


Fig. 6.36 Influence of reaction temperature,  $T$  on the rate constant of antimony leaching,  $k$  for  $Sb_2S_3$ , 1 - non-activated sample, 2 - sample activated for 20 min, leaching agent:  $Na_2S+NaOH$  [6.101].

The determination of temperature sensitivity of leaching is a contribution to elucidation of the mechanism of the process. The dependance of the rate constant  $k$  on leaching temperature is represented in Fig. 6.36 for non-activated stibnite as well as for stibnite activated for 20 min. While the dependence obtained for the non-activated sample (1) exhibits exponential character in accordance with the Arrhenius law, the course observed for the activated sample (2) at higher temperatures is near linear. The different temperature dependence observed for the activated sample is to be explained by the fact that the grains in this sample are present in the form of agglomerates. Thus they are less accessible to the molecules of lixiviant even if their surface and bulk disordering is greater when compared with a non-activated sample. This is confirmed by the Arrhenius plots in Fig. 6.37 which show a fall in experimental activation energy of leaching from the  $28 \text{ kJ mol}^{-1}$  for the non-activated sample to a value of  $13 \text{ kJ mol}^{-1}$  for the activated sample. The value calculated for the non-activated  $\text{Sb}_2\text{S}_3$  can be attributed to a process in which the rate-determining step is chemical reaction [6.38]. The inaccessibility of internal surface of the aggregates formed by mechanical activation causes a decrease in temperature sensitivity such that the activation energy approaches the range typically observed for a process where diffusion is rate-determining. Because of the absence of a solid reaction product we may assume that self diffusion in the bulk of stibnite could be the rate determining step in this case.

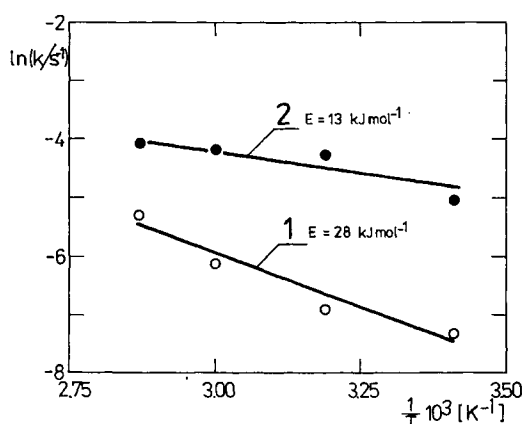


Fig. 6.37 Arrhenius plot for  $\text{Sb}_2\text{S}_3$  leaching, 1 - non-activated sample, 2 - sample activated for 20 min, leaching agent:  $\text{Na}_2\text{S}+\text{NaOH}$  [6.101].

The samples of  $\text{Sb}_2\text{S}_3$  leached for 5 and 20 min at  $20^\circ\text{C}$  were subjected to morphological investigation by scanning electron microscopy. The scanning electron micrographs are presented in Fig. 6.38 A-D. The residual stibnite exhibits a laminated structure with the weaker bonding between layers causing perfect cleavability of the mineral [6.102]. The smallest grains are the first to react in the course of leaching at laboratory temperature (Fig. 6.38A) and the compact structure of the larger grains simultaneously starts to disintegrate. At lower temperature, the disintegration predominantly proceeds in layers corresponding to the perfect cleavage plane (010) pertaining to weak bonds of the van der Waals type [6.102]. Besides peeling of whole layers we can also observe pits which occur at surface dislocations (Fig. 6.38B). At higher temperatures the disintegration also proceeds in the direction perpendicular to parallel planes which is shown by the increasing number of cracks (Fig. 6.38C - 6.38D).

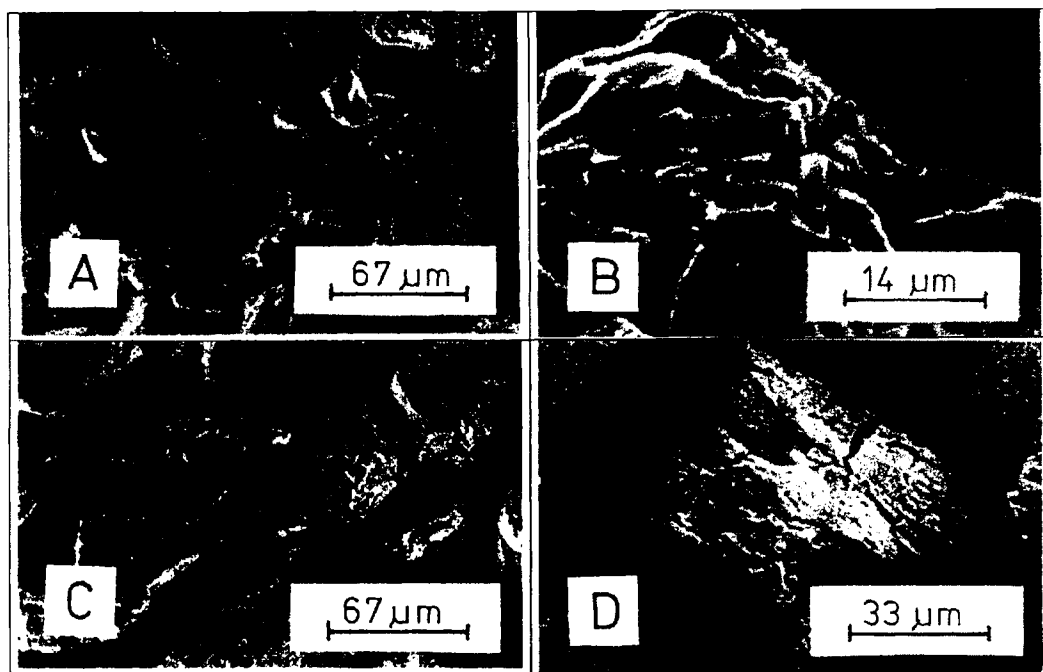


Fig. 6.38 Scanning electron micrographs of  $\text{Sb}_2\text{S}_3$  after leaching. Leaching conditions: A, B :  $T = 20^\circ\text{C}$ ,  $t_L = 20$  min; C, D:  $T = 60^\circ\text{C}$ ,  $t_L = 5$  min [6.101].

#### *Tetrahedrite $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$*

Tetrahedrites represent the important source of copper (40-46 %) and antimony (27-29 %) and are also of interest due to their content of silver and mercury. Alkaline leaching of tetrahedrite in solution of  $\text{Na}_2\text{S}$  gives a soluble complex salts of antimony and mercury. The reaction chemistry between sodium sulfide and tetrahedrite is described in Chapter 8.

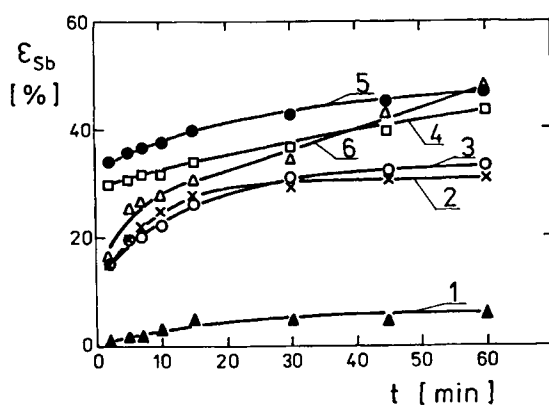


Fig. 6.39 Recovery of antimony into leach,  $\epsilon_{\text{Sb}}$  vs. time of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  leaching,  $t$ . Mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, 4 - 15 min, 5 - 20 min, 6 - 30 min. Leaching agent:  $\text{Na}_2\text{S} + \text{NaOH}$  [6.103].

Figures 6.39-6.40 represent the leaching plots for antimony and mercury as a function of time. It is clear from the plots that the mechanical activation of tetrahedrite accelerates the leaching of both metals.

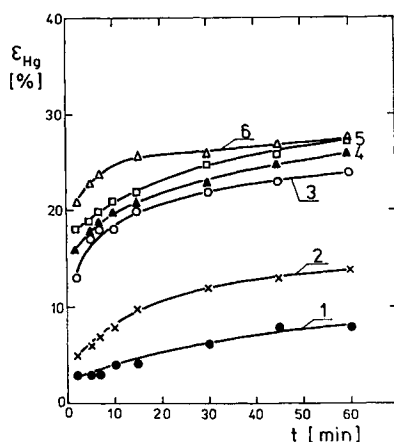


Fig. 6.40 Recovery of mercury into leach,  $\epsilon_{\text{Hg}}$  vs. time of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  leaching,  $t$ . Mechanical activation: 1 - 0 min, 2 - 5 min, 3 - 10 min, 4 - 15 min, 5 - 20 min, 6 - 30 min. Leaching agent:  $\text{Na}_2\text{S}+\text{NaOH}$  [6.103].

A sample of tetrahedrite with time of mechanical activation equal to 30 min was used to investigate the temperature sensitivity of antimony and mercury leaching for the temperature region 25-90°C. An Arrhenius treatment of the leaching plots for both metals is presented in Fig. 6.41. The linear nature of the graphs indicate that the mechanism of antimony and mercury leaching did not change in the investigated temperature interval. The calculated activation energies,  $E = 7 \text{ kJmol}^{-1}$  for mercury and  $E = 33 \text{ kJmol}^{-1}$  for antimony show that the rate determining step of the leaching reaction was diffusion and mixed diffusion/chemical control for Hg and Sb respectively [6.104].

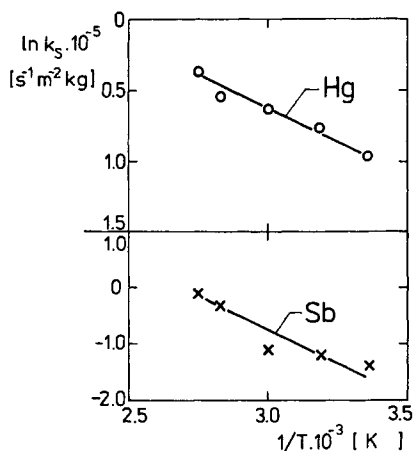


Fig. 6.41 Arrhenius plots for  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  leaching, mechanical activation: 30 min, leaching agent:  $\text{Na}_2\text{S}+\text{NaOH}$  [6.103].

## Enargite $\text{Cu}_3\text{AsS}_4$

Enargite  $\text{Cu}_3\text{AsS}_4$  belongs to a group of minerals with very low extractibility of copper. By Christoforov [6.105] it was stated that the order of various sulfides leachability was



Both acid [6.89, 6.106] and ammonia [6.107] leaching were examined for copper extraction, however, these processes were not selective because the arsenic passed into solution with the copper.

On the other hand, the leaching of enargite in alkaline sodium sulfide offers the possibility of selective leaching. The chemistry of selective solubilization of arsenic can be described by the simplified equation



Copper in the form of  $\text{Cu}_2\text{S}$  is the solid reaction product and arsenic is selectively extracted into solution and can appear in pentavalent or trivalent forms of thioarsenic compounds according to the reaction conditions [6.108]. Mechanical activation has been shown to enhance the rate of arsenic extraction [6.109 - 6.110].

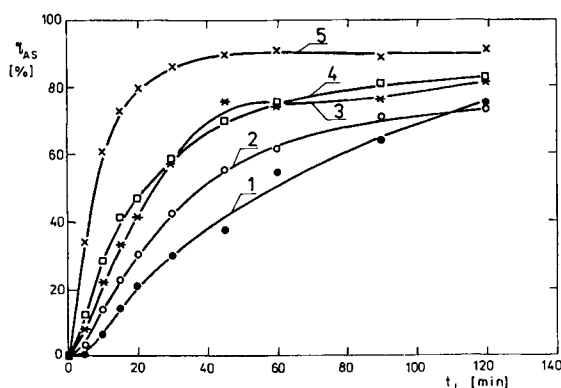


Fig. 6.42 Arsenic recovery,  $\eta_{\text{As}}$  vs. leaching time,  $t_L$  for non-activated  $\text{Cu}_3\text{AsS}_4$ .  $\text{Na}_2\text{S}/\text{NaOH}$  ratio: 1 = 20, 2 = 15, 3 = 10, 4 = 5, 5 = 2 [6.110].

Fig. 6.42 represents the recovery of arsenic to solution for an as-received sample as a function of leaching time for various  $\text{Na}_2\text{S}/\text{NaOH}$  ratios. From these leaching curves it can be seen that changing the ratio has a major effect on the As extraction of enargite. An arsenic solution recovery of 91 % can be obtained under optimum conditions for a leaching time of 60 min. The most efficiency results were obtained with leaching solution of the ratio  $\text{Na}_2\text{S}/\text{NaOH} = 2$ .

This ratio was verified for different concentrations of  $\text{Na}_2\text{S}$  and  $\text{NaOH}$ . The recovery of arsenic in leach,  $\eta_{\text{As}}$  after leaching for 120 min is quoted in Table 6.9.

Table 6.9 Recoveries of arsenic,  $\eta_{As}$  from  $Cu_3AsS_4$  for different  $Na_2S$  and  $NaOH$  concentrations [6.110]

| $Na_2S$ ( $g\ l^{-1}$ ) | $NaOH$ ( $g\ l^{-1}$ ) | $\eta_{As}$ (%) |
|-------------------------|------------------------|-----------------|
| 40                      | 20                     | 11.10           |
| 60                      | 30                     | 44.74           |
| 80                      | 40                     | 86.48           |
| 100                     | 50                     | 91.27           |

From the view-point of process selectivity recoveries of arsenic and copper are given in Table 6.10 as a function of leaching time  $t_L$ . Clearly, the leaching of arsenic may be regarded as selective with the average  $< 0.5$  % of copper passing into solution.

Table 6.10 Recoveries of arsenic,  $\eta_{As}$  and copper,  $\eta_{Cu}$  vs. leaching time,  $t_L$  for  $Cu_3AsS_4$ .  
Leaching agent:  $100\ g\ l^{-1}\ Na_2S + 50\ g\ l^{-1}\ NaOH$ , [6.110]

| $t_L$ (min) | $\eta_{As}$ (%) | $\eta_{Cu}$ (%) |
|-------------|-----------------|-----------------|
| 5           | 34.08           | 0.78            |
| 10          | 60.74           | 0.58            |
| 15          | 72.94           | 0.46            |
| 20          | 80.01           | 0.46            |
| 30          | 86.08           | 0.49            |
| 45          | 89.62           | 0.39            |
| 60          | 90.73           | 0.32            |
| 90          | 88.75           | 0.10            |
| 120         | 91.27           | 0.32            |

The leaching conditions used for the as-received sample were also applied for sample activated in an attritor for 60 minutes. The resulting recoveries are summarized in Table 6.11 and confirm the favourable influence of mechanical activation on the recovery of arsenic in the leach liquor. 96 % recovery of arsenic in the leach solution is obtained for a leaching time of 10 min by using mechanically activated sample. On the other hand, the value obtained for as-received sample is only 61 % As.

Table 6.11 Recoveries of arsenic,  $\eta_{As}$  vs. leaching time,  $t_L$  for  $Cu_3AsS_4$  [6.110]

| $t_L$ (min) | $\eta_{As}$ (%)      |                              |
|-------------|----------------------|------------------------------|
|             | Non-activated sample | Mechanical activation 60 min |
| 5           | 34.08                | 91.02                        |
| 10          | 60.74                | 96.43                        |
| 15          | 72.94                | 91.44                        |
| 20          | 80.01                | 88.11                        |
| 30          | 86.08                | 87.28                        |

X-ray photoelectron spectra of enargite samples support the efficiency of alkaline leaching. Arsenic is being no longer present in surface of enargite after leaching. The presence of  $Fe(3p)$  is a consequence of iron wear by grinding (Fig. 6.43).

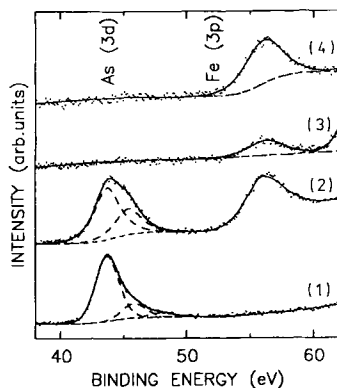


Fig. 6.43 XPS As (3d) and Fe (3p) spectra of  $\text{Cu}_3\text{AsS}_4$ : 1 - as received sample, 2 - sample mechanically activated for 60 min, 3 - sample mechanically activated for 60 min and subsequent leached, 4 - solid residue after mechanical activation, leaching and washing with  $\text{H}_2\text{O}$ .

#### 6.4. Leaching of sulfides containing gold and silver

The most frequent sulfides in which gold and silver are present are pyrite, arsenopyrite and stibnite, other minerals, such as chalcopyrite, sphalerite and galena also contain small amounts of gold and silver.

Selezneva [6.111] claimed that the grinding of pyrite and arsenopyrite in a planetary mill lasting 20-40 seconds raised the extraction of gold by subsequent cyanide leaching from 77 % to 86 %. Further prolongation of mechanical activation made possible to increase the recovery of gold even to 90-94 %.

The sulfidic minerals which occur in the form of sulfosalts (proustite, pyrargyrite, tetrahedrite etc.) cause considerable problems in the leaching of silver. In this case, the classical cyanide leaching does not allow to extract more than 5-10 % Ag [6.112]. However, experiments involving mechanical activation of proustite  $\text{Ag}_3\text{AsS}_3$  and pyrargyrite  $\text{Ag}_3\text{SbS}_3$  have shown a significant improvement of leachability of these minerals [6.113 - 6.114].

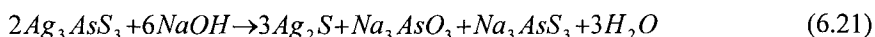
Smagunov [6.114] analyzed the influence of mechanical activation of proustite in different media on the extraction of silver. The results expressed by silver recovery during subsequent cyanidation are summarized in Table 6.12.

Table 6.12 Recovery of silver from mechanically activated proustite  $\text{Ag}_3\text{AsS}_3$  after 360 minutes cyanidation [6.114]

| Mechanical activation | Grinding medium      | $\varepsilon_{\text{Ag}}$ (%) |
|-----------------------|----------------------|-------------------------------|
| -                     | -                    | 1.5                           |
| 5                     | air                  | 15-18                         |
| 60                    | $\text{H}_2\text{O}$ | 70-75                         |
| 60                    | NaOH                 | 55-60                         |
| 60                    | $\text{FeCl}_3$      | 75-80                         |

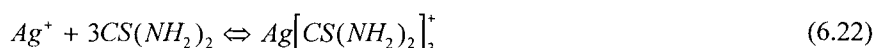
Only 1.5 % Ag was extracted from non-activated mineral after 6 hours cyanidation. X-ray phase analysis has shown that phase transformations take place in  $\text{Ag}_3\text{AsS}_3$  during activation

in air. During activation in water lasting 5-30 min proustite partially decomposes and completely decomposes to give metallic silver after 45 min activation. The following mechanochemical reaction takes place in the course of activation in NaOH



If the activation lasts longer, the arising acanthite ( $Ag_2S$ ) undergoes partial decomposition. As the case of activation in water metallic silver appears as a decomposition product. Activation in the presence of  $FeCl_3$  brings about amorphization of proustite and simultaneous formation of silver sulfide.

The acid non-cyanide leaching of silver from tetrahedrite mechanically activated in an planetary mill or an attritor was studied in papers [6.115 -6.117]. Thiourea,  $CS(NH_2)_2$  as an attractive alternative for NaCN stabilizes silver ions in solution as a complex [6.118 - 6.119] by the equation



Pesic and Seal [6.120] have stated that the dissolution of silver in thiourea also requires ferric ion as the oxidizing agent in the solution. The reported advantages of acidic thiourea solution over classical cyanide leaching are: low toxicity, faster dissolution rate and higher selectivity [6.121].

The mechanically activated samples of tetrahedrite were subjected to thiourea leaching and these results are summarized in Figs. 6.44 and 6.45. Under the activation and leaching conditions used the maximum recovery was achieved from the samples activated in a planetary mill [6.115]. In this case recovery of 48 % Ag was obtained for a sample ground for 45 min and leached for 120 min. The recoveries from the samples activated in an attritor were lower with < 30 % Ag recovery attained. The silver recoveries obtained for the “as received” sample (without mechanical pretreatment) were < 10 % Ag [6.122]. These results indicate that the disordering of the structure of tetrahedrite is a decisive process from the viewpoint of silver extraction.

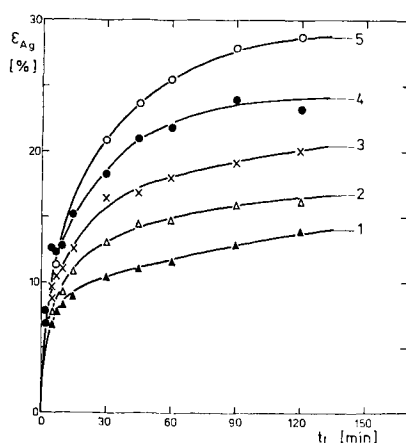


Fig. 6.44 Silver recovery,  $\epsilon_{Ag}$  vs. leaching time,  $t_L$ , for tetrahedrite mechanically activated in an attritor. Time of activation: 1 = 10 min, 2 = 20 min, 3 = 40 min, 4 = 80 min, 5 = 160 min, leaching agent:  $CS(NH_2)_2$  [6.115].

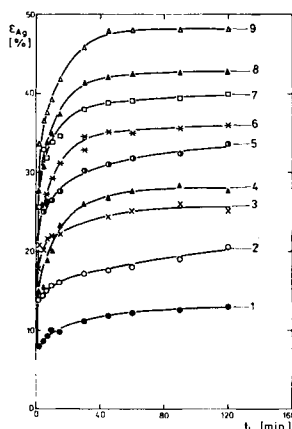


Fig. 6.45 Silver recovery,  $\varepsilon_{Ag}$  vs. leaching time,  $t_L$  for tetrahedrite mechanically activated in planetary mill. Time of activation: 1 = 2 min, 2 = 5 min, 3 = 10 min, 4 = 30 min, 5 = 15 min, 6 = 20 min, 7 = 60 min, 8 = 90 min, 9 = 45 min, leaching agent:  $CS(NH_2)_2$  [6.115].

Fig. 6.46 represents the quantitative relationship between rate of thiourea leaching and surface/bulk properties of the mechanically activated samples investigated. The rate constant has been correlated with the empirical coefficient  $S_A/(1-R)$ , which represents the surface/bulk disordering ratio for the mineral. The plot in Fig. 6.46 shows that the extraction of silver from tetrahedrite is a structure sensitive reaction. Simple proportionality expresses the equal influence of surface increase and volume disordering of the thiourea leaching of silver. An equal rate of leaching can be attained by mechanical activation either in an attritor (i.e. in a mill producing larger surface and smaller disordering in bulk), or in planetary mill (where the disordering in bulk is great and the formation of new surface is minor). This observation is also of prognostic character because it enables us to propose suitable grinding equipment according to the demand for fineness or reactivity of the solid substances.

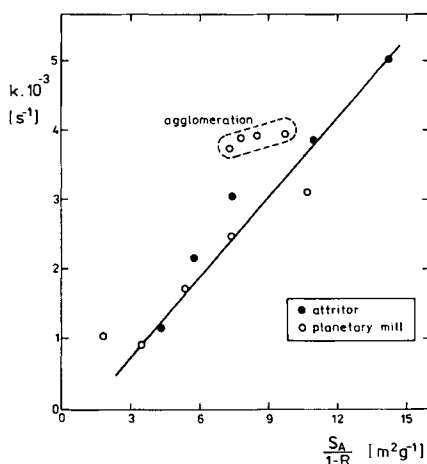
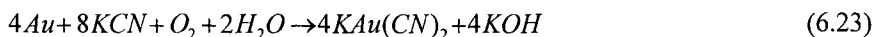


Fig. 6.46 Rate constant of silver leaching,  $k$  from tetrahedrite vs. surface/bulk disordering ratio,  $S_A/(1-R)$ ,  $S_A$  - specific surface area,  $R$  - disordering of tetrahedrite structure [6.115].

From the view-point of the extractibility of gold by cyanidation according to the classical Elsner equation



it is interesting that the rate of gold cyanidation increases in the presence of some sulfides. It can be assumed that microgalvanic cells of the type gold-sulfide arise, if the cathodic part is made up by sulfide. The increased surface of cathode is responsible for an increase in the rate of the electrochemical processes controlling the transfer of gold into the cyanide complex [6.123 - 6.124]. According to [6.125] the gold itself passes into KCN leach in 24 hours and its recovery amounts to 10 %. However, if gold is in contact with galenite, chalcopyrite or pyrite during leaching, its recovery reaches 67-91 %.

Varencova [6.126 - 6.127] investigated the system gold-pyrite-sodium cyanide from the electrochemical point of view. It has appeared that one of the possibilities of accelerating the rate of gold extraction is based on the control of electrochemical potential of the cathodic part of the cell. Pyrite was mechanically activated for 0.5-10 minutes and afterwards a paste electrode with surface ratio  $FeS_2 : Au = 10 : 1$  was made. The results of measurement of the electrode potential of  $FeS_2$  in NaCN solution are given for different activated times in Fig. 6.47. The potential of activated samples increases with the time of activation. At same time the rate of gold extraction grows (Tab. 6.13).

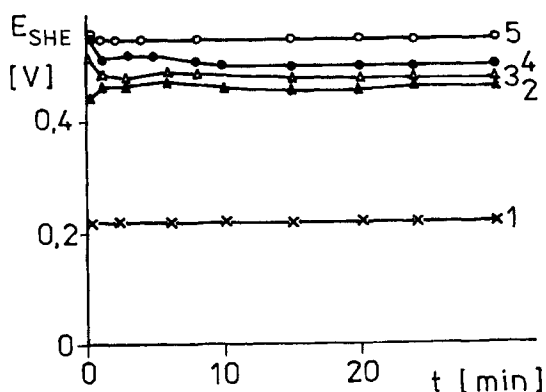


Fig. 6.47  $FeS_2$  electrode potential,  $E_{SHE}$  in NaCN solution vs. time,  $t$ . Time of mechanical activation: 1 - 0 min, 2 - 0.5 min, 3 - 2 min, 4 - 5 min, 5 - 10 min [6.127].

Table 6.13 Values of electrode potentials,  $E$  and rate of gold extraction,  $v_{Au}$  in the system Au- $FeS_2$ -NaCN as functions of the time of mechanical activation  $t_M$  [6.127]

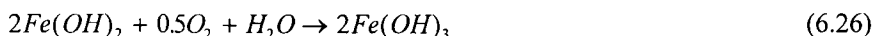
| $t_M$ (min) | $E^*$ (V) | $v_{Au}$ ( $mg\ cm^{-2}\ h^{-1}$ ) |
|-------------|-----------|------------------------------------|
| 0           | 0.20      | 0.75                               |
| 0.5         | 0.46      | 0.85                               |
| 2           | 0.47      | 1.85                               |
| 5           | 0.50      | 1.85                               |
| 10          | 0.55      | 2.05                               |

\* After 30 minutes contact with NaCN solution ( $1.5\ g\ l^{-1}$ )

The 100 % recovery of gold calculated on the basis of electrochemical measurements according to eq. (6.24) was achieved



If the galvanic cell Au-FeS<sub>2</sub>-NaCN works, the surface of pyrite gets covered by a precipitate in which the trivalent iron was identified. Varencova [6.127] alleges that the cathodic reaction proceeds in two steps



## 6.5. Electrochemical aspects of leaching of mechanically activated sulfides

The leaching of sulfides is governed by the laws of electrochemical processes the character of which is determined by the properties of aqueous solutions and solid phase. If a mixture of several sulfides is subjected to leaching, the so-called galvanic cells arise at the contact places between individual sulfides. In a cell comprising two sulfides with different values of electrode potential the mineral exhibiting lower potential shall dissolve more rapidly. After its consumption or passivation the mineral with higher value of potential starts to dissolve. The minerals with lower value of potential make up the anodic part of galvanic cell while the minerals with higher value of potential form its cathodic part. The difference between electrode potentials of a cell is the driving force of electrochemical processes.

The electrode potentials of some sulfides are given in Table 6.14.

Table 6.14 Electrode potentials, E of sulfides measured in 1N-KCl solution [6.128]

| Sulfide      | E (V) |
|--------------|-------|
| Marcasite    | 0.56  |
| Pyrite       | 0.44  |
| Chalcopyrite | 0.36  |
| Arsenopyrite | 0.35  |
| Bornite      | 0.32  |
| Pyrrhotite   | 0.30  |
| Galena       | 0.25  |
| Pentlandite  | 0.22  |
| Molybdenite  | 0.14  |
| Sphalerite   | 0.12  |

Sato [6.129] published the equation for electrode potential  $E_{MeS}$  in a system binary sulfide - metal ion - sulfide ion

$$E_{MeS} = E_{MeS}^0 + \frac{RT}{4F} \ln \frac{(a_{Me}^{2+})_L (a_S)_{MeS}}{(a_S^{2-})_L (a_{Me})_{MeS}} \quad (6.28)$$

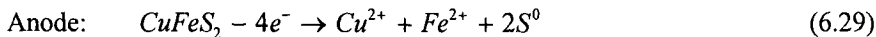
The value of  $E_{MeS}$  depends on activities (a) of metal and sulfide ions in the solid (MeS) and liquid (L) phase. If the liquid phase contains other components (acids, dissolved oxygen etc.) the relations in the system sulfide - aqueous solution of electrolyte are still more complicated [6.130].

Paper [6.131] is concerned with the influence of mechanical activation on the values of electrode potentials of  $FeS_2$ ,  $PbS$  and  $Cu_{12}Sb_4S_{13}$ . The results have shown in all cases that the deformation of mineral brings about a shift in potential to more negative values (in comparison with non-deformed minerals). The values of electrode potentials relax in the course of time. The process of relaxation of potential is dependent on the kind of electrolyte and extent of deformation of mineral surface as well as on the kind of mineral.

It may be assumed that the mechanical deformation gives rise to additional microcorrosion cells between activated and non-activated portions of the surface. A similar shift in the values of electrode potentials in the system  $ZnS/H_2SO_4$  was observed by Baláz et al. [6.132].

The investigation of galvanic effects at the contact of minerals is not a new topic. Gottschalk and Buchler [6.133] published the pioneer paper where they disclosed the important role of galvanic effects in oxidation of minerals in the open air. Dutrizac [6.3] investigated these effects in mixtures of sulfides while Berry and Mehta emphasized their significant influence on bacterial leaching [6.134 - 6.135].

One of these galvanic systems is the mixture chalcopyrite - pyrite which frequently occurs as a mineral association in nature. The decomposition of this mixture in acid medium can be described by the following equations



The electrochemical description of the decomposition by eqs. (6.29) and (6.30) is not perfect owing to complications due to secondary reaction, e.g.



or to depolarization processes, e.g.



Paper [6.136] is concerned with the influence of mechanical activation on behaviour of the galvanic cell chalcopyrite-pyrite with respect to the reaction involving copper dissolution in acid medium. The results are in terms of dependence of copper recovery in leach on leaching time present in Fig. 6.48.

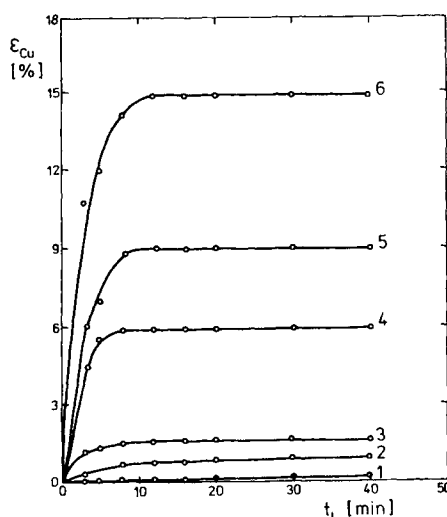


Fig. 6.48 Recovery of copper,  $\epsilon_{\text{Cu}}$  vs. leaching time,  $t_L$  for mechanical activation of  $\text{CuFeS}_2$  and mixture ( $\text{CuFeS}_2 + \text{FeS}_2$ ), 1 -  $\text{CuFeS}_2$ , 2 -  $\text{CuFeS}_2 + \text{FeS}_2$ , 3 -  $\text{CuFeS}_2^*$ , 4 -  $\text{CuFeS}_2 + \text{FeS}_2^*$ , 5 -  $\text{CuFeS}_2^* + \text{FeS}_2$ , 6 -  $(\text{CuFeS}_2 + \text{FeS}_2)^*$ , \* - mechanical activation 60 min, leaching agent:  $\text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4$  [6.136].

The presented results bring the following pieces of knowledge

- verification of galvanic effect for non-disordered samples,
- positive influence of separate disordering of anodic ( $\text{CuFeS}_2$ ) or cathodic ( $\text{FeS}_2$ ) part of galvanic cell on the rate of leaching and
- multiple intensification of the galvanic effect in the case of combined disordering in the mixture  $\text{CuFeS}_2\text{-FeS}_2$ .

Varencova [6.137] studied the galvanic cell chalcopyrite-pyrite-copper after its activation in a planetary mill. It has been found that  $\text{CuFeS}_2$  dissolves in acid medium better if it is in contact with metals exhibiting more negative electrode potential (Pb, Fe, Cu). This fact is likely to be due to the work of the galvanic cell. The measurement of electrode potentials has shown that the potential of  $\text{CuFeS}_2$  shifts to negative values and the potential of Cu to more positive values if the galvanic cell has been closed. This change in potentials may be a consequence of electrode polarization. The authors have stated that the mechanical activation has positive influence on the rate of electrochemical corrosion of components of the reaction mixture.

The system chalcopyrite-silver and tetrahedrite-silver [6.138 - 6.140] were investigated later. It has appeared that like in preceding cases, the electrode potentials of mechanically activated sulfides are shifted to more negative values. However, other applied method of mechanical activation - engraving of mineral surface by ruby cone - affects the rate of electrochemical processes only for a short time.

The study of galvanic effects in mechanically activated systems was not limited only to combinations with chalcopyrite. Paper [6.140] is concerned with the results of investigations of the rate of lead transfer from the system galena-pyrite-perchloric acid. As for mechanically non-activated mixture, the expected effect of accelerated transfer of lead from the  $\text{PbS-FeS}_2$

mixture into solution in comparison with PbS itself was confirmed (for comparison see Tab. 6.14). An interesting phenomenon was observed in context with these disordered minerals. It was revealed that the influence of FeS<sub>2</sub> disordering on the rate of lead transfer into solution was more significant than the influence of PbS disordering. The authors attributed these effects not only to surface increase of the minerals but also to number increase of the energetically excited sites in the zone of mechanical violation. The situation is illustrated in Fig. 6.49.

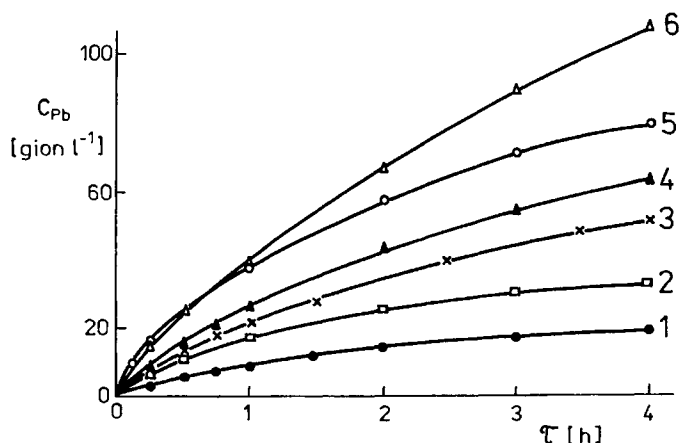
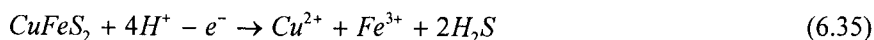


Fig. 6.49 Lead concentration,  $c_{Pb}$  vs. leaching time,  $\tau$  for PbS-FeS<sub>2</sub> system, 1 - without deformation, 2 - deformation of PbS in solution, 3 - deformation of FeS<sub>2</sub> in solution, 4 - deformation of PbS on air, 5 - deformation of FeS<sub>2</sub> on air, 6 - common deformation of FeS<sub>2</sub> and PbS on air [6.140].

Recently the method of cyclic voltammetry was recommended for characterizing the surface of mechanically activated sulfides in some electrochemical papers [6.141 - 6.143]. It has appeared in the electrochemical experiments that the polarization of the mineral electrode at the anodic (cathodic) side gives rise to the current peaks corresponding to oxidation (reduction) on the surface of mineral. The merit of cyclic voltammetry consists in possibility of studying the redox behaviour within a wide range of potentials as well as in registration of leaching intermediates.

Some cyclic voltammograms of CuFeS<sub>2</sub> taken in the medium of H<sub>2</sub>SO<sub>4</sub> with the samples mechanically activated for 5 and 15 min are presented in Fig. 6.50 (the dashed line corresponds to the non-activated mineral). It was observed that activation raised the electrochemical activity. The current corresponding to the anodic leaching of copper



increased for an activated sample activated for 5 min 10-times and for an sample activated for 15 min 40-times while the cathodic peak of electric current corresponding to reduction of the oxidized copper according to eq. (6.36)



increased 58-times and 80-times, respectively [6.141].

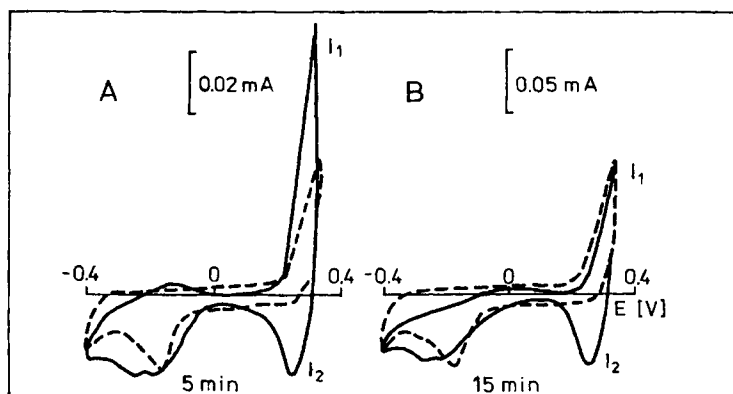


Fig. 6.50 Cyclic voltammograms of  $\text{CuFeS}_2$ , time of mechanical activation: A - 5 min, B - 15 min, interrupted line = non-activated sample [6.141].

The cyclic voltammograms of mechanically activated  $\text{ZnS}$  taken in the medium of  $\text{H}_2\text{SO}_4$  are represented in Fig. 6.51 [6.142]. Like in the case of chalcopyrite we can observe an increase in cathodic and anodic effects for activated samples. This fact is quite comprehensible because the current response of the mineral is dependent on surface area of this mineral [6.130] which is many times larger after 30 minutes' activation of sphalerite than it is in the case of non-activated sample.

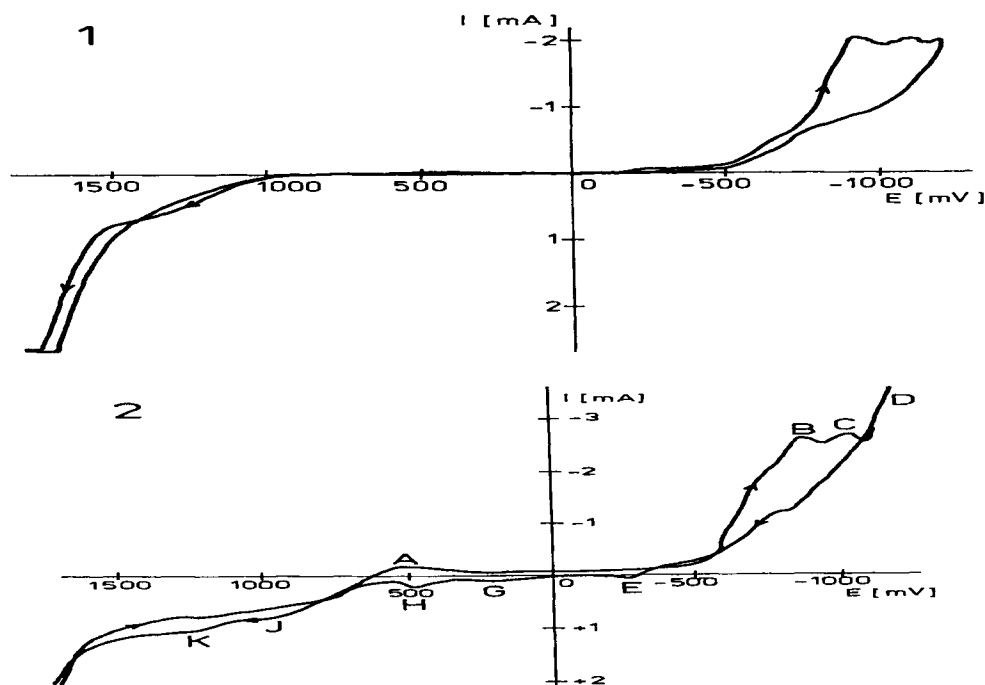


Fig. 6.51 Cyclic voltammograms of  $\text{ZnS}$ , time of mechanical activation: 1 - 0 min, 2 - 30 min [6.142].

The investigations of the surface changes in mechanically activated tetrahedrite are illustrated by cyclic voltammograms in Fig. 6.52. The voltammograms are shaped by the sum of effects in anodic ( $A_1$ ,  $A_2$ ) and cathodic ( $K_1$ ) region. These effects are much more significant in the case of mechanically activated samples. The magnitude of anodic effect  $A_1$  increases up to the time of mechanical activation equal to 10 min. At this time the specific surface area reaches the maximum value. The corresponding value of voltage  $E$  is near to the thermodynamic potential of copper oxidation to  $\text{Cu}^{2+}$  form. At higher times of mechanical activation effect  $A_1$  decreases in coherence with specific surface area decrease as a consequence of generation of agglomerates. Simultaneously, both anodic effect  $A_2$  as well coupled effect  $K_1$  increase. The position of  $A_2$  corresponds to antimony which was registered on the cyclic voltammogram of stibnite  $\text{Sb}_2\text{S}_3$  at equal potential under equal experimental conditions. We assume that the electrochemical activity of copper is screened by greater activity of antimony at higher values of potential. These data can be supported by differences in copper and antimony leaching from the same tetrahedrite in paper [6.94].

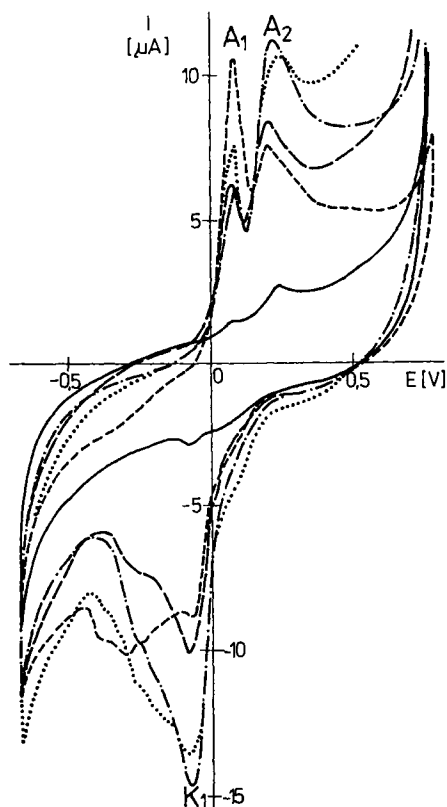


Fig. 6.52 Cyclic voltammograms of  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , time of mechanical activation: (—) 0 min, (----) 10 min, (.....) 15 min, (-.-.-) 20 min, (— —) 30 min [6.143].

The electrochemical aspects manifest themselves not only in the leaching process of sulfides but also during grinding. The wet grinding and application of iron balls bring about not only structural surface transformations of sulfides due to close contact between sulfide and grinding balls but also other effects. Adam [6.144] has alleged that wet grinding brings about a loss in weight of the balls as a consequence of corrosion and abrasion. However, it is difficult to estimate the relevance of this effect. Moreover, it is known that the sulfidic mineral

are nobler than most steels used for making the grinding balls and must therefore accelerate the anodic dissolution of metals [6.145]. The results of investigation of the wet grinding of pyrrhotite were used for designing the model of corrosion of grinding balls which is represented in Fig. 6.53. This model assumes the corrosion on the surface itself of grinding ball (A) and the corrosion in the course of interaction between grinding ball and sulfide [6.146]. These effects are likely still more significant in the case of mechanical activation in wet medium.

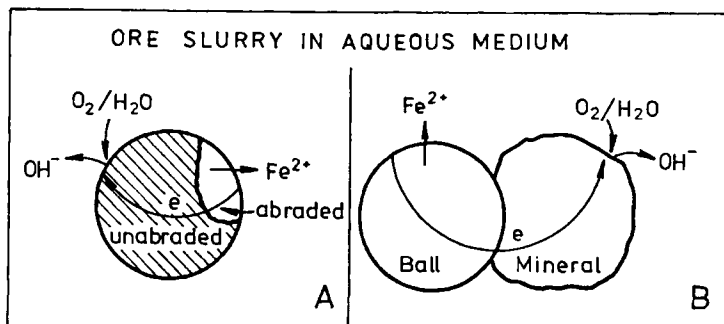


Fig. 6.53 Corrosion model for grinding balls, A - the differential abrasion cell, B - the ball - mineral cell [6.146].

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## **Chapter 7 INFLUENCE OF MECHANICAL ACTIVATION ON BACTERIAL LEACHING OF MINERALS**

**7.1. Chalcopyrite  $\text{CuFeS}_2$**

**7.2. Arsenopyrite  $\text{FeAsS}$**

**7.3. Pyrite  $\text{FeS}_2$**

**7.4. Sphalerite  $\text{ZnS}$**

**7.5. Tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$**

**7.6. References**

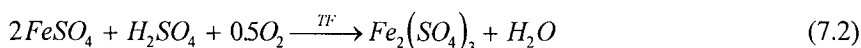
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Bacterial leaching is based on processes which occur at atmospheric pressure and low temperatures and are a part of the group of processes called biohydrometallurgy [7.1]. The leaching medium is primarily composed of diluted  $H_2SO_4$  and iron in both ferric and ferrous forms. There are also a range of organic compounds, such as organic acids, proteins and polysaccharides which may be products of bacterial metabolism [7.2 - 7.3].

The microorganism, *Thiobacillus ferrooxidans* (TF), the most frequently studied with respect to biohydrometallurgical treatment of sulfide-bearing minerals is a motile, non-sporeforming, gram-negative, rod-shaped bacterium [7.4]. TF is a chemolithotropic bacterium and oxidizes virtually all known metal sulfides to sulfate and elemental sulfur to sulfuric acid



Furthermore, it oxidizes ferrous ion to ferric ion



Eight electrons need to be removed from the sulfide species to form sulfate, and it has been suggested that the ferric ion reduction system of the bacteria is involved in this process [7.4]. The energy available (in form of electrons) from the above oxidation reactions is captured by TF in form of adenosine triphosphate, a high energy yield compound and used to supply its energy needs.

One of the drawbacks of the application of bacteria is the time of leaching which is typically days as opposed to minutes or hours for chemical leaching. Mechanical activation may give an increase in the rate of leaching due to an increase in the surface area where the attachment of bacteria can occur and by disordering the mineral structure resulting in an overall increase in reactivity.

The pioneer work in this field was published by Kulebakin et al. [7.5] who pointed out that the oxidizability of iron, antimony, copper, bismuth, molybdenum, zinc, nickel and lead sulfides in acid solutions with thion bacteria present is increased after grinding of these minerals.

## 7.1. Chalcopyrite $CuFeS_2$

Kulebakin, by studying the influence of mechanical activation on the leaching of a chalcopyrite flotation concentrate with bacteria TF observed the phase  $Fe_3(SO_4)_2 \cdot (OH)_5 \cdot 2H_2O$  on the surface of mineral which was a consequence of the effect of bacteria. He stated the mechanical activation accelerated both chemical and bacterial leaching of  $CuFeS_2$  [7.5].

The mechanism by which TF leaches the sulfide minerals is a complex one. It is assumed either that the bacteria acts directly, i.e. that its enzymes disrupt the crystal lattice of minerals or indirectly, where the products of the bacterial oxidation (i.e. ferric sulfate and sulfuric acid) attack the mineral. The mechanism of oxidation of chalcopyrite by TF can be described by the reactions [7.3]





where reactions (7.3) and (7.4) are typical examples of direct and indirect bacterial oxidation of chalcopyrite, respectively. The bacteria will reoxidize ferrous ions to ferric ions according to reaction (7.5) and elemental sulfur to sulfuric acid as shown in equation (7.6).

The leaching of the metal is achieved at a low pH and low to medium temperature. Chalcopyrite concentrates can be leached in acid aqueous solutions with TF at pH values of 1.5-3.0 and temperature 28°C [7.6].

In paper [7.7] the bacterial leaching of mechanically activated  $\text{CuFeS}_2$  mineral was studied using *Thiobacillus thiooxidans* (TT). According to the literature [7.8], these bacteria can oxidize elemental sulfur to sulfuric acid without intermediate oxidation products, but are unable to oxidize ferrous ions

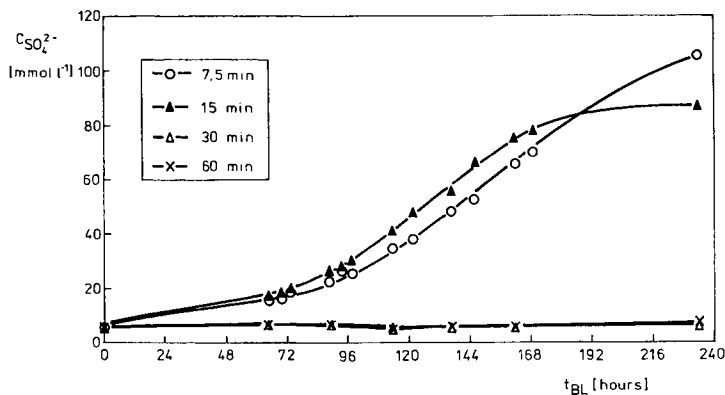


Fig. 7.1 Sulfate concentration,  $c_{\text{SO}_4^{2-}}$  vs. duration of bacterial leaching,  $t_{\text{BL}}$  for  $\text{CuFeS}_2$  mechanically activated for different times and chemically preleached to  $\varepsilon = 25\%$  Cu [7.7].

Samples of  $\text{CuFeS}_2$  ground for 3, 7.5, 15, 30 and 60 min were leached with ferric sulfate until a recovery of  $\varepsilon_{\text{Cu}} = 25\%$  was attained. The solid residues were filtered, dried and bacterially leached. The results of bacterial leaching are presented in Fig. 7.1. The bacterial leaching is effective only for the samples ground for 7.5 and 15 min. For the samples ground for a longer time, there does not appear to be any effect on bacterial leaching, this is consistent with the pH values of the medium (Table 7.1). However, for all grinding times, the oxidation process of non-sulfidic sulfur to sulfate by bacteria, i.e. Eq. (7.7), proceeds with minimum solubilization of copper and iron. This solubilization is a consequence of the chemical leaching of the mineral [7.3]. In this context, the zero content of soluble iron in the samples discussed is also remarkable.

Table 7.1 Rate constant,  $k$ , doubling time,  $t$ , in the exponential phase and the final pH value of the medium (initially pH 4.3) after 12 days bacterial leaching [7.7]. The doubling time is the time taken for the bacterial population to double; it is the natural logarithm of two (0.639) divided by the specific growth rate ( $\ln 2/k$ ).

| Grinding time<br>(min) | $k$<br>(hours <sup>-1</sup> ) | $t$<br>(hours) | pH   |
|------------------------|-------------------------------|----------------|------|
| 7.5                    | 0.0156                        | 44.4           | 1.05 |
| 15                     | 0.0170                        | 40.8           | 1.17 |
| 30                     | -                             | -              | 4.27 |
| 60                     | -                             | -              | 4.36 |

The differences between the results obtained for the two groups of ground samples (i.e. 7.5 and 15 min vs. 30 and 60 min grinding) can be explained by analysing the samples by X-ray photoelectron spectroscopy (XPS) [7.7]. The spectra for the sulfur S2p electrons of the samples ground for 7.5 min (1) and 60 min (3) and the same samples after chemical and bacterial leaching, spectra (2) and (4), are displayed in Fig. 7.2. The relative atomic concentrations of elements in the surface layer are summarized in Table 7.2. From the differences, the information about sulfur and iron is clearly important. The values found for sulfur correspond to the relationships represented in Fig. 7.1. The  $S^0/S^{2-}$  ratio is equal to 2.1 (0.51:0.24) for the 7.5 min sample and 2.9 (0.60:0.21) for the sample ground for 60 min.

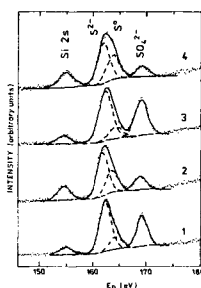


Fig. 7.2 Sulfur S2p spectra of  $CuFeS_2$  samples: 1 - mechanically activated for 7.5 min, 2 - sample 1 after combined chemical and bacterial leaching, 3 - mechanically activated for 60 min, 4 - sample 3 after combined chemical and bacterial leaching [7.7].

Examination of the 2p lines of iron shows a much larger effect due to grinding. Because of the overlap of the oxide (O) and sulfate ( $S^{6+}$ ) 2p lines for iron [7.9], their differentiation was not feasible. Therefore, only the ratio of Fe (oxide + sulfate) to iron in chalcopyrite is given in Table 7.2. While this ratio is 0.8 for the sample ground for 7.5 min, it is equal only to 0.4 (2.34:6.41) for the sample ground for 60 min. Thus, it can be seen that the sample ground for 60 minutes, which was bacterially inert, exhibits a two-fold deficit of surface iron when compared with the active sample (7.5 min). However, solution analysis of the leachate did not detect any soluble iron at all. We can assume that not only was there a change in surface heterogeneity of the 30 and 60 min ground samples, but that a change in the chemical composition of the surface had also occurred.

Hydroxide or hydroxysulfate compounds are likely to be formed with  $Fe(OH)SO_4$  present at chalcopyrite surface after long-term oxidation [7.10]. Removal of these compounds by bacterial leaching could be responsible for the increase in pH of the leach, as well as for the decrease in iron content in the solid phase (Table 7.2) for the samples ground for 30 min and

more. A negative influence of the fine fractions of other sulfides on bacterial oxidation kinetics was also observed for leaching pyrite by *Thiobacillus ferrooxidans* [7.11]. In order to explain these phenomena in more detail, a thorough study of the mechanisms of microbial adhesion at various surface area would be necessary.

Table 7.2 Relative atomic concentrations of elements in  $\text{CuFeS}_2$  samples, concentrations of elements are referred to copper concentration [7.7]

| Grinding time | Combined leaching | S                             |                            | Fe(oxide+sulfate) | Si   | N    |
|---------------|-------------------|-------------------------------|----------------------------|-------------------|------|------|
|               |                   | $\text{S}^{6+}/\text{S}^{2-}$ | $\text{S}^0/\text{S}^{2-}$ | Fe (chalcopyrite) |      |      |
| 7.5           | -                 | 0.56                          | 0.24                       | 6.15              | 0.63 | 0.00 |
| 7.5           | +                 | 0.26                          | 0.51                       | 4.84              | 2.17 | 2.25 |
| 60            | -                 | 0.64                          | 0.21                       | 6.41              | 0.68 | 0.00 |
| 60            | +                 | 0.29                          | 0.60                       | 2.34              | 1.55 | 0.35 |

## 7.2. Arsenopyrite $\text{FeAsS}$

By mechanical activation of arsenopyrite series of samples with different specific surface area and different lability of arsenic in the arsenopyrite structure were prepared. The results of bacterial leaching of these samples with TF are presented in Fig. 7.3. This information makes clear the dependence of the instantaneous rate of arsenic extraction into leach ( $v_0$ ) on the time of mechanical activation ( $t_M$ ). In agreement with literature [7.12] the process of arsenic solubilization may be described by the equation

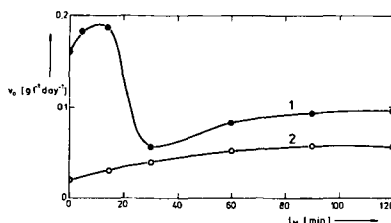
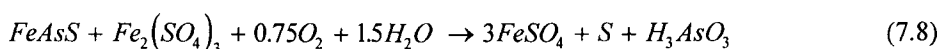


Fig. 7.3 Dependence of the instantaneous rate of arsenic leach,  $v_0$  vs. time of mechanical activation,  $t_M$  of  $\text{FeAsS}$ , 1 - bacterial leaching, 2 - sterile control.

The course of leaching (curve 1) can be divided into three regions:

1. In the initial 15 min the values of  $v_0$  increase up to  $0.185 \text{ g l}^{-1} \text{ day}^{-1}$  which results in 100 % recovery of As for the time of leaching  $t_L = 14$  days. The concentration of bacteria is  $10^9 - 10^8 \text{ cells ml}^{-1}$  in this region and a combined bacterial - chemical leaching takes place showing a positive influence due to mechanical activation.
2. Between 15 and 30 min, a rapid decrease in  $v_0$  occurs and concentration of living bacteria decreases to  $10^1 \text{ cells ml}^{-1}$ . The toxicity of arsenopyrite as substrate for bacteria increases with lability of arsenic in the  $\text{FeAsS}$  structure owing to more rapid passage of arsenic from the surface of mineral into the liquid phase. The higher concentrations of arsenic inhibit oxidation and lead to decay of bacteria. The number of bacteria decreases and their

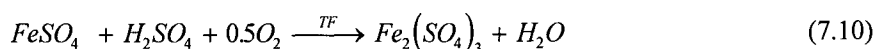
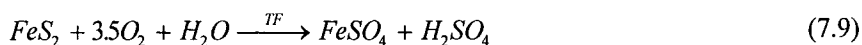
ability to regenerate  $\text{Fe}_2(\text{SO}_4)_3$  or oxidize elemental sulfur to soluble sulfate form diminish. All these factors contribute to the observed decrease in the rate of leaching.

3. Beyond 30 min the presence of living bacteria was not observed. The values of  $v_0$  increase with the time of mechanical activation and their course resembles the course of  $v_0$  in the control experiment (curve 2). In this case only chemical leaching with  $\text{H}_2\text{SO}_4$  which was a component of leaching agent took place. The higher values of curve 1 in this region can be explained by the fact that the  $\text{Fe}^{3+}$  ions introduced by inoculum were also present in the agent for bacteria leaching.

The results of the bacterial leaching of mechanically activated arsenopyrite enable the appreciate of some aspects of its mechanism. Combined bacterial/chemical leaching is operative at lower degrees of disordering of mineral, while only the chemical leaching is effective at higher degrees of disordering. The increase in surface area of mineral and the weakening of bonds by mechanical activation have favourable effect on the rate of chemical leaching. As for biological leaching, the toxicity of arsenic has to be eliminated by adaptation of bacteria and the mineral should be activated only below a certain degree of disordering of its structure. In paper [7.13] the conditions of selective leaching of arsenopyrite with *Thiobacillus ferrooxidans* partially adapted to high arsenic content in liquor were studied.

### 7.3. Pyrite $\text{FeS}_2$

The products of oxidation of pyrite by *Thiobacillus ferrooxidans* (TF) are sulfuric acid and ferric sulfate. The overall course of decomposition may be described in agreement with literature [7.14] as follows



Besides the direct oxidation of pyrite by the bacteria attached on the mineral surface (7.9), bacterial regeneration of the  $\text{Fe}^{3+}$  ions also takes place in the solution (7.10). The generated ferric sulfate is a strong oxidation agent and leaches pyrite according to equation (7.11). The elemental sulfur formed is bacterially oxidized according to (7.12).

In accordance with (7.10), the reaction of pyrite with bacteria TF involves the transfer of the  $\text{Fe}^{2+}$  ions into solution and the decrease in pH-value of the leach (Fig. 7.4).

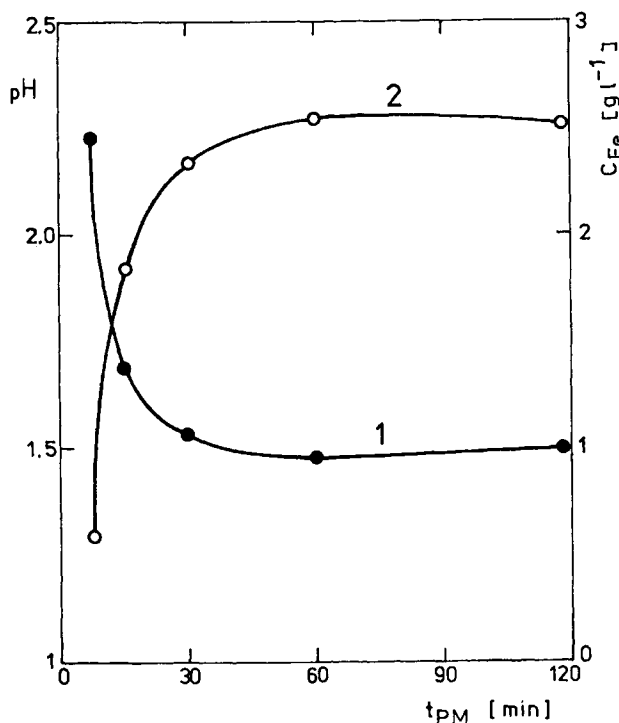


Fig. 7.4 Dependence of pH (1) and iron concentration,  $c_{Fe}$  (2) vs. time of mechanical activation,  $t_{PM}$  of FeAsS.

The plot in Fig. 7.5 shows the dependence of iron concentration  $c_{Fe}$  on the time of bacterial leaching  $t_{BL}$  for pyrite mechanically activated for different times. From these plots it is clear that the bacterial decomposition of pyrite is accelerated by the influence of mechanical activation. These curves exhibit a character analogous to that of the growth curve of bacteria. The maximum rate of bacterial leaching increases with mechanical activation and surface area and the values of  $t_{inf}$  shift to lower values ( $t_{inf}$  represents the time of bacterial leaching where the rate is maximum) (Fig. 7.6). It follows from this figure that the process of bacterial leaching is retarded when the specific surface of samples  $S_A > 0.5 \text{ m}^2 \text{ g}^{-1}$  (corresponding to  $t_{PM} > 30 \text{ min}$ ). The slowing of leaching is confirmed by the changes in the values of  $v_{max}$  and  $t_{inf}$ . In this region, pH-values of about pH 1.5 can also be observed (Fig. 7.4). It is stated in literature that the optimum pH for TF is pH 2.0 - 3.0 [7.15]. The variation of the solution concentration of iron on the same figure indicates that the process of leaching practically comes to a standstill.

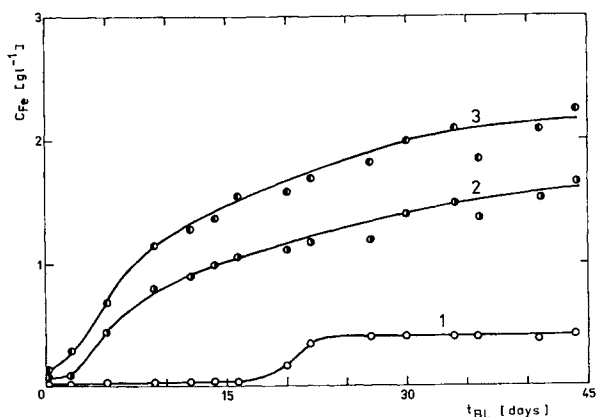


Fig. 7.5 Variation of iron concentration,  $c_{Fe}$  with time of bacterial leaching,  $t_{BL}$  of  $FeS_2$ .

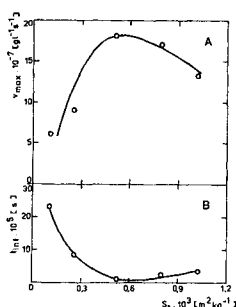


Fig. 7.6 Dependence of the maximum rate of iron,  $v_{max}$  (A) and the inflex point,  $t_{inf}$  (B) of bacterial leaching curves on the surface area  $S_A$  of mechanically activated  $FeS_2$ .

The retardation of bacterial oxidation can be explained by a change in the mechanism of leaching (eqn. 7.9 - 7.12) and changing disordering in the pyrite structure caused by mechanical activation.

A coating of elemental sulfur on the surface of fine pyrite particles arises during the course of chemical oxidation (eqn. 7.11) and the pH decreases simultaneously, mainly because of reaction (7.12). The high concentration of sulfuric acid inhibiting the oxidizing ability of bacteria. The equilibrium in reaction (7.12) shifts to the left under these conditions and the reaction is retarded.

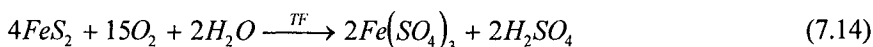
The structural disorder of pyrite increases with the time of mechanical activation. In addition to an increase in overall surface, new boundaries and cracks, accompanied by the formation of lattice defects and imperfections on a submicroscopic scale come into existence. According to Shewmon [7.16] diffusion of sulfur atoms through pure crystalline solids is typically of the order  $10^{-16} \text{ cm}^2 \text{ s}^{-1}$  whereas diffusivities along dislocations and grain boundaries are of the order  $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ . From the energetic point of view, a sufficient supply of sulfur on these sites, produces an increased metabolic activity of bacteria which manifests itself by pitting on the surface of pyrite [7.17]. Such explanation can be used for the samples mechanically activated for up to 30 min, where the rate of bacterial leaching increases with grinding time (Fig. 7.6). At longer activation times the favourable effect of defects is suppressed by the formation of agglomerates of pyrite (Fig. 7.7) with the consequent, lower accessibility of surface defect sites for the bacteria. For this reason the metabolic activity of bacteria is decreased and this manifests itself as a decreased rate of leaching.



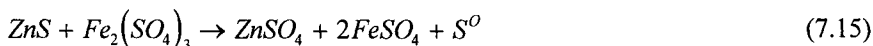
Fig. 7.7 Scanning electron micrographs of  $\text{FeS}_2$ , time of mechanical activation,  $t_{\text{PM}}$ : A - 0 min, B - 7.5 min, C - 15 min, D - 30 min, E - 60 min, F - 120 min [7.18].

## 7.4. Sphalerite ZnS

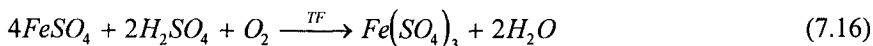
Sphalerite ZnS is the most frequent occurring zinc sulfide and is often accompanied by pyrite in ore deposits. Choi and Torma [7.19] published a paper on the leaching of sphalerite-pyrite mixture by bacteria *Thiobacillus ferrooxidans* (TF). In this system, sphalerite represents the anodic part and pyrite the cathodic part of galvanic cell. According to the authors the chemistry of leaching may be described by the following equations



Ferric sulfate arising in reaction (7.14) is a strong oxidant and can oxidize sphalerite indirectly according to the equation



The reduced forms of iron and sulfur may be continuously reoxidized by direct bacterial attack



The results of bacterial leaching of a pure sphalerite and a sphalerite-pyrite mixture by *Thiobacillus ferrooxidans* are summarized by the zinc recovery into solution, shown in Fig. 7.8. At the end of the leaching experiment,  $\epsilon_{\text{zn}}$  values of 9 % and 17 % were obtained for non-activated sphalerite and non-activated sphalerite-pyrite mixture, respectively. In this figure the time course of the mineral leaching is represented for inoculated samples (1,2) and sterile controls (3,4).

The application of mechanical activation brings about a significant increase in recovery. The recovery obtained by bacterial leaching ( $t_L = 357$  h) of the samples mechanically activated for 30 min (Fig. 7.9) is 3-4 times greater than that obtained for non-activated samples under equal conditions (Fig. 7.8). The more rapid leaching of zinc from the sphalerite-pyrite mixture compared with pure sphalerite remains as with for the non-activated samples.

The maximum rate of bacterial leaching  $v_{\text{max}}$  is plotted against time of mechanical activation in Fig. 7.10. The curves, for a mechanical activation  $t_G > 20$  min exhibit an exponential course with only small differences between the values  $v_{\text{max}}$  obtained for sphalerite and sphalerite-pyrite mixture. For higher values of  $t_G$  the differences in the maximum leaching rate increase more rapidly for the mixture. In order to elucidate this behaviour, examination of the surface-structure and electrochemical properties of the samples of sphalerite and sphalerite-pyrite mixture was made.

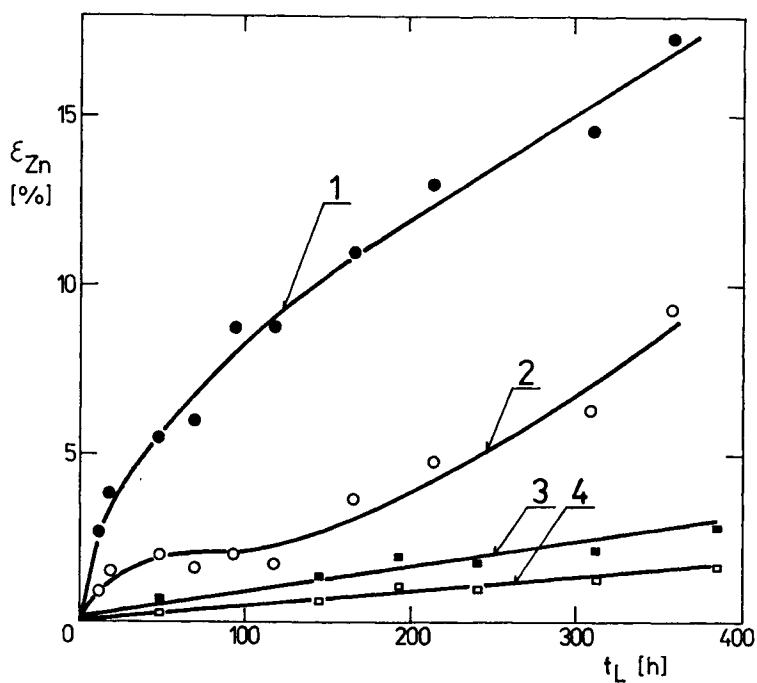


Fig. 7.8 Variation of zinc recovery,  $\epsilon_{Zn}$  during time of bacterial leaching,  $t_L$  of non-activated ZnS (2,4) and ZnS+FeS<sub>2</sub> (1,3), 1,2: inoculated samples; 3,4: sterile control [7.20].

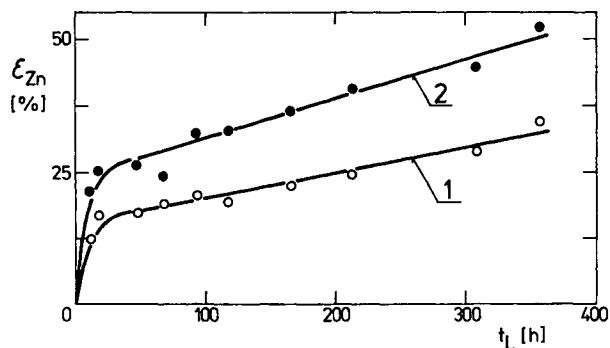


Fig. 7.9 Variation of zinc recovery,  $\epsilon_{Zn}$  during bacterial leaching,  $t_L$ , 1: ZnS, 2: ZnS+FeS<sub>2</sub>. Time of mechanical activation  $t_G = 30$  min [7.20].

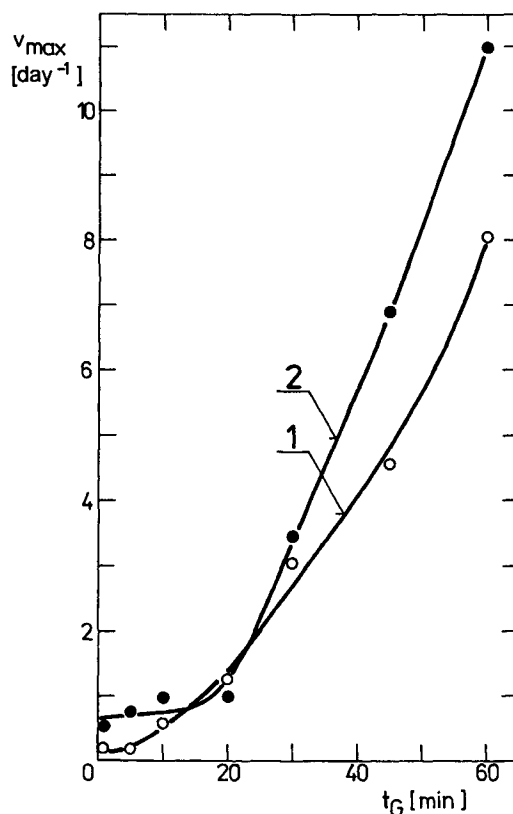


Fig. 7.10 Influence of the time of mechanical activation,  $t_G$  on the maximum rate of bacterial leaching,  $v_{\max}$ , 1: ZnS, 2: ZnS+FeS<sub>2</sub> [7.20].

The specific surface area and the content of X-ray amorphous phase of sphalerite are plotted against the time of mechanical activation in Figs 7.11 and Fig. 7.12, respectively. The surface area  $S_A$  (Fig. 7.11, curves 1,2) increase with the time of mechanical activation with a larger increase evident for pure sphalerite. The aggregation of particles may be characterized by the values of specific granulometric surface  $S_G$  (Fig. 7.11, curves 3,4). In the case of aggregates formation, a stagnation or decrease in  $S_G$  appears, as has been observed in the grinding of sphalerite [7.21]. In this case, the agglomeration of both sphalerite and the mixture is evident at  $t_G \geq 30$  min. Fig. 7.12 shows that the fraction of amorphous sphalerite differs whether the sphalerite was pure or mixed with pyrite. Pure sphalerite undergoes amorphization only during the initial 20 min where the content of amorphous phase reached 53 %. Longer grinding times did not produce a significantly higher amorphous content, this is possibly due to the discussed agglomeration. In contrast to pure sphalerite, the amorphization of sphalerite in the mixture continued for  $t_G > 20$  min. Microscopic observation showed that the size of sphalerite grains decreases more rapidly than the pyrite grains with activation. Because of the different hardnesses of both minerals ( $H(\text{FeS}_2) = 6.0$ ,  $H(\text{ZnS}) = 3.5$ ) it can be assumed that pyrite disintegrates slowly and functions as a mineral lubricant in the process of mechanical activation. A similar effect was observed during grinding the softer material in the presence of harder one [7.22-7.26]. It seems, from Figs. 7.10 and 7.12, that the influence of structure on the differences in leaching between sphalerite and the sphalerite-pyrite mixture begin to occur at  $t_G > 20$  min.

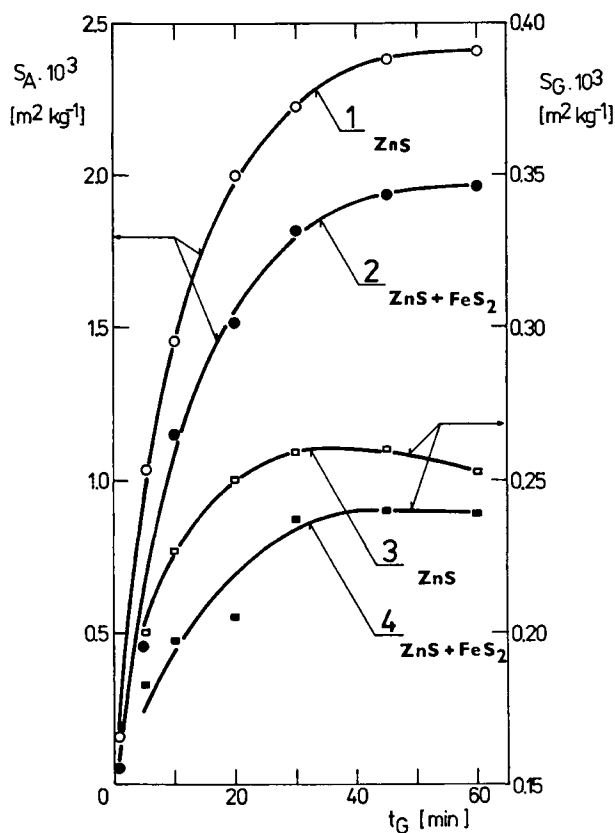


Fig. 7.11 Variation of specific adsorption surface,  $S_A$  (1,2) and specific granulometric surface,  $S_G$  (3,4) with the time of mechanical activation,  $t_G$ ; 1,3: ZnS; 2,4: ZnS+FeS<sub>2</sub> [7.20].

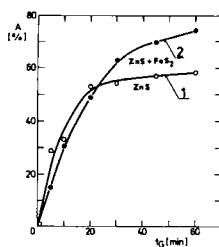


Fig. 7.12 Amorphization of sphalerite,  $A$  as a function of the time of mechanical activation,  $t_G$ , 1: ZnS, 2: ZnS+FeS<sub>2</sub> [7.20].

It is usual in the kinetics of dissolution of heterogeneous phases to consider the rate of process as a function of the specific surface of the particles. Such approach enables us to appreciate the true effect of the nature of the mineral on the dissolution [7.27]. The relation between the specific rate of bacterial leaching  $v_{max}/S_A$  and the disordering of sphalerite structure expressed by the quantity of amorphous phase is represented in Fig. 7.13. This plot revealed two regions, both of which are present for sphalerite and the sphalerite-pyrite mixture. In the first region,  $A \leq 53\%$  for sphalerite and  $A \leq 63\%$  for sphalerite-pyrite

mixture, the specific rate of leaching is practically independent on disordering within the sphalerite structure. In the second region ( $A > 53$  % for sphalerite and  $A > 63$  % for the mixture) the specific rate of dissolution increases abruptly and kinetics of leaching cannot be appreciated without taking the solid-phase transformations of sphalerite into consideration. This region also begins with the formation of agglomerates (marked by the dashed lines).

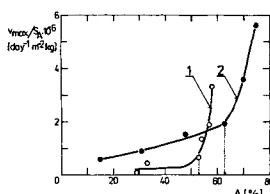


Fig. 7.13 Relation between the maximum specific rate of bacterial leaching,  $v_{\max}/S_A$  and the extent of amorphization,  $A$  of sphalerite, 1: ZnS, 2: ZnS+FeS<sub>2</sub> [7.20].

The results of electrode potential measurements, expressed as a function of the time of mechanical activation, are given in Table 7.3 along with literature data for non-activated sphalerite and pyrite. It seems that the differences between the electrode potential for the sphalerite-pyrite mixture and pure sphalerite are greatest at  $t_G \geq 30$  min i.e. where the increase of the bacterial leaching rate occurred.

Table 7.3 Electrode potentials  $E$  of ZnS, FeS<sub>2</sub> and (ZnS+FeS<sub>2</sub>) mixture [7.20]

| E (vs. Ag/AgCl)<br>(mV) |                  |                      | Medium                                | Time of<br>mechanical<br>activation, $t_G$<br>(min) | References  |
|-------------------------|------------------|----------------------|---------------------------------------|-----------------------------------------------------|-------------|
| ZnS                     | FeS <sub>2</sub> | ZnS+FeS <sub>2</sub> |                                       |                                                     |             |
| 166                     | 531              |                      | 1.0 M KCl                             | -                                                   | [7.29]      |
| 238                     | 378              |                      | H <sub>2</sub> SO <sub>4</sub> (pH 4) | -                                                   | [7.30]      |
| 11                      | 346              |                      | uninoculated                          |                                                     | [7.31-7.32, |
|                         |                  |                      | 0.9 K [7.24]                          |                                                     | 7.34]       |
| 26                      | 386              |                      | inoculated                            | -                                                   | [7.31-7.32, |
|                         |                  |                      | 0.9 K [7.24]                          |                                                     | 7.34]       |
| 155                     |                  | 125                  | 1.0 M H <sub>2</sub> SO <sub>4</sub>  | -                                                   | [7.20]      |
| 100                     |                  | 25                   | -                                     | 5                                                   | -           |
| 75                      |                  | 205                  | -                                     | 10                                                  | -           |
| 122                     |                  | 200                  | -                                     | 20                                                  | -           |
| 50                      |                  | 250                  | -                                     | 30                                                  | -           |
| 72                      |                  | 300                  | -                                     | 45                                                  | -           |
| 75                      |                  | 290                  | -                                     | 60                                                  | -           |

If a galvanic cell consisting of an anodic ZnS half-cell and a cathodic FeS<sub>2</sub> half-cell is not under external voltage, it holds in accordance with literature [7.33]

$$\sum i_a S_a = \sum i_k S_k \quad (7.18)$$

where  $i_a$ ,  $i_k$ ,  $S_a$  and  $S_k$  are anodic current, cathodic current, surface area of anode and cathode, respectively. According to Eq. (7.18), changes in the values of  $S_a$  and  $S_k$  produce changes in galvanic currents  $i_a$  and  $i_k$ . The changes in these galvanic currents, as well as the changes in electrode potentials, are the main driving force of the process of bacterial leaching [7.31-7.32,7.34]. We assume that the changes in properties of the investigated mixture bring about an increasing flux of electrons in pyrite leading to increased dissolution of zinc from the anodic ZnS half-cell.

Thus the mechanical activation of sphalerite-pyrite mixture has a combined effect comprising changes in surface and in bulk properties of both minerals. These changes manifest themselves most significantly at the contact of the mineral mixture with a leaching medium and have some influence on the electrochemical properties which determine the galvanic effect.

## 7.5. Tetrahedrite Cu<sub>12</sub>Sb<sub>4</sub>S<sub>13</sub>

Bacterial leaching of tetrahedrite in order to recover copper, antimony and silver was studied by Frenay [7.35]. From these experiments it can be concluded that copper was recovered by bacterial leaching and pregnant solution can be easily processed by cementation or solvent extraction.

The possibility to extract copper by bacteria from mechanochemically pretreated tetrahedrite concentrate was studied in [7.36-7.37]. The application of *Thiobacillus ferrooxidans* over 21 days led to extraction of 61-83 % of Cu (Fig. 7.14). Recoveries in control (non-activated) sample under the identical conditions were under 30 %. The recoveries obtained for copper are sensitive to disordering of the tetrahedrite structure as a result of combined mechanical and chemical pretreatment. The presence of easily filtrable jarosite  $KFe_3(SO_4)_3(OH)_6$  was identified in the products of bacterial leaching.

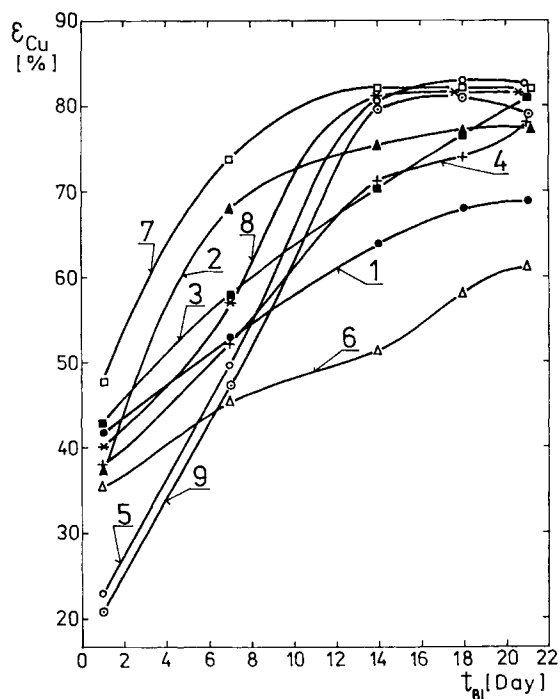


Fig. 7.14 Variation of copper recovery,  $\epsilon_{Cu}$  during time of bacterial leaching,  $t_{BL}$  for  $Cu_{12}Sb_4S_{13}$  mechanochemically pretreated for 60 min. Temperature ( $T$ ) and  $Na_2S$  concentration ( $c$ ) for pretreated samples: 1:  $T = 60^\circ C$ ,  $c = 100 \text{ g l}^{-1}$ , 2:  $T = 60^\circ C$ ,  $c = 150 \text{ g l}^{-1}$ , 3:  $T = 60^\circ C$ ,  $c = 200 \text{ g l}^{-1}$ , 4:  $T = 80^\circ C$ ,  $c = 100 \text{ g l}^{-1}$ , 5:  $T = 80^\circ C$ ,  $c = 150 \text{ g l}^{-1}$ , 6:  $T = 80^\circ C$ ,  $c = 200 \text{ g l}^{-1}$ , 7:  $T = 95^\circ C$ ,  $c = 100 \text{ g l}^{-1}$ , 8:  $T = 95^\circ C$ ,  $c = 150 \text{ g l}^{-1}$ , 9:  $T = 95^\circ C$ ,  $c = 150 \text{ g l}^{-1}$ .

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## **Chapter 8 MECHANICAL ACTIVATION IN TECHNOLOGY**

### **8.1. Effect of mechanical activation on the flotability of minerals**

### **8.2. Mechanical activation as pretreatment step for oxidative leaching**

#### **8.2.1. Attritors in hydrometallurgy**

#### **8.2.2. *Influence of grinding equipment and grinding medium on properties and reactivity of sulfidic concentrates***

#### **8.2.3. *Selective leaching of metals from complex sulfidic concentrates***

#### **8.2.4. *LURGI-MITTERBERG process***

#### **8.2.5. *ACTIVOX<sup>TM</sup> proces***

### **8.3. Mechanical activation as pretreatment step for gold and silver extraction**

#### **8.3.1. *IRIGETMET process***

#### **8.3.2. *SUNSHINE process***

#### **8.3.3. *METPROTECH process***

#### **8.3.4. *ACTIVOX<sup>TM</sup> proces***

### **8.4. Mechanochemical leaching**

#### **8.4.1. *MELT process***

### **8.5. Mechanical activation as a way of metallurgical calcine treatment**

#### **8.5.1. *Pyrite and arsenopyrite calcines***

#### **8.5.2. *Tetrahedrite calcines***

### **8.6. Economic evaluation of mechanical activation**

### **8.7. Sorption of metals from solutions by mechanically activated minerals**

### **8.8. References**

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The efficiency of both mineral processing and extractive metallurgy of minerals depends on the separation of individual mineral components and on the exposure of their surface [8.1]. The production of flotation concentrates, with particle sizes of tens of microns, is not sufficient for many hydrometallurgical processes to operate at their optimum. As a consequence, metallurgical plants require for the effective processing high temperatures and pressures and some sort of concentrate pretreatment.

Mechanical activation is an innovative procedure where an improvement in hydrometallurgical processes can be attained via a combination of new surface area and formation of crystalline defects in minerals.

The lowering of reaction temperatures, the increase of rate and amount of solubility, preparation of water soluble compounds, the necessity for simpler and less expensive reactors and shorter reaction times are some of the advantages of mechanical activation. The environmental aspects of these processes are particularly attractive [8.2 - 8.4].

This Chapter is devoted to the examples of application of mechanical activation in the treatment of sulfidic concentrates by different technological operations like flotation, leaching and sorption.

### **8.1. Effect of mechanical activation on the flotability of minerals**

It is well known that the degree of dispersion and other physico-chemical properties of minerals are changed by mechanical stress in grinding machines. These effects not only have significance in enhancing dispersion, but also affect particle sizes typically encountered in flotation since the structural defects may be concentrated within thin surface layers [8.5].

The sulfidic concentrates are ground to flotation fineness in industrial plants, as a rule, in ball mills where the grinding effect is achieved by rubbing and crushing. As vibratory mills often used for mechanical activation work by a similar regime, their application to modification of the surface properties of minerals was investigated [8.1].

Plaksin and Šafejev [8.6] found that the adsorption capacity of galena for the collector potassium butylxanthate decreases with decreasing size of particles. This may be due to a change in electron concentration in the surface layer of PbS. The higher electron concentration in the case of finer particles makes the electron transitions between the xanthate anions and the surface of galena energetically unfavourable owing to which the formation of a solid particle-xanthate bond is hindered. However, the relationship between size of the particles and their adsorption properties is not unambiguous [8.7]. In addition to the conditions of mechanical activation [8.8] a number of other factors play a role and many of these factors are antagonistic.

Ocepek [8.9] investigated the influence of vibratory grinding on the flotability of galena and sphalerite. Experiments performed in a flotation cell showed that there is an optimum degree of mechanical activation that increases the flotability of sulfides compared with non-activated sulfides. The content of amorphous material increases with the time of mechanical activation and results in a decrease in flotability. For PbS, the decrease in flotability can be explained by formation of anglesite  $\text{PbSO}_4$ .

Mechanical activation of a galena concentrate involving a closed cycle with classifier has been described in [8.10] which showed that greater selectivity and increased lead recovery could be achieved. Moreover, it was possible to reduce the consumption of electric energy by 17 %, the abrasion of mill lining to 68 % and the grinding flowsheet to a single stage. The increase in recovery and selectivity may be due to a considerable decrease in iron content in

the pulp due to abrasion reduction and the shorter contact time of particles with aqueous phase.

Čanturija et al. indicated that it is possible to influence the flotation properties of sulfidic ores by control of the electrochemical potential in the pulp during the grinding process [8.11 - 8.13]. These electrochemical experiments demonstrated the possibility of raising the concentration of defects and weakening the bonds at the interface of mineral grains and was shown to work on several sulfidic concentrates.

## 8.2. Mechanical activation as pretreatment step for oxidative leaching

The pilot-plant and plant application of mechanical activation as a method of pretreatment of sulfidic concentrates is primarily based on the research results of the German school [8.14 - 8.26].

The mechanical activation of sulfidic concentrates was intensively investigated and patented by Pawlek [8.18 - 8.21]. Wet grinding of chalcopyrite concentrate in an attritor reduces the particle size to 0.1 - 1  $\mu\text{m}$  in a short time with the efficiency of activation increased by addition of NaOH. During subsequent acid leaching in an autoclave (0.1 MPa and 110°C) full extraction of copper into solution was achieved in 30 min. The author published the technological flowsheet (Fig. 8.1) and considers the wet grinding to be convenient for the step of mechanical activation.

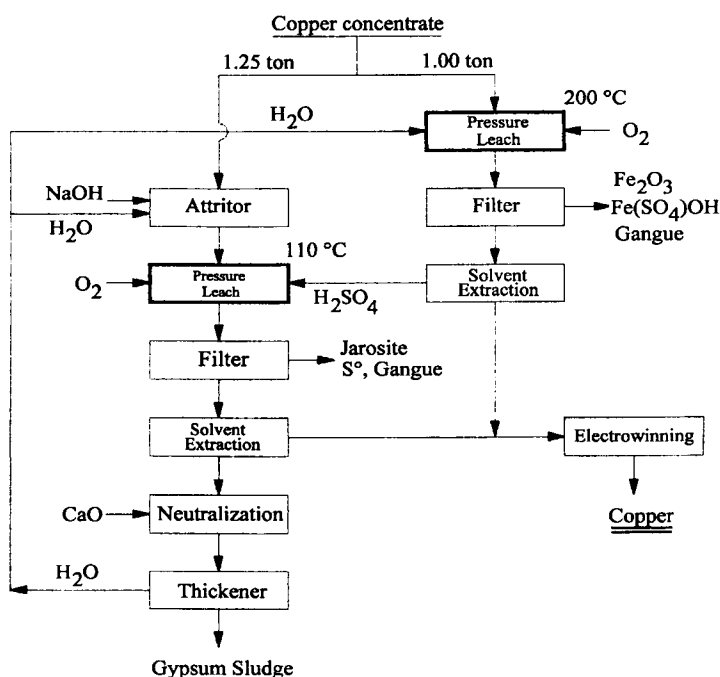


Fig. 8.1 Flowsheet for treatment of chalcopyrite concentrate by attrition grinding followed by high temperature oxidative pressure leaching and low temperature acid pressure leaching [8.18].

The technological parameters of the combined process of mechanical activation in vibration mill and subsequent oxidative leaching of sulfidic concentrates of chalcopyrite, sphalerite and molybdenite are summarized in Table 8.1.

Table 8.1 Technological parameters of mechanical activation in a vibration mill followed by oxidative leaching of flotation concentrates of  $\text{CuFeS}_2$ ,  $\text{ZnS}$  and  $\text{MoS}_2$  [8.14]

| Flotation concentrate                                                  | $\text{CuFeS}_2$                                 | $\text{ZnS}$                                    | $\text{MoS}_2$                                                |
|------------------------------------------------------------------------|--------------------------------------------------|-------------------------------------------------|---------------------------------------------------------------|
| Mechanical activation                                                  | Vibration mill                                   |                                                 |                                                               |
| Amplitude (mm)                                                         | 6                                                | 6                                               | 6                                                             |
| Revolutions ( $\text{s}^{-1}$ )                                        | 1000                                             | 1000                                            | 1000                                                          |
| Ball charge (%)                                                        | 85                                               | 85                                              | 85                                                            |
| Mass of balls to mass of ground material ratio                         | 47                                               | 47                                              | 47                                                            |
| Energy input of mill ( $\text{kWh t}^{-1}$ )                           | 224                                              | 75                                              | 224                                                           |
| Relative acceleration                                                  | 6.8                                              | 2.73                                            | -                                                             |
| Oxidative leaching                                                     | Cylinder autoclave                               |                                                 |                                                               |
| Content of solid phase ( $\text{g l}^{-1}$ )                           | 150                                              | 100                                             | 50                                                            |
| Initial concentration of $\text{H}_2\text{SO}_4$ ( $\text{g l}^{-1}$ ) | 65                                               | 185                                             | -                                                             |
| Temperature ( $^{\circ}\text{C}$ )                                     | 120                                              | 120                                             | 180                                                           |
| Partial pressure of oxygen (MPa)                                       | 2                                                | 1                                               | 1                                                             |
| Time of leaching (min)                                                 | 120                                              | 120                                             | 120                                                           |
| Results of leaching                                                    |                                                  |                                                 |                                                               |
| Solution                                                               | $\text{CuSO}_4$<br>$\text{Fe}_2(\text{SO}_4)_3$  | $\text{ZnSO}_4$<br>$\text{Fe}_2(\text{SO}_4)_3$ | $\text{H}_2\text{SO}_4$                                       |
| Residue                                                                | $\text{Fe}(\text{OH})\text{SO}_4 \cdot \text{S}$ | S                                               | $\text{MoO}_3$ or<br>$\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ |
| Recovery                                                               | 100 %                                            | 100 %                                           | 97.2 %                                                        |
| Metal output                                                           | Reductive electrolysis                           |                                                 | Reduction with carbon or hydrogen                             |

### 8.2.1. Attritors in hydrometallurgy

Attritors were patented in the fifties in the USA and in 1956 the license for their manufacturing was transferred to NETZSCH Company in Germany. This mill type was originally used for applications in chemical and pharmacy industry [8.27] and later for powder metallurgy [8.28] and mineral processing [8.29-8.31].

Attritors use the comminution intensity between the contact surfaces of moving balls, similar to the operation of conventional ball mills, but without the disadvantages of the latter [8.32-8.34]. An increase in contact points and therefore of contact surfaces is achieved by the use of small grinding balls (2-4 mm diameter). Unlike the ball motion in the rotating drum body of conventional ball mills, the balls in the attritor are brought to a higher degree of

acceleration by a rotating stirring device in a stationary mill container surrounded by a cylindrical cooling chamber Fig. 8.2.

A new series of attritors (Fig. 8.3) were developed by NETZSCH for continuous mode of operation. The main features of these are: completely enclosed design, newly developed separating elements, horizontally mounted grinding chamber, mechanical seal and improved cooling system [8.33].

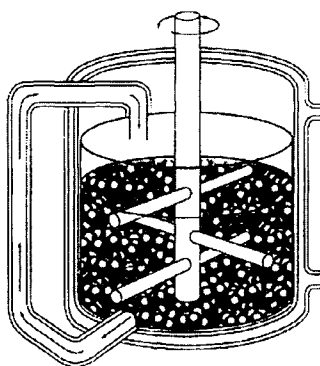


Fig. 8.2 Schematic arrangement of the UNION PROCESS Attritor - batch mode of operation [8.34].

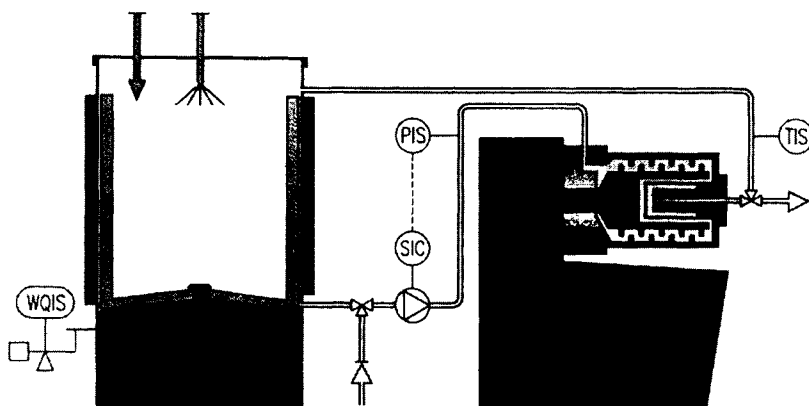


Fig. 8.3 Schematic arrangement of the NETZSCH Attritor - continuous mode of operation [8.27].

It is possible to vary the kinetic energy of attritor by varying the rotation rate of the stirring mechanism and the media mass by changing the density and diameter of the grinding balls. The parameters allow the mill may to be used so that particle size, surface area and size distribution may be optimised, but can also modify the structure of solids during grinding. Through special construction of the mill fitted with an eccentric annular discs, it is possible to imparts both centrifugal and a centripetal accelerative forces to the grinding elements, thereby resulting in highly intensive mechanical activation of the solids throughout the entire grinding chamber.

Beckstead et al. presented results on acid ferric sulfate leaching of a ground chalcopyrite concentrate which was  $\sim 80\%$  chalcopyrite, pyrite and quartz were the major impurities. As can be seen from Fig. 8.4, after 6 hours of grinding in the ball mill, the median particle size is reduced from 20 microns to 2 microns, further grinding does not result in further size reduction. On the other hand, continued size reduction does occur in the case of attrition grinding, at least to a median particle size of 0.5 microns. The grind limit for ball milling is reflected also in the limiting specific surface area of  $4 \text{ m}^2\text{g}^{-1}$ , whereas the specific surface area of attritor-ground products continues to increase to at least  $12 \text{ m}^2\text{g}^{-1}$  [8.35].

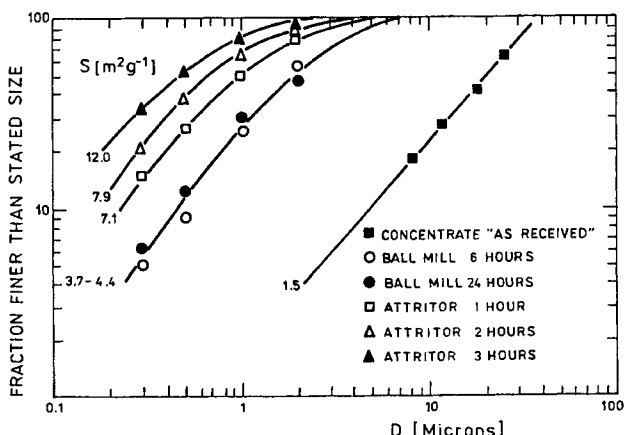


Fig. 8.4 A size distribution plot showing the change in particle size distribution of chalcopyrite concentrate effected by various methods of grinding and for various times of grinding [8.35].

Copper extraction of approximately 90 % was achieved after three hours leaching of sample attritor ground for 3.5 h. As can be seen from Fig. 8.5, leaching of the concentrate without size reduction is technologically unacceptable since only 12 % of the copper values were extracted after 3 hours of leaching.

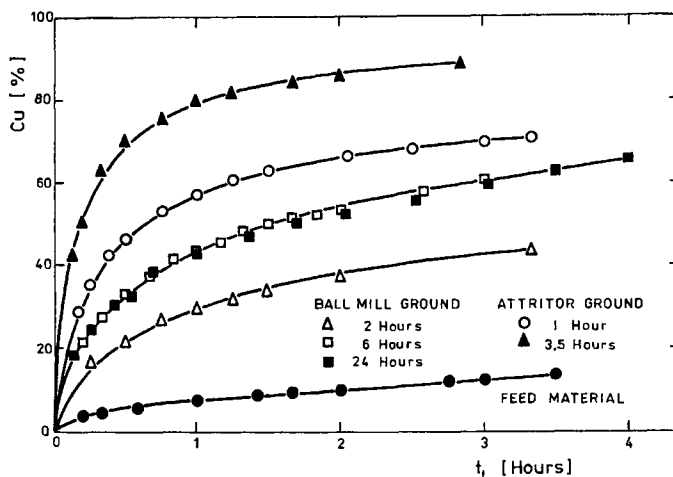


Fig. 8.5 A plot of copper extracted, Cu as a function of leaching time,  $t_L$  for various ground products at  $1\text{M H}_2\text{SO}_4$ , 5 % solids,  $93^\circ\text{C}$ , 1200 rpm and stoichiometric amounts of  $\text{Fe}_2(\text{SO}_4)_3$  for 100 % reaction [8.35].

Several investigations applying attritors in hydrometallurgy were performed with zinc, nickel and copper concentrates [8.36-8.40]. Wet grinding in a semi-industrial attritor gave rise to fines under 1 microns and sufficiently effects could be achieved for short comminution times using a power input of 20-50 kWh<sup>t</sup><sup>-1</sup> sphalerite concentrate [8.25]. The specific surface area of 3-4 m<sup>2</sup>g<sup>-1</sup> can be achieved in this region (Fig. 8.6).

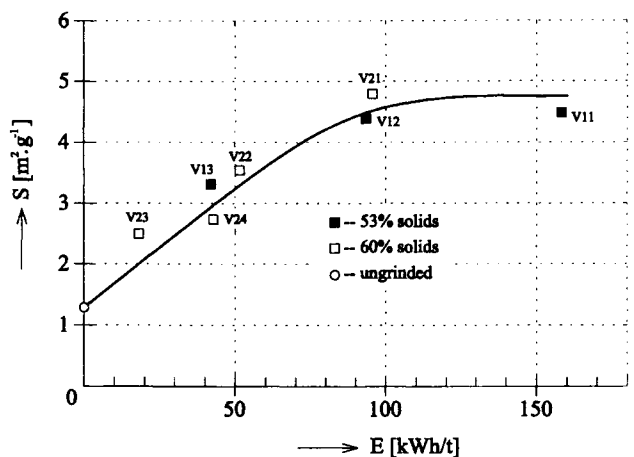


Fig. 8.6 A plot of specific surface area, S as a function of power input, E for sphalerite concentrate ground at various solid/liquid ratio [8.25].

Leaching tests with Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> indicated that after 15 minutes grinding a 95 % Zn extraction could be achieved after 60 minutes leaching whereas only 68 % was recovered by leaching the as-received concentrate (Fig. 8.7).

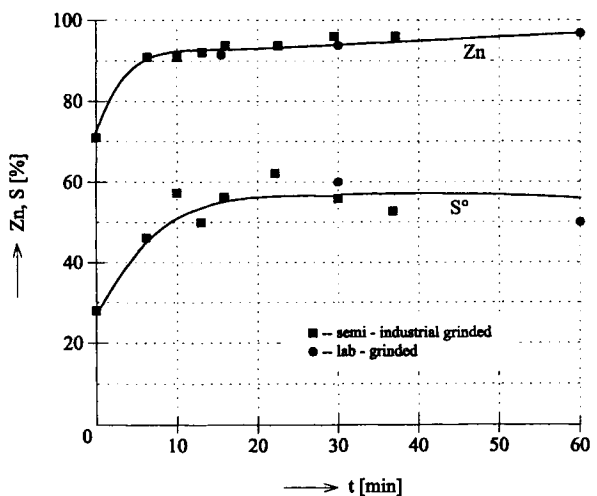


Fig. 8.7 A plot of zinc and elemental sulfur extraction as a function of leaching time, t for sphalerite concentrate mechanically activated in semi-industrial and laboratory attritor [8.25].

Investigations about the leachability of sulfides after attrition grinding were published by Stanczyk and Feld [8.41] who dealt with ultrafine grinding of several industrial minerals. Björling and Mulak have applied attrition grinding in order to produce active nickel sulfide surfaces [8.42].

It is clear from the presented data that the use of attritors or vibration mills should be appropriate. The real type of mill and the conditions of its application are dependent on the type of concentrate. The specification of these conditions can only be determined by laboratory and subsequent pilot-plant experiments. The economic evaluation of mechanical activation must be appraised in the context of the whole hydrometallurgical process and not just on the power consumed by the mill.

### ***8.2.2. Influence of grinding equipment and grinding medium on properties and reactivity of sulfidic concentrates***

For mechanical activation of solid substances all equipments designed for fine and ultrafine grinding are suitable in principle. The properties of grinding products are determined by intensity of stress and nature of the forces in individual equipment and can be significantly modified by changing the grinding medium.

For the investigation of the effect of mechanical activation conditions the mills with free-moving grinding bodies were chosen: rotary ball mill, vibration mill and attritor [8.43]. In these types of equipments the feed material is subjected to combined stress, whilst the predominant stress method changes in dependence on regime of their work. In the rotary drum mills and the vibrational type mills, material is mainly subjected to impact and compressive impulses imparted by grinding bodies. Attrition takes place between media moving at various speeds and between the grinding bodies and the drum wall whilst imparting shear stress. In the attritor, attrition is the main mode of operation, although some crushing also occurs [8.33]. In classical ball mills and in vibration mills it is possible to grind in gaseous atmosphere as well as in liquid medium. The grinding in attritor is generally performed in liquid medium.

For our purposes, the dry grinding was performed in nitrogen atmosphere. By grinding in inert atmosphere we endeavoured to eliminate the influence of potential mechanochemical reactions on the resulting properties of the product. Methanol and water were chosen as liquid media. Both substances perform as dispersant, i.e. they prevent aggregation of small particles. However, the probability of mechanochemical reactions involving chalcopyrite is greater in water than in methanol.

All three types of mill examined are of the batch type. The amount of work consumed in material grinding is determined by specific grinding output and grinding time. It follows from data in Table 8.2 that the attritor has the highest output and the ball mill has the lowest one. To provide an equal amount of grinding work a ball mill needs to run 14-times longer than a vibration mill and 1.7-times longer than an attritor.

This extended time requirement can have significance, especially when wet grinding, with the extended contact time between the ground substance and water increasing the probability of mechanochemical compounds formation.

Table 8.2 Specific surface area,  $S_A$  and XRD values,  $I/I_0$  (integral intensity) and HBW (halfwidth) for chalcopyrite concentrate activated in different mills [8.43]

| Mill           | Grinding medium    | Time of activation (h) | Power input (kWh <sup>-1</sup> ) | $S_A$ (m <sup>2</sup> g <sup>-1</sup> ) | XRD         |              |
|----------------|--------------------|------------------------|----------------------------------|-----------------------------------------|-------------|--------------|
|                |                    |                        |                                  |                                         | $I/I_0$ (%) | HBW (rel. %) |
| -              | as-received        | sample                 | 0                                | 0.5                                     | 100         | 1.00         |
| Attritor       | H <sub>2</sub> O   | 0.25                   | 240                              | 2.6                                     | 102         | 0.91         |
|                | H <sub>2</sub> O   | 0.50                   | 490                              | 3.7                                     | 88          | 1.09         |
|                | H <sub>2</sub> O   | 2.00                   | 1950                             | 5.9                                     | 62          | 1.36         |
|                | CH <sub>3</sub> OH | 0.50                   | 490                              | 3.0                                     | 84          | 1.09         |
| Ball mill      | N <sub>2</sub>     | 3.00                   | 210                              | 3.0                                     | 63          | 1.45         |
|                | N <sub>2</sub>     | 6.00                   | 420                              | 3.1                                     | 52          | 1.73         |
|                | H <sub>2</sub> O   | 3.00                   | 210                              | 4.9                                     | 72          | 1.14         |
|                | H <sub>2</sub> O   | 6.00                   | 420                              | 7.0                                     | 55          | 1.36         |
|                | H <sub>2</sub> O   | 15.00                  | 1050                             | 10.6                                    | 35          | 1.55         |
|                | CH <sub>3</sub> OH | 3.00                   | 210                              | 4.6                                     | 71          | 1.27         |
|                | CH <sub>3</sub> OH | 6.00                   | 420                              | 5.8                                     | 52          | 1.45         |
| Vibration mill | N <sub>2</sub>     | 0.25                   | 140                              | 2.8                                     | 65          | 1.45         |
|                | N <sub>2</sub>     | 0.50                   | 280                              | 3.8                                     | 60          | 1.45         |
|                | N <sub>2</sub>     | 1.00                   | 560                              | 4.6                                     | 46          | 2.05         |
|                | H <sub>2</sub> O   | 0.25                   | 140                              | 3.1                                     | 103         | 0.91         |
|                | H <sub>2</sub> O   | 0.50                   | 280                              | 2.7                                     | 95          | 1.00         |
|                | H <sub>2</sub> O   | 1.00                   | 560                              | 4.0                                     | 81          | 1.00         |

#### Physico-chemical transformations of chalcopyrite concentrate at grinding in various mills

Table 8.2 and Fig. 8.8 and 8.9 show the changes of the physical properties of chalcopyrite in the course of grinding. The values of specific surface of chalcopyrite concentrate (Fig. 8.9) increase with the power input. For an equal amount of power input, the greatest surface is in material ground in either water or methanol in the ball mill. This can be attributed to the dispersant effect of liquid medium and to mechanochemical reactions between ground substance and polar medium. Whilst the former has been verified by extensive investigation [8.44-8.46], the latter was confirmed by infrared spectroscopy. A more detailed discussion of these results are presented in Chapter 3. The presence of sulfate as a product of chemical reaction of chalcopyrite with grinding medium was demonstrated in the only case, namely in the sample ground in the ball mill in water for 15 hours. The fact that this sample has the greatest specific surface area of the all ground samples indicates that the formation of a surface compound during long-time contact of chalcopyrite with water may be one of the causes of the specific surface increase.

During the course of grinding disintegration of particles of polycrystalline material occurs. Plastic deformation of the structure takes place by the action of microstresses which are in balance within a small volume or an entire particle. Both disintegration and plastic deformation cause the broadening of X-ray diffraction lines. The structural disorder due to the increasing abundance of X-ray amorphous material is manifested by decreases in the integral intensity of diffraction lines.

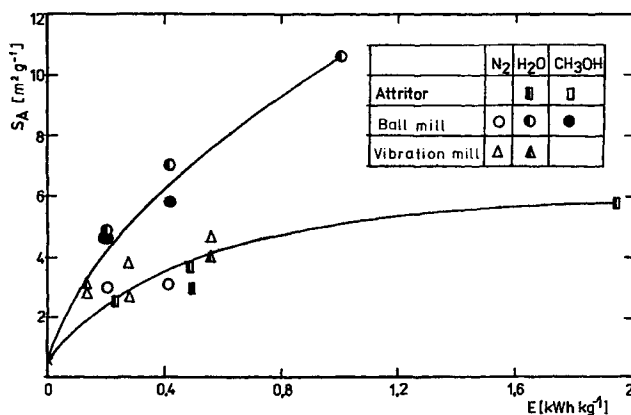


Fig. 8.8 The specific surface area,  $S_A$  vs. power input,  $E$  for chalcopyrite concentrate activated in different mills [8.43].

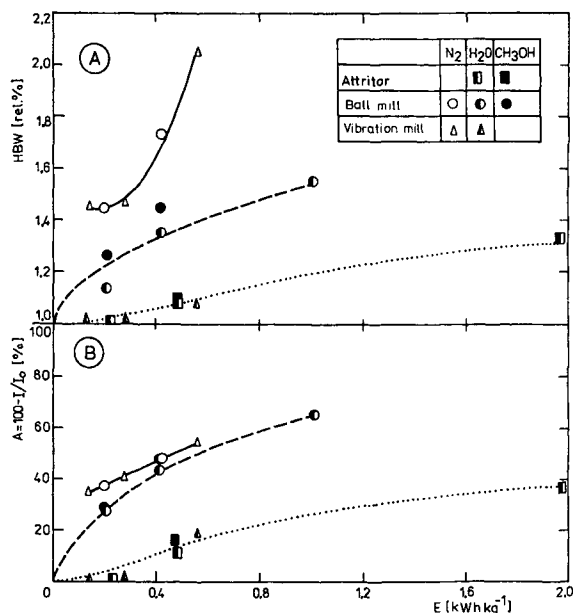


Fig. 8.9 The integral halfwidth, HBW and amorphization,  $A$  vs. power input,  $E$  for chalcopyrite concentrate activated in different mills [8.43].

The dependence of the fraction of X-ray amorphous phase and integral halfwidth of the (112) diffraction line of chalcopyrite on the power input, shown in Fig. 8.9, enable the classification of the grinding products into three major groups. The samples wet ground in either attritor or vibration mill show the least structural change. The most greatest structural damage takes place by dry grinding in nitrogen in ball and vibration mills. The products ground wet in ball mill are between these two extremes.

From the extent of amorphization, the broadening of diffraction lines and the specific surface relationships characterizing the well-known differences between dry grinding and wet grinding are clear (Fig. 8.10). In the course of dry grinding, a greater degree of amorphization occurs than in wet milling. The amorphization of material during wet milling only occurs when the surface area is high indicating that the major role of the liquid consists in suppressing of fine grains.

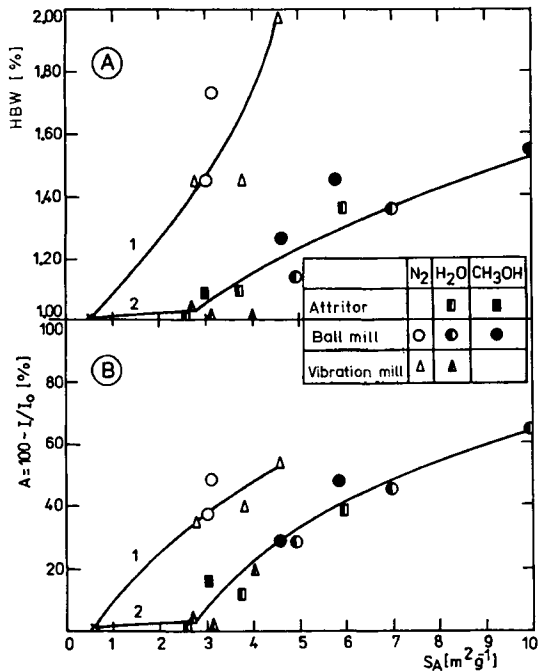


Fig. 8.10 The integral halfwidth, HBW and amorphization, A vs. the specific surface area,  $S_A$  for chalcopyrite concentrate activated in different mills [8.43].

Influence of grinding equipment and grinding medium on chalcopyrite concentrate leaching

Samples of ground chalcopyrite differing in their structure disordering were leached in a 4 %  $H_2O_2$  solution. The leaching rate was characterized by rate constant  $k_{AJ}$ . The reactivity of mechanically activated samples in this case was also examined by leaching in sulfuric acid medium. The leachability of the samples was characterized by copper and iron yields to the liquor after a constant reaction time 2 hours. These experimental results are shown in Fig. 8.11 and 8.12.

It is evident from the comparison of Fig. 8.10 and 8.13 that under conditions of oxidative leaching the specific rate of copper leaching changes in accordance with the structural damage within the sample. There is a linear relationship between the amorphization and/or integral halfwidth HBW of the diffraction line and the rate constant of the reaction between activated chalcopyrite and  $H_2O_2$  (Fig. 8.14)

$$k_{AJ} = (k_{AJ})_0 + k \cdot X \tag{8.1}$$

where  $(k_{AJ})_0$  - the rate constant of the reaction of  $H_2O_2$  with non-disordered  $CuFeS_2$ ,  $X$  – amorphization or halfwidth HBW,  $k$  – proportionality constant, the value of which depends on the nature of the observed reaction, however it does not depend on the conditions of the chalcopyrite activation.

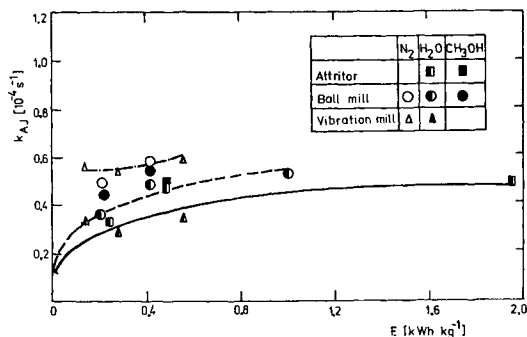


Fig. 8.11 The rate constant of leaching,  $k_{AJ}$  vs. power input,  $E$  for chalcopyrite concentrate activated in different mills, leaching agent:  $H_2O_2$  [8.43].

Under mild acid leaching conditions the yields of copper and iron both increase linearly with the surface area (Fig. 8.15).  $Cu/Fe$  ratio is less than 1 for the majority of samples. The exception is the sample ground in water for 15 hours in a ball mill. The copper yield to the liquor was 2-10-times greater than any of the other samples and the  $Cu/Fe$  ratio characterizing the process selectivity equals to 1.9. The exceptional behaviour of this sample can be explained by surface oxidation of chalcopyrite to  $CuSO_4$ , this is confirmed by the detection of sulfate by infrared spectroscopy (see Chapter 3).

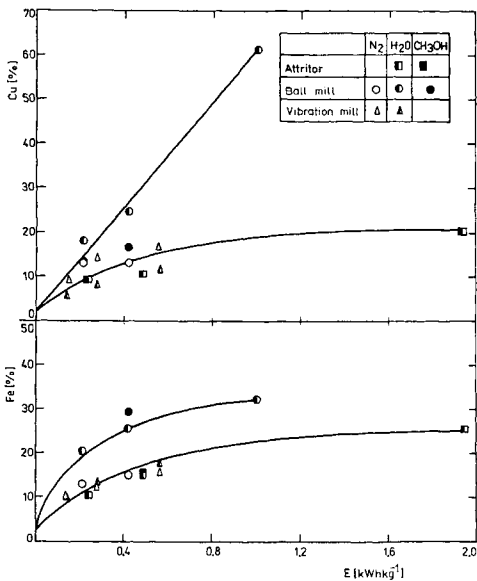


Fig. 8.12 Copper and iron recovery vs. power input,  $E$  for chalcopyrite concentrate activated in different mills, leaching agent:  $H_2SO_4$  [8.43].

It follows from these results that the choice of the activation conditions depends on the type of the reaction. For the effective mechanical activation of chalcopyrite it is necessary to

choose such conditions under which disordering of the chalcopyrite structure takes place. By comparison of Fig. 8.11 with Fig. 8.8 and 8.9 it can be seen that the required effect will be reached for the least power input by grinding dry under nitrogen in either a vibration or a rotary ball mill.

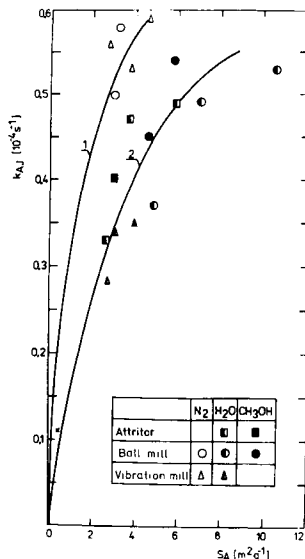


Fig. 8.13 The rate constant of leaching,  $k_{AJ}$  vs. specific surface area,  $S_A$  for chalcopyrite concentrate activated in different mills: 1 - dry grinding, 2 - wet grinding, leaching agent:  $H_2O_2$  [8.43].

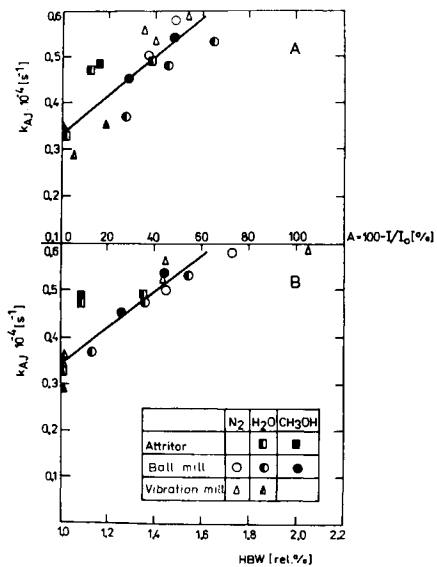


Fig. 8.14 The rate constant of leaching,  $k_{AJ}$  vs. amorphization,  $A$  and halfwidth,  $HBW$  for chalcopyrite concentrate activated in different mills, leaching agent:  $H_2O_2$  [8.43].

For the acid leaching the critical factor is the size and quality of the surface. Therefore it is appropriate to use the rotary ball mill, compare Fig. 8.8 and 8.9 with Fig. 8.12, and to wet grind. Water is a better grinding medium than methanol as oxidation of the chalcopyrite surface to  $\text{CuSO}_4$  occurring during milling. This effect accelerates the copper transfer to the liquor and improves the process selectivity even under conditions when the leaching agent does not react selectively with copper in chalcopyrite.

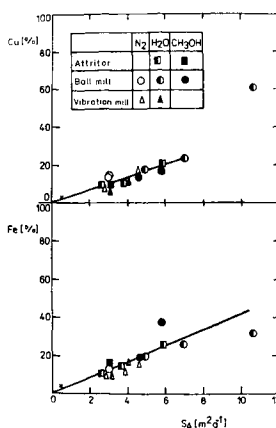


Fig. 8.15 Copper and iron recovery vs. specific surface area,  $S_A$  for chalcopyrite concentrate activated in different mills, leaching agent:  $\text{H}_2\text{SO}_4$  [8.43].

#### Influence of grinding equipment and grinding medium on physico-chemical properties of a tetrahedrite concentrate

In Figs. 8.16-8.18 the percentage of particles under  $10\ \mu\text{m}$ ,  $\Delta R_{10}$  specific surface area  $S_A$  and amorphization  $A$  of tetrahedrite concentrate samples are plotted against the time of mechanical activation for dry grinding in a planetary mill (1) and wet grinding in an attritor (2). Clearly, grinding in water favours the formation of finer particles (Fig. 8.16) giving a greater surface area (Fig. 8.17) which continues to increase with milling time, unlike the surface area obtained by dry grinding in a planetary mill which reaches a constant values after  $\sim 15$  min. The formation of a powder with constant surface area during dry grinding has been observed for tetrahedrite, chalcopyrite and pyrite [8.47-8.48], and since the present tetrahedrite concentrate was composed of these minerals, it can be expected that the same mechanism would apply.

The particle size distribution and surface area, however, have little influence on the structural disorder of mechanically activated samples in this case. It follows from Fig. 8.18 that activation in a planetary mill brings about a much more disordering of the tetrahedrite structure. For all samples the values of the structural disorder due to the planetary grinding is at least twice larger than from an attritor.

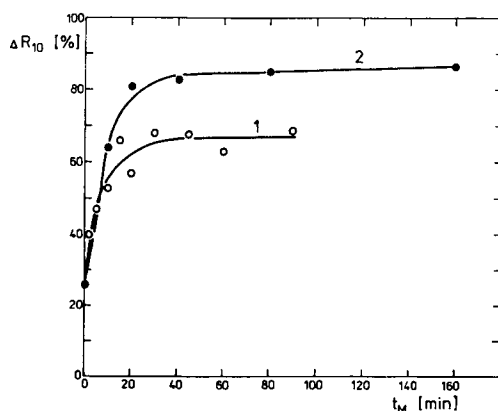


Fig. 8.16 The value of  $\Delta R_{10}$  vs. grinding time,  $t_M$  for tetrahydrate concentrate activated in planetary mill (1) and attritor (2) [8.49].

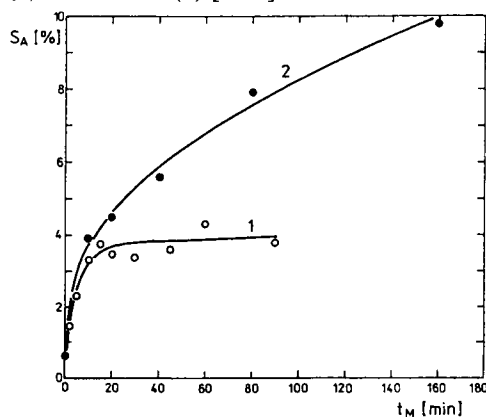


Fig. 8.17 The specific surface area,  $S_A$ , vs. grinding time,  $t_M$ , for tetrahydrate concentrate activated in planetary mill (1) and attritor (2) [8.49].

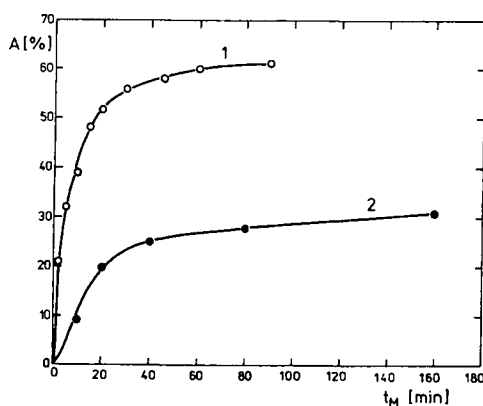


Fig. 8.18 The amorphization of tetrahydrate,  $A$  vs. grinding time,  $t_M$ , for tetrahydrate concentrate activated in planetary mill (1) and attritor (2) [8.49].

### 8.2.3. Selective leaching of metals from complex sulfidic concentrates

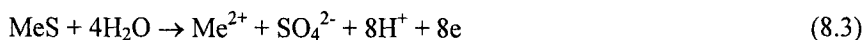
Complex Cu-Pb-Zn sulfide ores represent an important source of non-ferrous metals and typically consist of fine grains of chalcopyrite, galena and sphalerite dispersed in a matrix of pyrite, phyllites and quartz [8.50].

Flotation of such ores may cause some complications. Liberation of the individual minerals occurs during energy intensive fine grinding, typically to below 75  $\mu\text{m}$ . The finely ground ore has large surface area leading to a high reagent consumption during flotation. Selective flotation is multistage and produces low grade concentrates with low metal recoveries making a single sulfide flotation stage a far more convenient way of ore dressing prior to metal extraction.

Due to the complex nature of these ores, hydrometallurgical techniques seem to be the most convenient way of extracting metals [8.51]. In comparison with pyrometallurgical techniques the hydrometallurgical way offers greater flexibility and, more importantly, can process low-grade ores, will extract major metals and trace elements and is amenable to automatic control. However, hydrometallurgical processing is energy intensive, highly corrosive towards the equipment and forms solid residue [8.52]. The ore can be leached in a variety of aqueous media e.g. sulfate (SHERRIT-GORDON), ammonia (SHERRIT-GORDON, LURGI), chloride (ARBITER, MINEMET, USB) and less frequently in nitric acid or alkaline cyanide. The use of very strongly oxidising leaching agents has also been tried [8.53-8.54]. The leaching step is usually carried out at elevated temperatures and pressures to aid the rates of dissolution. When chlorides are present, the corrosion of the leaching unit becomes a serious problem unless very expensive materials are used in construction. So far a low pollution process for extracting the valuable metals from complex sulfide ores containing copper, lead and zinc has not been found.

Mechanical activation seems to be a favourable process for the treatment of minerals prior to leaching with significantly enhanced metal recoveries reported. This increase in leachability may well be due to a combination of mechanically induced structural defects and chemical reactions involving the mineral and the local environment. The differences in reactivity of the mineral components of ore, as well as the differences in solubility of the reaction products, can be used to selectively leach metals [8.4, 8.55].

The possibility of applying both these principles to selective extraction of zinc from a complex Cu-Pb-Zn concentrate was investigated [8.54, 8.56] using hydrogen peroxide as a model strong oxidative lixiviant. In accordance with data from the literature [8.57] the overall reactions of sulfide MeS with  $\text{H}_2\text{O}_2$  can be described by the following two equations



Reaction (8.3) manifests itself to a lesser extent. The Cu-Pb-Zn concentrate reacts with hydrogen peroxide to give soluble copper and zinc sulfates, insoluble  $\text{PbSO}_4$  and partially soluble iron hydroxide.

Fig 8.19 depicts the recoveries of copper and zinc from as-received complex Cu-Pb-Zn concentrate plotted versus duration of leaching in 4 and 30 % hydrogen peroxide. After five hours of leaching 61 % Zn and 40 % Cu enter the solution. The metal recoveries are relatively low and the reagent consumption high.

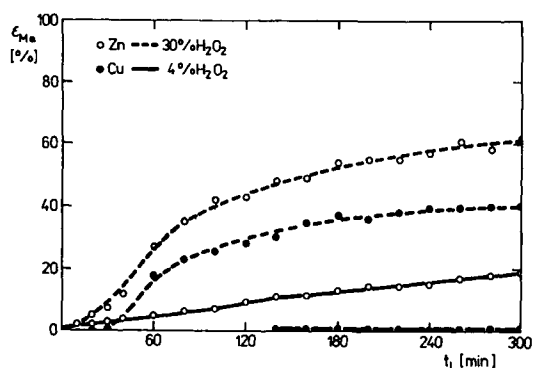


Fig. 8.19. Zinc and copper recovery,  $\epsilon_{Me}$  vs. leaching time,  $t_L$  for as-received Cu-Pb-Zn concentrate [8.56].

Fig. 8.20 shows the results of leaching in  $H_2O_2$  the same concentrate after mechanical activation in a vibration mill. With 30 %  $H_2O_2$  as a leaching agent, 96 % Zn and 90 % Cu entered the solution.

The tests represented in Fig. 8.20 by full curves seem to be very promising as they suggest that the more dilute leaching agent (4 %  $H_2O_2$ ) can extract metals with high recoveries. Furthermore, the curves depicted in Fig. 8.20 also suggest that the weaker leaching agent has a favourable effect on selectivity of leaching, particularly during the initial stages of leaching. For instance, after 60 minutes of leaching by 30 %  $H_2O_2$  the ratio Zn/Cu equals 1.1 whereas when leaching in 4 %  $H_2O_2$  it amounts to 24.5. The beneficial effect of mechanical activation of the concentrate at randomly selected conditions of activation is documented in Fig. 8.20.

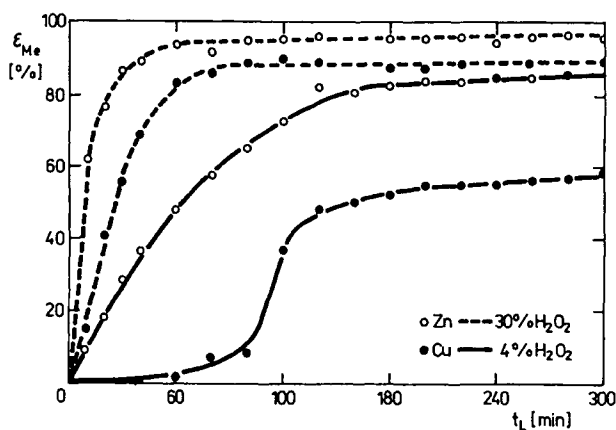


Fig. 8.20 Zinc and copper recovery,  $\epsilon_{Me}$  vs. leaching time,  $t_L$  for mechanically activated Cu-Pb-Zn concentrate [8.56].

A systematic study on the effect of the milling conditions on the recoveries of copper and zinc into the solution by leaching concentrate in 4 %  $H_2O_2$  was carried out following the  $2^2$  plan of experiments (Table 8.3).

Table 8.3 Plan of experiments 2<sup>2</sup> (vibration mill, grinding time 60 min)

| Test No. | Parameters of the mill |                                |
|----------|------------------------|--------------------------------|
|          | Amplitude (mm)         | Frequency (min <sup>-1</sup> ) |
| 1        | 3.9                    | 590                            |
| 2        | 5.8                    | 590                            |
| 3        | 3.9                    | 1100                           |
| 4        | 5.8                    | 1100                           |

The effect of mechanical activation was studied at four levels of the energy input to the mill which were adjusted by selecting the amplitude and the speed of rotation of the mill. Table 8.4 summarizes the results for grinding times of 0.125 - 8 hours. High metal recoveries suggest that leaching is feasible even in the strong diluted lixiviant (4 % H<sub>2</sub>O<sub>2</sub>).

Table 8.4 Copper and zinc recovery vs. grinding time,  $t_M$  for Cu-Pb-Zn concentrate mechanically activated in accordance with conditions in Table 8.3 (leaching time 300 min)

| $t_M$<br>(min) | Copper (%) |       |       |       | Zinc (%) |       |       |       |
|----------------|------------|-------|-------|-------|----------|-------|-------|-------|
|                | No.1       | No.2  | No.3  | No.4  | No.1     | No.2  | No.3  | No.4  |
| 0              |            | 0.92  |       |       |          | 18.61 |       |       |
| 7.5            | 2.30       | 17.02 | 4.15  | 44.10 | 24.99    | 63.37 | 45.16 | 83.50 |
| 15             | 3.12       | 19.87 | 44.27 | 56.40 | 40.81    | 71.28 | 79.12 | 85.00 |
| 30             | 13.56      | 39.82 | 44.29 | 68.40 | 64.46    | 82.15 | 86.62 | 86.70 |
| 60             | 33.70      | 54.63 | 54.12 | 67.00 | 71.70    | 81.83 | 86.05 | 89.90 |
| 120            | 42.90      | 61.21 | 57.39 | 58.50 | 79.45    | 87.50 | 88.39 | 89.20 |
| 240            | 66.46      | 63.00 | 65.87 | 57.34 | 86.31    | 90.78 | 97.11 | 91.79 |
| 480            | 65.44      | 75.44 | 70.14 | 69.00 | 89.09    | 98.03 | 88.80 | 83.00 |

Fig. 8.21 shows the dependence of the dissolution of copper, zinc and iron with time for the most intensively activated sample i.e. test No. 4 milled for 480 min. The temperature of the solution measured during this tests showed two maxima (at  $t = 10$  min and  $t = 240$  min) which corresponded with the highest rates of recovery of zinc and copper respectively.

Leaching of sphalerite or chalcopyrite from the concentrate by H<sub>2</sub>O<sub>2</sub> solution is an exothermic process hence the temperature of the solution rises. Of great importance is the fact that zinc is selectively leached out at  $t_L < 180$  min and the solubilization of iron is minimal (2 % after 6 hours of leaching).

Mechanical activation of the sample brings about reduction of the particle size of the concentrate. Table 8.5 summarizing the fraction passing 40  $\mu$ m in the ground samples. For all grinding times and conditions the fraction of concentrate below 40  $\mu$ m was 2-3 times greater than in the as-received sample.

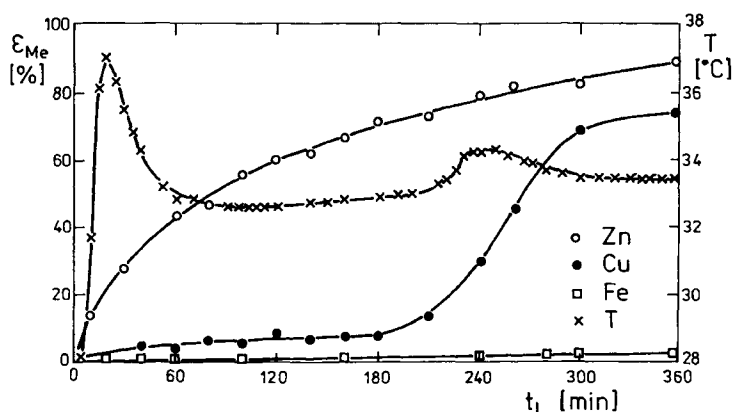


Fig. 8.21 Zinc, copper and iron recoveries,  $\epsilon_{Me}$  and temperature of leach solution,  $T$  vs. leaching time,  $t_L$  for mechanically activated Cu-Pb-Zn concentrate (Test No.4,  $t_M = 480$  min) [8.56].

Table 8.5 Percent of occurrence of fines passing 40  $\mu m$  for Cu-Pb-Zn concentrate mechanically activated in accordance with conditions in Table 8.2

| Test No. | Grinding time (min) |    |    |    |     |     |     |
|----------|---------------------|----|----|----|-----|-----|-----|
|          | 7.5                 | 15 | 30 | 60 | 120 | 240 | 480 |
| -        |                     |    |    | 31 |     |     |     |
| 1        | 76                  | 92 | 90 | 84 | 84  | 81  | 80  |
| 2        | 77                  | 78 | 74 | 69 | 69  | 69  | 65  |
| 3        | 85                  | 79 | 63 | 56 | 67  | 55  | 64  |
| 4        | 73                  | 73 | 62 | 62 | 61  | 61  | 64  |

The reaction of Cu-Pb-Zn concentrate with  $H_2O_2$  solutions represents a convenient model system to study the conditions of selective dissolution of a particular metal from mechanically activated complex concentrates. Hydrogen peroxide reacts with galena and iron to give insoluble or poorly soluble products which can be separated from soluble sulfates in a single leaching stage. The selective separation of soluble zinc and copper sulfates can be accomplished by multi-step leaching process, provided the differences in reactivity of sphalerite and chalcopyrite are conveniently regulated by mechanical activation [8.54].

Cu-Ni complex concentrates also serve as a suitable model for selectivity study. The mechanical activation of pentlandite concentrate results in increased specific surface area and amorphization of individual mineral components. The dissimilar behaviour of pentlandite  $(Fe,Ni)_9S_8$  and chalcopyrite  $CuFeS_2$  after mechanochemical treatment towards ferric sulfate leaching may be used to selective leach of nickel and copper [8.58]. The differences between cobalt and iron during oxidative sulfuric leaching of mechanically activated complex Cu-Ni concentrate from Akarema (Egypt) were described in paper [8.59].

#### 8.2.4. LURGI-MITTERBERG process

The leaching of chalcopyrite flotation concentrate was tested on an industrial scale in the LURGI-MITTERBERG process [8.60-8.61]. Chalcopyrite  $\text{CuFeS}_2$  is among the most refractory minerals with respect to leaching agents [8.62] and even under high pressures and temperatures the recovery of copper is only to about 20 %. According to proposers of the process, the leachability of copper can be improved by mechanical activation of the concentrate in a vibration mill. If the performance of the mill is sufficient a complete extraction of copper can be achieved in single step at temperatures below the melting point of sulfur. The flowsheet of the process is represented in Fig. 8.22. The chalcopyrite flotation concentrate from the Mitterberg deposit was dried to  $\sim 1$  % moisture and activated in a vibration mill. The energy necessary for copper extraction is dependent upon the mineralogical composition of the concentrate. For the Mitterberg concentrate, an energy input of about  $300 \text{ kWh t}^{-1}$  was needed for the recovery of 96 % of copper. If a predominantly chalcocite  $\text{Cu}_2\text{S}$  concentrate was tested, the energy input necessary for obtaining at minimum 95 % of copper decreased to  $100 \text{ kWh t}^{-1}$ .

The product obtained after grinding the chalcopyrite concentrate is mixed with the reversible electrolyte from the extraction of copper. The electrolysis proceeds at pressures of 1-2 MPa and residence time of 2 hours, the efficiency being  $0.6 \text{ t m}^{-3}$  for 24 hours. The partially dissolved iron is precipitated in the autoclave together with arsenic, antimony, bismuth and other contaminants and remains in the solid residue. The solution obtained by pressure leaching is pure enough to be electrolysed following the solid-liquid separation. The cathode copper is produced using a current density of  $200 \text{ A m}^{-2}$ .

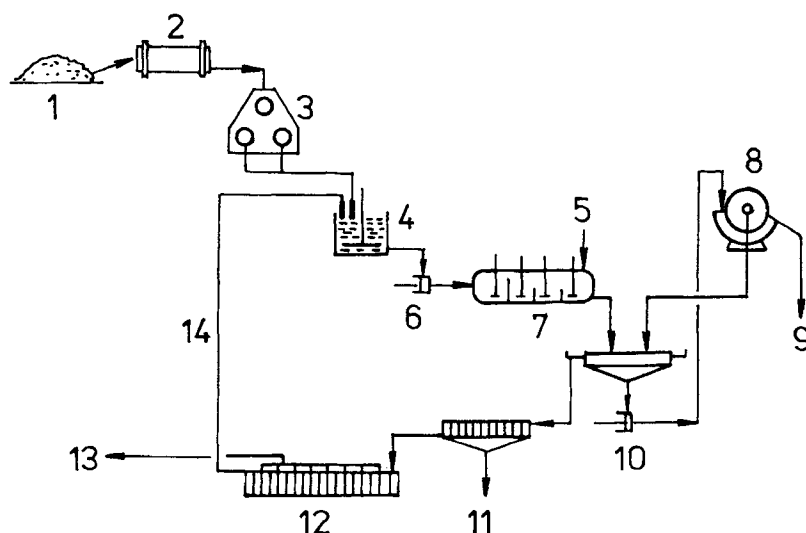


Fig. 8.22 Flowsheet of the LURGI-MITTERBERG process: 1 - flotation concentrate, 2 - drum drier, 3 - vibration mill, 4 - stirrer, 5 - oxygen inlet, 6 - slurry pump, 7 - autoclave, 8 - filter, 9 - waste, 10 - thickener, 11 - waste, 12 - electrolyzer, 13 - cathode copper, 14 - reversible electrolyte [8.60].

This process was in operation in 1974-76, the capacity was 1t of cathode copper daily. The plant was closed because of high operational costs with the concentrate transport and high power consumption.

### 8.2.5. ACTIVOX™ process

The ACTIVOX™ process was developed in the the past decade in Australia as an alternative to the pretreatments of sulfidic concentrates by roasting and bacterial oxidation [8.63-8.66]. The process has been applied to the recovery of non-ferrous and precious metals from concentrates and calcines. A typical ACTIVOX™ flowsheet is shown in Figure 8.23.

ACTIVOX™ combines two unit operations - ultra-fine grinding and pressure oxidation under mild conditions. The mechanical activation proceeds usually in the first operation. The concentrate is ground to 80 % 5-15 microns using a METPROTECH vertical stirred pin mill with a power input of 55-180 kWh<sup>t</sup><sup>-1</sup>. The power input is dependent on the nature of the concentrate [8.65-8.66]. In the second operation, diluted slurry from the mill flows to the autoclave where oxygen pressure oxidation proceeds. The oxidative leaching conditions are typically: pulp temperature 98-100°C, oxygen pressure of 1000 kPa and residence time between 1-2 hours [8.66].

An example of the ACTIVOX™ process is the application to recovery of nickel from pentlandite concentrate from Western Australia. The concentrate was ground to various sizes in a stirred mill and subsequently oxidised in an autoclave for one hour at oxygen pressures of below 1000 kPa and temperatures below 100°C [8.65]. After grinding to 80 % - 5 microns and mild oxidation for 40-60 minutes the recovery was 97 % Ni. The recovery of nickel under the same leaching conditions but without grinding was no more than 50 % Ni.

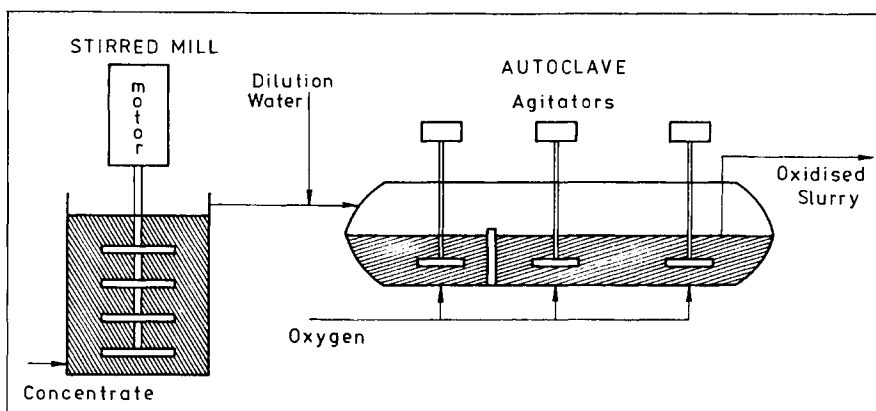


Fig. 8.23 Flowsheet of the ACTIVOX™ process [8.66].

It has been found that it is not necessary to totally oxidise all the reduced species to achieve these results. Elemental sulfur in the leach residues can be recovered as a valuable by-product. The second advantage is the reduction in oxygen demand by the mild conditions of oxidation. Oxygen is one of the major operational costs in oxygen-leaching and typical data for oxygen consumption are given in Table 8.6.

Table 8.6 Oxygen consumption during pressure oxidation of nickel concentrate [8.65]

|                                             | Conventional pressure<br>oxidation | ACTIVOX <sup>TM</sup> pressure<br>oxidation |
|---------------------------------------------|------------------------------------|---------------------------------------------|
| Sulfide sulfur (%)                          | 22.5                               | 22.5                                        |
| O <sub>2</sub> /sulfide sulfur (mass ratio) | 2.2:1                              | 1.3:1                                       |
| Reduction ratio of O <sub>2</sub> usage     | 1                                  | 0.6                                         |

The ACTIVOX<sup>TM</sup> process offers a number of potential advantages [8.64]. Some of them are

- the required moderate temperatures and pressures result in a plant that is simpler and less expensive to build and operate than a conventional pressure oxidation plant. The leaching units can be made from less expensive materials, without the need to resort to exotic alloys,
- less oxygen is required (see Table 8.6) and
- arsenic in the residue from the process is in a stable form.

There are some disadvantages of the ACTIVOX<sup>TM</sup> process with an additional ultra-fine grinding step added to the flowsheet and the power consumption by the grinding step.

A new technology for the hydrometallurgical treatment of sulfide ores was developed recently in Australia under the name “The Yakabindie Nickel Process”. This process represents a unique combination of the ACTIVOX<sup>TM</sup> leaching and well established solvent extraction - electrowinning unit operations. The Yakabindie Process was extensively tested and proved on a continuous basis in a fully integrated plant during 1995.

### 8.3. Mechanical activation as pretreatment step for gold and silver extraction

The technologies hitherto used encounter a problem in processing complex sulfide ores containing gold and silver in an economic way providing sufficient recovery. One of the problems of gold and silver extraction from sulfidic minerals is associated with the form in which the precious metals occur.

Gold and silver are frequently physically-locked within sulfides, may form defects in their structure or can be chemically bonded in the form of solid solutions or compounds [8.67-8.68]. Different types of associations of gold with sulfidic minerals are given in Fig. 8.24.

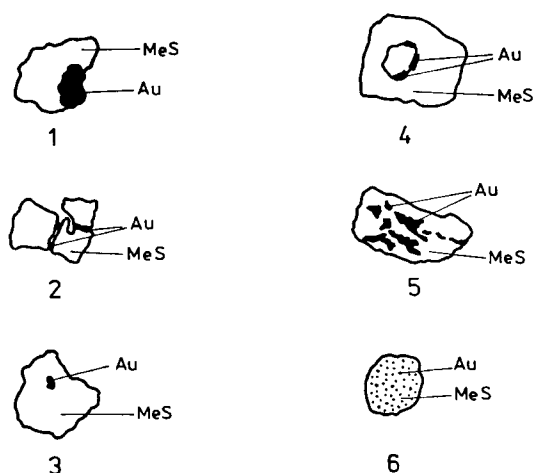


Fig. 8.24 Gold associations with sulfide minerals, 1 - readily liberatable gold, 2 - gold along crystal grain boundaries, 3 - gold grain enclosed in pyrite/sulfide (random position), 4 - gold occurrence at the boundary between sulfide grains, 5 - gold in concretionary pyrite (or other sulfide) along fractures and/or crystal defects, 6 - gold as colloidal particles or in solid solution in sulfide [8.68].

Sulfides are also a considerable natural resource of silver. Gasparini mentions 200 minerals bearing silver in major, minor and variable amounts [8.69]. However, of these, only 10-12 minerals are of practical importance. These are, in order of leachability: elemental silver, silver halides and silver sulfides [8.70].

The contact of gold and silver (in form of metals or compounds) with leaching reagent plays a fundamental role in the hydrometallurgical extraction of the precious metals. An improvement of the contact can be achieved by pretreatment. The choice of pretreatment method significantly depends on locality and mineralogy of the ore deposit. The oxidizing pretreatment, which can, in principle, proceed in the pyrometallurgical or hydrometallurgical way, belongs among classical methods [8.68]. Pyrometallurgical pretreatment is the oldest application and consists of an oxidizing roast to convert sulfides to oxides. However, because of environmental demands roasting is becoming more and more suppressed, irrespective of technical innovations [8.71].

Chemical and biological pretreatments are applied in hydrometallurgical processes, the goal of these processes is to disintegrate the sulfide and thus to facilitate the subsequent extraction of gold and silver. Pressure oxidation can be used for this but has high capital and operating costs. At present, one of the increasingly used processes is biological oxidation, this is considered acceptable from the view-point of environmental considerations and lower economic demands (see Table 8.7). However, long reaction times and appropriate design of bioreactors can make difficulties.

Table 8.7 Relative costs of pretreatment processes [8.72]

| Pretreatment         | Costs     |           |
|----------------------|-----------|-----------|
|                      | Capital   | Operating |
| Roasting             | 1.0-1.5   | 0.75-0.80 |
| Pressure oxidation   | 1.20-1.25 | 0.90-0.95 |
| Biological oxidation | 1.0       | 1.0       |

The process of fine and ultra-fine grinding for pretreating gold and silver concentrates has been used very often in recent years. This process requires finer grinding than that attained in the ball mills typically used in comminution for flotation. Particle size of 1-20  $\mu\text{m}$  can be produced in intensive milling where size reduction is accompanied by mechanical activation of mineral components. The economics of milling is dependent on the metal content of ore, energy and reagent consumptions and amortization of the process plant. Vibration, planetary, jet impact mills and attritors have all been used in ultrafine grinding.

Minejev et al. [8.73] studied the mechanical activation of arsenopyrite concentrate containing 21  $\text{g t}^{-1}$  of gold by a jet impact mill. The subsequent processing with protein hydrolyzate in mixture with 0.15 % solution of cyanide made it possible to solubilize 85 % of gold.

Jet mill treatment of Au-Ag-As concentrate containing 40 % of sulfides gave a size range of 8-30  $\mu\text{m}$  after activation [8.74]. After arsenopyrite decomposition, cyanidation of the residue resulted in the 96-97 % recovery of gold.

Syratlanova et al. [8.75] studied the possibilities of intensification of the cyanide leaching of refractory pyrite-arsenopyrite concentrates. In this case gold was associated in the form of fine dispersion and direct cyanidation was ineffective with only 8-10 % gold recovery. A combination of mechanical activation, alkaline leaching and cyanide leaching resulted in 81 % decomposition of the arsenopyrite during the alkaline leaching and in significant improvement in gold extraction in the second stage of leaching. The results obtained by different methods of activation are summarized in Table 8.8.

Table 8.8 Influence of different methods of mechanical activation on FeAsS destruction and subsequent gold extraction [8.75]

| Mechanical activation | FeAsS decomposition (%) | Au cyanidation (%) |
|-----------------------|-------------------------|--------------------|
| -                     | 12.5                    | 8-10               |
| Ball mill             | 15.0                    | -                  |
| Vibration mill        | 21.2                    | -                  |
| Planetary mill        | 81.2                    | 48-50              |
| Jet impact mill       | -                       | 62-80              |

It is clear that the jet impact mill proved to be the most effective. These mills are widely used in industry, they have high capacity (25  $\text{th}^{-1}$  and more), simple construction and are not expensive. It seems that planetary milling is less effective because of surface passivation of gold particles as has been shown to occur during mechanical activation [8.76, 8.77].

Kušnierová et al. [8.76] investigated a pyrite-arsenopyrite concentrate of Slovak origin. Mechanical activation in a vibration mill showed relatively little improvement in the recovery of gold, despite considerable amorphization of  $\text{FeS}_2$  and FeAsS. Mechanical activation brought about an increase in gold recovery from 4 to 29 %. A similar experiment carried out

with biologically pretreated concentrate resulted in a recovery increase from about 66 % to 93 % Au after activation.

Jusupov et al. [8.77] studied the influence of particle size of an arsenopyrite-pyrite concentrate activated in the centrifugal-planetary mill and subsequently classified. The results are summarized in Table 8.9.

Table 8.9 Results of gold extraction from mechanically activated and classified arsenopyrite-pyrite concentrate [8.77]

| Grain size<br>( $\mu\text{m}$ )      | Leaching agent |               |
|--------------------------------------|----------------|---------------|
|                                      | Cyanide        | Thiocarbamide |
|                                      | Au (%)         |               |
| Non activated concentrate            | 72.5           | -             |
| - 50 + 40                            | 80.1           | 98.0          |
| - 40 + 20                            | 83.6           | 95.8          |
| - 20 + 10                            | 92.3           | 95.2          |
| - 10 + 5                             | 100.0          | 89.7          |
| - 5                                  | 100.0          | 58.5          |
| Non classified activated concentrate | 93.6           | 87.6          |

The optimal range of particle size for gold extraction is clearly different for cyanide and thiourea leaching. For cyanide leaching particles of 5-10  $\mu\text{m}$  appeared to be the most efficient. When employing thiocarbamide as the lixiviant, the decrease in gold extraction can be explained by the presence of a surface layer of elementary sulfur formed during dissolution of arsenopyrite and pyrite in acid medium. The particle size range 40-50  $\mu\text{m}$  appeared to be the most favourable size for leaching of the concentrate.

Pawlek studied the effect of combination of fine grinding in ball mill with classification and mechanical activation in attritor on gold and silver recovery from a chalcopyrite concentrate [8.18]. The proposed flowsheet is in Fig. 8.25.

Mechanical activation was used to examine whether intensification of gold and silver leaching from arsenopyrite concentrates with high carbon content could be achieved [8.78]. It was found that after activation the concentrate can effectively be leached at 100-120°C and an oxygen pressure of 0.5-1.0 Mpa. Arsenic and iron quantitatively pass into the leaching solution and the residue is enriched with gold and silver. After decarbonization of the residue by roasting the precious metals can be completely extracted by cyanidation. The applied activation-leaching process bypasses the drawbacks of traditional pyrometallurgical pretreatment of arsenopyrite concentrates such as emission of  $\text{SO}_2$  and  $\text{As}_2\text{O}_3$  and gold losses. According to Gock [8.79] the roasting of arsenopyrite at 802°C leads to the loss of 33.7 % of gold with fly ashes.

Besides the chemical, biological and physical pretreatment of concentrates the concept of mechanochemical pretreatment was effectively applied to silver extraction from sulfides (Fig. 8.26). This concept is based on the synergetic effect of mechanical activation and leaching and is more thoroughly discussed in Chapter 8.4.

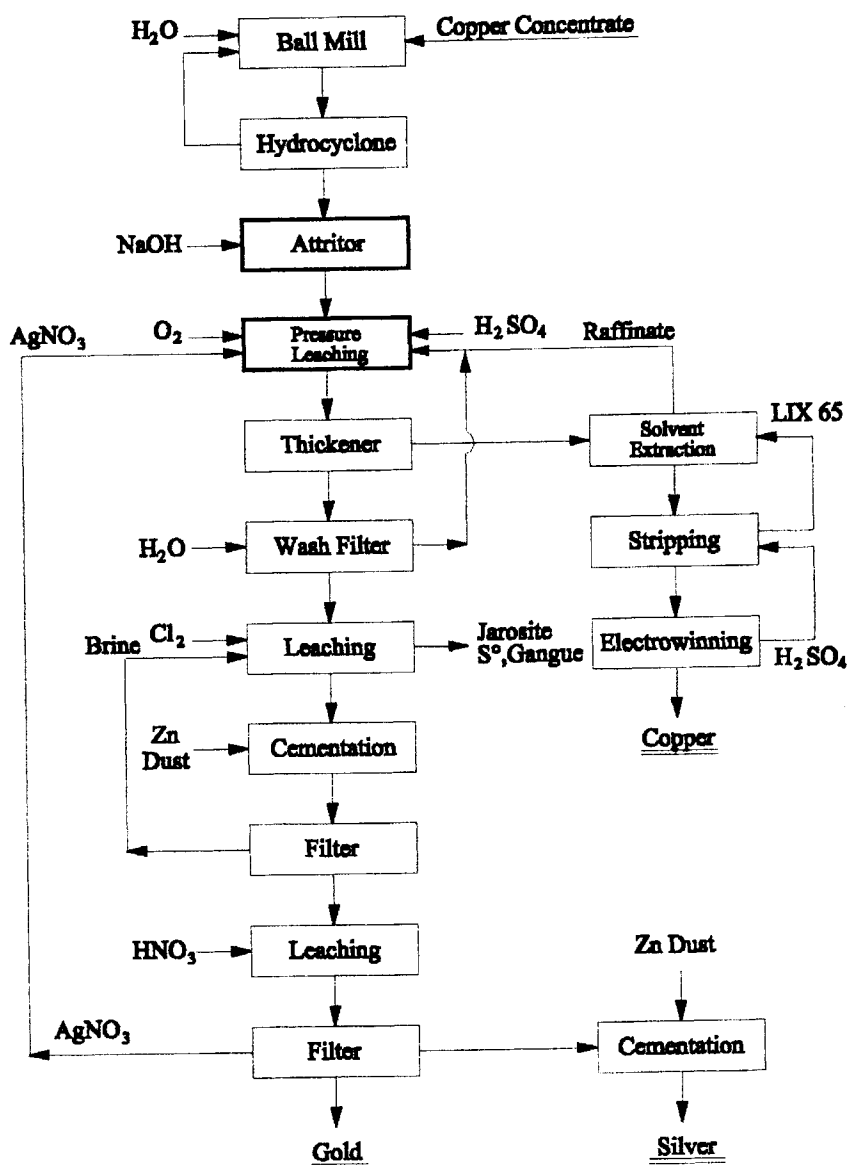


Fig. 8.25 Flowsheet for the treatment of chalcopyrite concentrate by attrition grinding and acid pressure leaching with catalyst ( $\text{AgNO}_3$ ) including recovery of Ag and Au [8.18].

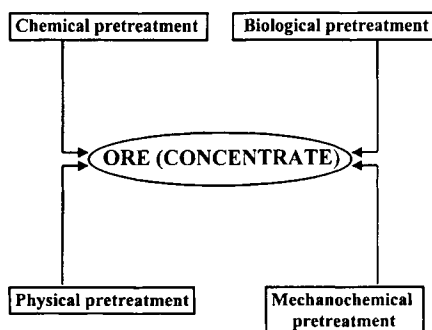


Fig. 8.26 The different ways of sulfidic ore (concentrate) pretreatment.

The mineral tetrahedrite, ideally  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  has a rather variable and complex composition with copper substituted by various metals, most importantly silver and antimony substituted by arsenic. In literature there are only a few papers dealing with the leaching of silver from tetrahedrite. The recovery of silver by cyanide or thiourea did not exceed 5-10 % showing to refractory character of the mineral [8.80]. The leachability of silver can be significantly raised by mechanical activation in a planetary mill, subsequent thiourea leaching enabled the dissolution of as much as 48 % Ag [8.49]. The mechanochemical pretreatment of tetrahedrite produces disordering of the mineral structure and has positive effect on silver extraction with non-cyanide lixiviants [8.49, 8.81-8.84].

In Fig. 8.27 recovery of silver into solution is plotted against leaching time. It can be seen that the application of thiourea for silver extraction from tetrahedrite without pretreatment is not effective and amounts to < 10 % even after 120 minutes of leaching.

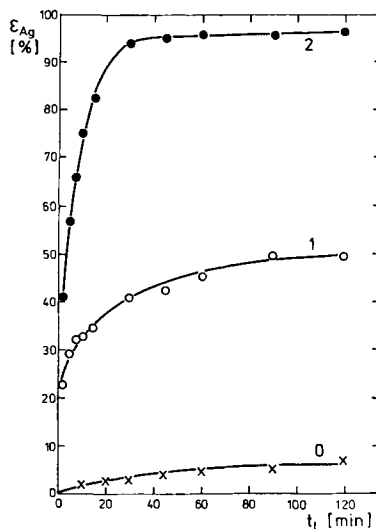
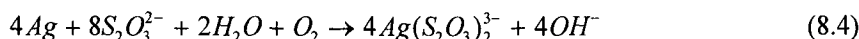


Fig. 8.27 Influence of leaching time,  $t_L$  on the recovery of silver,  $\epsilon_{Ag}$  from a mechanochemically treated tetrahedrite concentrate. Degree of mechanochemical decomposition of tetrahedrite: 0 - 0 %, 1 - 52 %, 2 - 100 %, leaching agent:  $\text{CO}(\text{NH}_2)_2$  [8.81].

The recoveries from the solid residues after mechano-chemical leaching are substantially improved. The extraction values depend on degree of tetrahedrite disordering and can vary from 50 % to 96 % Ag.

In ammonium thiosulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  silver predominantly reacts to form the thiosulfate complex



However a small amount of the amine complex is also formed in the process [8.85, 8.86]



Fig. 8.28 shows the structural sensitivity of the leaching of silver from tetrahedrite by thiosulfate. The leaching of the most disordered tetrahedrite sample shows a dissolution of 93 % Ag after 120 min whereas without pretreatment silver recovery did not exceeded 3 % .

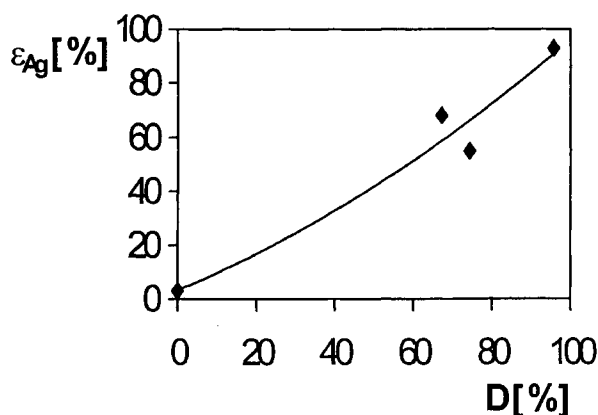


Fig. 8.28 Influence of the destruction of tetrahedrite, D on the recovery of silver,  $\epsilon_{\text{Ag}}$  from mechanochemically pretreated tetrahedrite, leaching agent:  $(\text{NH}_4)_2\text{S}_2\text{O}_3$  [8.84].

Ultrafine grinding as a method of physical pretreatment of the minerals is continuously examined in Australia [8.4, 8.30-8.31, 8.55, 8.63-8.66, 8.87-8.100]. In Perth The Special Research Centre for Advanced Mineral and Materials Processing (SRCAMMP) was established in 1991 [8.98-8.100]. One of the focuses of the SRCAMMP is “the development of new value added processing techniques based on ultrafine grinding and mechanochemistry, applicable to the processing of minerals and advanced materials” [8.99].

Of the equipment used for ultrafine grinding, the best results have been achieved with attritors which show the lowest consumption of energy, high rates of grinding and good recovery of gold in the subsequent cyanide leaching. If the gold encapsulated within the matrix of sulfide minerals is somewhat coarser in size, ranging from 1 to 20 microns, then liberation can be achieved by ultrafine grinding in a vertical stirred mill (attritor) [8.63]. Gold contained in pyrites is generally coarser and ultrafine grinding has significant effect on gold recovery (Fig. 8.29).

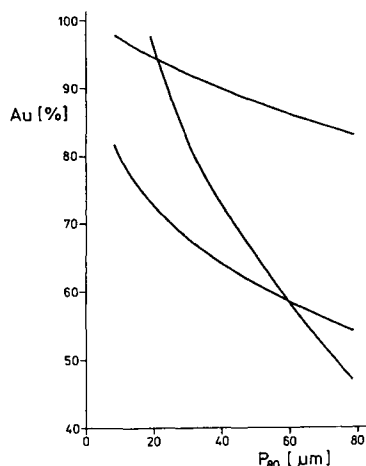
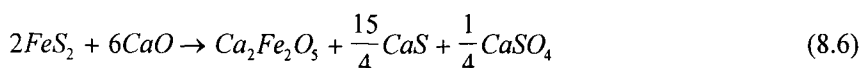


Fig. 8.29 The gold recovery in cyanide leaching from pyrite concentrates mechanically activated in METPROTECH mill [8.63].

The behaviour of pyrite and arsenopyrite in the process ultrafine grinding and the potential for exsolution of gold was studied in paper [8.94]. The positive effect of the gold liberation from the sulfide structures may be retarded by locking the gold up in aggregates of arsenopyrite.

There is the possibility to influence the properties of gold bearing pyrite by selective mechanochemical reaction. Warris and McCormick [8.95] have studied the reaction between pyrite and calcium oxide in a vertical stirred mill



The CaS can be oxidised in the second step to CaSO<sub>4</sub> by heating the sample in air at 500°C. The main advantage of the process under study is the potential to treat the refractory pyritic gold ores without any SO<sub>2</sub> evolution.

Welham pointed out on the different behaviour of pyrite and arsenopyrite during grinding [8.4, 8.55]. Study of pure pyrite and arsenopyrite has shown that selective dissolution was possible by a simple leaching process directly after grinding. The separation of both minerals is possible by grinding in oxygen, the arsenopyrite decomposing and the pyrite remaining essentially unreacted. This has great potential for processing gold bearing pyrite/arsenopyrite ores where selective oxidation of the gold bearing arsenopyrite would liberate the gold for cyanide leaching [8.4].

### 8.3.1. IRIGETMET process

Extensive studies of the influence of mechanical activation on the efficiency of subsequent cyanide leaching of some sulfidic concentrates containing gold were made in IRIGETMET in the former Soviet Union [8.101]. It was found that the time of cyanization can be decreased severalfold after optimum mechanical activation. Optimizing the regime of grinding was essential because the consumption of NaCN increased with the extent of activation owing to mechanochemical destruction of sulfidic minerals. The optimum regime of grinding consisted

of attaining 95 % 20-40  $\mu\text{m}$ . A continuous planetary mill working at relative acceleration of 50-70 using a revolution rate of  $1500\text{ min}^{-1}$  and rate of pulp feed of  $2\text{ dm}^3\text{h}^{-1}$  proved to be satisfactory. The recovery of gold increased by 11 % while the time of cyanidation shortened threefold. It is interesting that a significant increase in NaCN consumption did not appear.

IRIGETMET subsequently developed an amalgam-free technology for gold extraction from sulfidic gravity concentrates. The technology comprises thermal decomposition of sulfides followed by grinding and gravity separation of free gold. A planetary mill proved to be the best for the selective grinding. In the course of testing an arsenopyrite concentrate a gold recovery of 97.9 % was achieved with practically all gold particles larger than 20  $\mu\text{m}$  recovered. By cyanidation of the finely ground residue the total gold recovery was  $> 99.9\%$ . This technology offers the possibility that besides an increase in gold extraction the highly toxic process of amalgamation can be eliminated from the technological cycle.

### **8.3.2. *SUNSHINE process***

In 1984 the Sunshine Mining and Refining Company introduced a new concept to the hydrometallurgical treatment of complex sulfidic concentrates with antimony, copper and silver content. The concept is based on sulfuric acid oxygen pressure leaching with the application of nitric acid [8.102]. This treatment allows the recovery of silver and copper from the solid residue after alkaline leaching of tetrahydrite.

It was shown that the grinding had an important role by the introduction of a regrind circuit before the pressure leach improving the overall recovery of silver. The grinding in tube mill led to size reduction from original 80 % - 25 micron to 80 % - 10 micron. The installation of the regrind circuit and application of sodium nitrite in the plant allowed the silver recovery to increase from the historically recorded value of 87.5 % to 92.1 %. At full production, these enhancements allow recovery of an extra 230,000 troy ounces of silver per year [8.102].

### **8.3.3. *METPROTECH process***

After extensive laboratory and pilot plant investigations a suitable mill for mining and metallurgical applications has been developed by METPROTECH [8.87-8.91] with the grinding process producing submicrons particles. In the course of the investigations it was found that a large number of gold-bearing materials are amenable to fine grinding [8.31]. A special feature of the METPROTECH process is that it is possible to add cyanide to the mill feed slurry so that cyanidation of the gold occurs in within the mill. The regime of mechanochemical leaching (see also Chapter 8.5) enables the recovery of part of the gold directly in the mill. This fact has an advantageous influence on the cost of a subsequent gold recovery by chemical leaching with cyanide. The critical parameter by grinding is the enhanced cyanide consumption in the subsequent leaching step. Liddell verified that maintaining high dissolved in the mill oxygen levels oxidizes ferrous ions to ferric ions thus allowing some oxidative leaching to occur also during the milling step.

The first industrial installation of the METPROTECH process was commissioned in 1988 [8.31] and was designed to grind tonnage quantities of a gold bearing calcine to 90 % - 8 microns and 50 % - 3 microns in a single pass prior to carbon-in-pulp section. The mills commissioned during the years 1988-98 in South Africa, Australia and New Zealand have installed power of up to 400 kW and grinding chamber volumes up to 6000 litres. Energy

inputs over  $100 \text{ kWm}^{-3}$  are achieved, compared to approximately  $25 \text{ kWm}^{-3}$  in classical ball or tower mills.

#### 8.3.4. ACTIVOX™ process

The ACTIVOX™ process was described in Chapter 8.2.5 as a method for the enhancing leachability of nickel from pentlandite concentrate. The process is also able to achieve the liberation of encapsulated gold from milled sulfide minerals [8.64]. A typical flowsheet of the processing of sulfidic gold ores by ACTIVOX™ technology is shown in Figure 8.30.

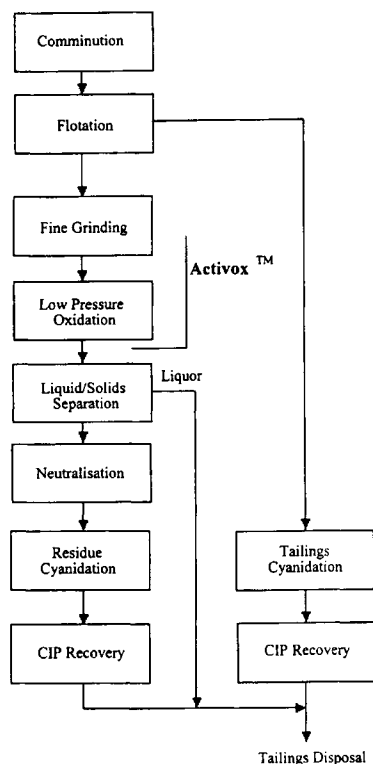


Fig. 8.30 Flowsheet incorporating ACTIVOX™ process for the recovery of gold from sulfide concentrates [8.64].

An arsenopyrite-pyrite concentrate was fine ground and treated by the cyanidation process (Table 8.10)

Table 8.10 Cyanidation of arsenopyrite-pyrite concentrate [8.65].

| Process       | Grind size P80<br>( $\mu\text{m}$ ) | NaCN<br>( $\text{kg t}^{-1}$ ) | Au recovery<br>(%) |
|---------------|-------------------------------------|--------------------------------|--------------------|
| -             | 75                                  | 16.1                           | 60                 |
| Fine grinding | 17.6                                | 19.2                           | 66                 |
| Fine grinding | 3.7                                 | 19.2                           | 68                 |
| ACTIVOX™      | 5                                   | 14                             | 91                 |

It can be seen from the data in Table 8.10 that fine grinding on its own does not substantially improve the gold extraction over the as-received concentrate, whereas fine grinding and relatively mild conditions ( $P < 1000 \text{ kPa O}_2$ ,  $T < 100^\circ\text{C}$ ) improved the gold recovery to 91 % during the subsequent cyanidation. Generally 60 to 90 minutes retention time (in milling or leaching) is required to effect liberation of the gold by oxidation of the sulfides [8.64-8.66].

Many other arsenopyrite-pyrite concentrates have been treated by this method. Cyanide leaching of gold usually exceeds 90 % and is often above 95 %. The commercialisation of ACTIVOX<sup>TM</sup> in Australia proceeded with the construction of two continuous pilot plants [8.66].

#### 8.4. Mechanochemical leaching

The possibility of integrating the individual operations within a whole technological flowsheet is not new. The process CIL (carbon-in-leach) is used in hydrometallurgy for gold recovery [8.68, 8.103]. Granular activated carbon is added to the leaching tanks so that it can adsorb the gold cyanide complex as soon as it is formed thus integrating leaching and sorption into a common operation.

The synergistic effect of grinding and leaching operations has the important theoretical background, as can be deduced from Figure 8.31 which shows that are differences between the excitation period and the duration of excitation states. If the mechanical activation is separated from the chemical process (e.g. leaching) in time, then a number of highly excited states would have decayed before leaching.

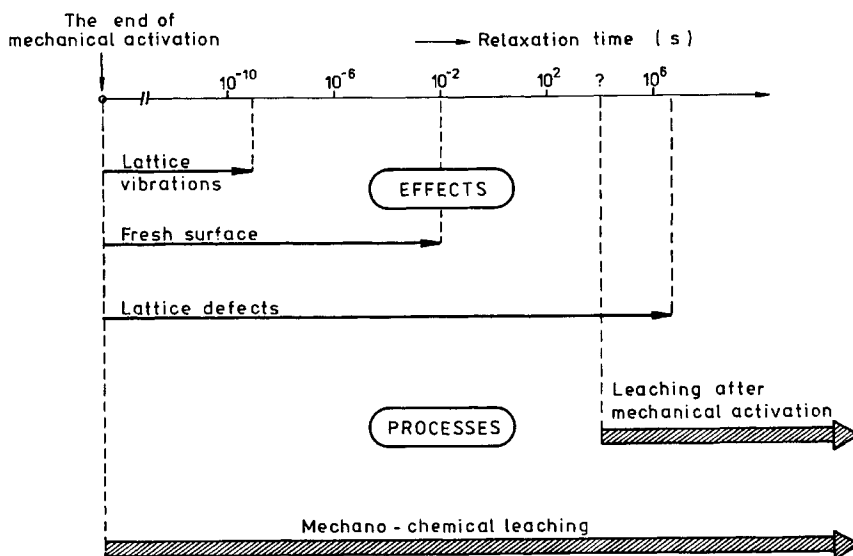


Fig. 8.31 The period and the duration of excitation states after termination of mechanical activation.

On the other hand, if the mechanical activation and leaching are integrated into a common step all the excitation states may be utilized. In addition to the improvement of grinding performance (the leaching agent works also as grinding additive) there is the possibility that a common grinding and leaching step contributes to operation benefits and to economy of the overall process.

The cyanide adding directly into a grinding circuit, as described in Chapter 8.3, represents a typical example of mechanochemical leaching [8.31, 8.87-8.88] with the goal being to improve the gold recovery in the cyanide leaching flowsheet.

#### 8.4.1. MELT process

Tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  is one of the most common sulfominerals. The general formula which describes the tetrahedrite-tennantite series occurring in nature is  $(\text{Cu},\text{Ag})_{10}(\text{Cu},\text{Zn},\text{Fe},\text{Cd},\text{Hg},\text{Cu})_2(\text{Sb},\text{Bi},\text{As})_4\text{S}_{13}$  [8.104]. Tetrahedrites represent the most important source of copper and antimony and are also of interest due to their content of silver and mercury.

In the industrial complex at Krompachy (Slovakia) copper is produced by a pyrometallurgical method. For this process, chalcopyrite concentrates, waste copper and tetrahedrite concentrates from Rožňava and Rudňany are all considered as suitable material for processing. The tetrahedrite concentrates from the Rožňava deposit are produced by non-selective sulfide flotation and have a high content of copper ( ~ 27 %), antimony ( ~ 16 %) and silver ( ~ 4000  $\text{gt}^{-1}$ ) [8.105]. However, operational requirements at Krompachy necessitate that the content of antimony in the tetrahedrite concentrate must not exceed 1 %.

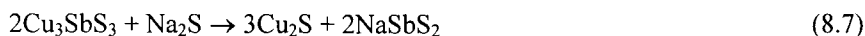
In order to satisfy this prerequisite, several pyrometallurgical processes were proposed and volatilizing roasting, chloridizing roasting and cyclone smelting were tested [8.106]. However, the obtained results indicate that these processes cannot reduce the antimony in the treated tetrahedrite concentrates under 1 %.

With the aim to developing an alternative processing route which allows extraction of most of the metal values from these tetrahedrite concentrates various hydrometallurgical methods have been considered too. The variable presence and proportions of metals in the tetrahedrite and the accompanying sulfides complicate the leaching and subsequent metal recovery steps. The devise a method for solving this problem requires a multistep hydrometallurgical process which exhibits high selectivity in individual stages.

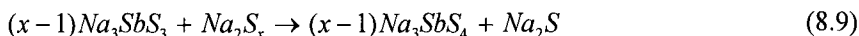
Hydrometallurgical treatment of tetrahedrite is possible in acid oxidative [8.107-8.110] or in alkaline solution [8.81, 8.111-8.113]. By acid oxidative leaching, e.g. in acidified ferric chloride solutions, copper and iron enter into solution, while antimony is partially precipitated as a compound with the composition similar to the mineral tripuhyite  $\text{FeSbO}_4$ . The overall leaching reaction proceeds very slowly and the kinetics are complicated [8.110].

Alkaline leaching in sodium sulfide medium dissolves selectively antimony leaving copper and iron in the solid residues. Arsenic and mercury are also solubilized as complex anions. This process has a high selectivity with copper and precious metals remaining in the solid residue which is suitable for smelter treatment.

The chemistry of the reaction between tetrahedrite and  $\text{Na}_2\text{S}$  can be described in simplified form by equations [8.114]



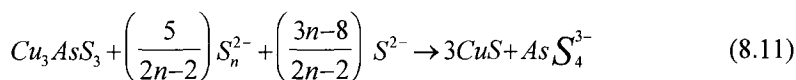
The soluble  $\text{Na}_3\text{SbS}_3$  containing trivalent antimony is oxidized to a product containing pentavalent antimony by the polysulfide ions present in the leaching liquor



The behaviour of arsenic leaching from tennantite by  $Na_2S$  may be described by equation



or in the presence of polysulfide anions by equation [8.115]



However in addition to tennantite, arsenic derived from tetrahedrite, orpiment and realgar is also solubilised in the alkaline solution - arsenopyrite is resistant to leaching in this medium.

The leaching of mercury sulfide with sodium sulfide gives a soluble complex too, according to the equation [8.112]



This salt is prone to hydrolysis and its solution stability necessitates the presence of a base, usually NaOH.

The refractoriness of tetrahedrite requires the application of concentrated leaching agents, high temperatures and long leaching times for efficient dissolution of the valuable antimony content. The recovery of antimony into alkaline leach is not higher than 40 % after two hours of leaching (Fig. 8.32).

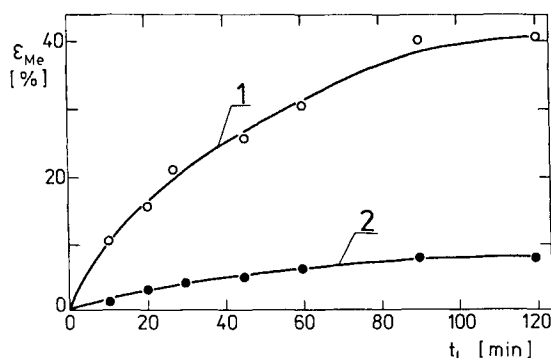


Fig. 8.32 Recovery of antimony (1) and mercury (2) into leach,  $\epsilon_{Me}$  vs. time of leaching,  $t$ , for as received tetrahedrite concentrate, temperature 90°C.

Alkaline leaching of tetrahedrite with a solution of  $Na_2S$  has been applied by the Sunshine Mining and Refining Company [8.116, 8.117]. Leaching is carried out using a 280-300  $gl^{-1}$  sodium sulfide solution at boiling point (104°C) and atmospheric pressure. The process is run in batch mode with a 12 hour residence time solubilising 90-95 % Sb and 60 % As [8.118].

In 1992, the Institute of Metallurgy of Technical University Berlin and the Institute of Geotechnics, Slovak Academy of Sciences Košice tested a new method which combined

grinding and leaching in a batch process within a stirred ball mill (attritor). The results, summarized in Table 8.11, reveal 52-99 % recoveries of antimony after 60 minutes of mechanochemical action [8.81, 8.119]. Antimony is selectively leached while the other valuable metals remain almost entirely in the solid residue.

Table 8.11 Experimental conditions (temperature, T, Na<sub>2</sub>S concentration, c) and recoveries of metals by mechanochemical leaching of tetrahedrite concentrate [8.81]

| T<br>(°C) | c<br>(gl <sup>-1</sup> ) | Metal in leach (%) |      |      |      |      |
|-----------|--------------------------|--------------------|------|------|------|------|
|           |                          | Sb                 | Cu   | Fe   | Hg   | Ag   |
| 60        | 100                      | 52.09              | <0.1 | <0.1 | <0.1 | 0.60 |
| 60        | 150                      | 83.90              | <0.1 | <0.1 | 0.16 | 0.46 |
| 60        | 200                      | 82.64              | <0.1 | <0.1 | 0.33 | 0.45 |
| 80        | 100                      | 99.64              | <0.1 | <0.1 | 0.62 | 0.40 |
| 80        | 150                      | 99.78              | <0.1 | <0.1 | 0.11 | 0.47 |
| 80        | 200                      | 92.76              | <0.1 | <0.1 | 0.11 | 0.38 |
| 95        | 100                      | 84.31              | <0.1 | <0.1 | 0.12 | 0.45 |
| 95        | 150                      | 95.02              | <0.1 | <0.1 | <0.1 | 0.49 |
| 95        | 200                      | 92.96              | <0.1 | <0.1 | 0.14 | 0.74 |

This new process, called MELT (mechanochemical leaching of tetrahedrite) was further developed and tested in semi-industrial and industrial scale attritors using a continuous mode of operation in Slovakia [8.40, 8.81-8.82, 8.119-8.125]. The principal flowsheet of operation, in which mechanochemical (I) leaching is followed by chemical (II) leaching, is shown in Figure 8.33.

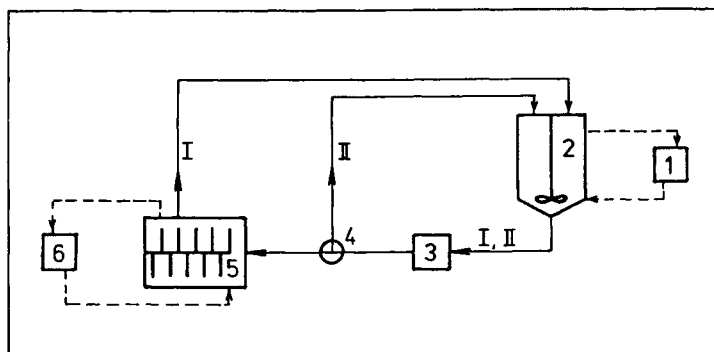


Fig. 8.33 Flowsheet of leaching unit: 1 - heating, 2 - chemical reactor, 3 - pump, 4 - valve, 5 - attritor, 6 - cooling. The working regimes: I - mechanochemical leaching, II - chemical leaching [8.121].

The mechanochemical leaching of the concentrate is characterized by the typical leaching plots for antimony, arsenic and mercury in Fig. 8.34 as well as by the data in Table 8.11. The process was performed in the combined regime of grinding and leaching. The initial stage of mechanochemical leaching (I) for 18 minutes was succeeded by the combined

mechanochemical and chemical leaching (I+II). The presented results show that almost total extraction of antimony can be achieved by leaching for 40 minutes leaving 0.25 % Sb in the solid residue (Table 8.12).

Table 8.12 Chemical composition of tetrahedrite concentrate Rožňava (Slovakia) [8.124]

| Element | Me (%)      |                           |
|---------|-------------|---------------------------|
|         | As received | Mechanochemically treated |
| Cu      | 27.36       | 26.00                     |
| Sb      | 15.93       | 0.25                      |
| Fe      | 14.58       | 16.46                     |
| Bi      | 0.33        | 0.33                      |
| As      | 1.02        | 0.27                      |
| Hg      | 0.74        | 0.11                      |

The behaviour of mercury is not consistent with its expected solubility in the alkaline leaching solution. The effect of a hindered mercury extraction was thought to be due to electrochemical effects, e.g. mercury cementation with iron balls or iron wear [8.81-8.82]. This effect was confirmed by experiments with separate mechanochemical and chemical leaching stages. After interruption of the attritor operation at 70 min (Fig. 8.35) mercury starts to dissolve with higher rates compared to its rate in the mechanochemical regime. At  $t > 200$  min nearly total mercury extraction is attained, and its amount in solid residue after leaching is below 0.01 %.

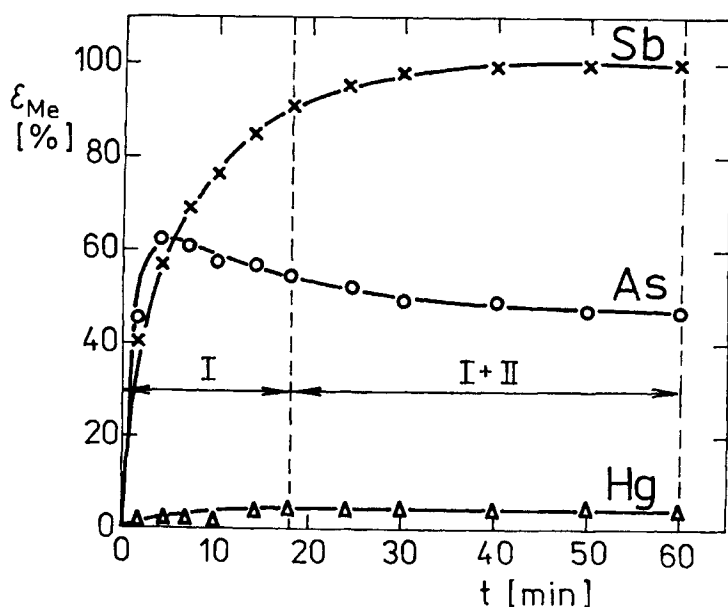


Fig. 8.34 Recovery of Sb, As and Hg into leach,  $\epsilon_{Me}$  vs. time of leaching,  $t$ . I - mechanochemical leaching, II - chemical leaching. Leaching conditions:  $300 \text{ g l}^{-1} \text{ Na}_2\text{S} + 50 \text{ g l}^{-1} \text{ NaOH}$ ,  $T = 88^\circ\text{C}$ , liquid/solid ratio 3.3, power input  $245 \text{ kWh t}^{-1}$  [8.124].

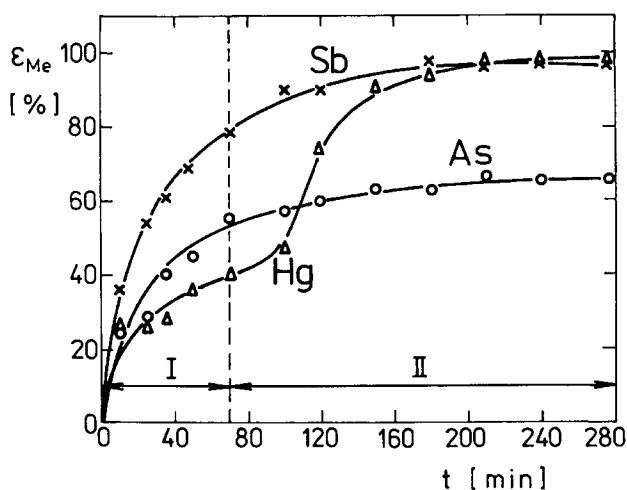


Fig. 8.35 Recovery of Sb, As and Hg into leach,  $\epsilon_{Me}$  vs time of leaching,  $t$ . I - mechano-chemical leaching, II - chemical leaching. Leaching conditions:  $300 \text{ gl}^{-1} \text{ Na}_2\text{S} + 50 \text{ gl}^{-1} \text{ NaOH}$ ,  $T = 95^\circ\text{C}$ , liquid/solid ratio 3.8, power input  $120 \text{ kWh}^{-1}$  [8.124].

The behaviour of arsenic in the alkaline leaching process depends on arsenic origin. The recovery of this metal is always lower than 70 % as indicated in Fig. 8.36 and it can be assumed that probably only the arsenic present in tetrahedrite or tennantite is extracted, the remaining arsenic ( $\sim 30 \%$ ) occurs in other minerals which are insoluble in alkaline sulfide solution (e.g. arsenopyrite) [8.114, 8.126].

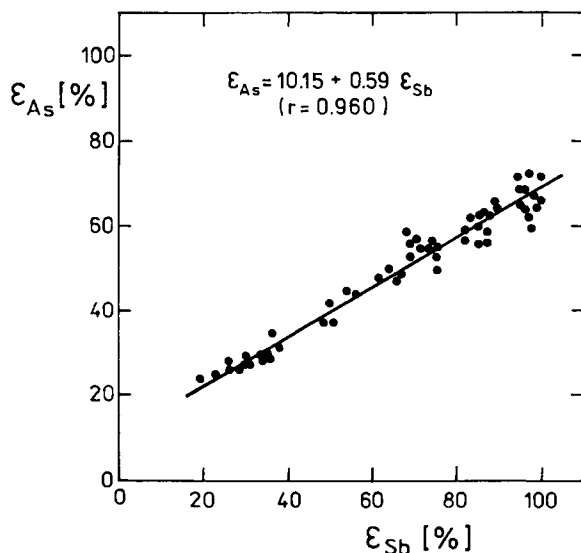


Fig. 8.36 Recovery of arsenic,  $\epsilon_{As}$  vs. recovery of antimony,  $\epsilon_{Sb}$  in experiments of chemical leaching. Leaching conditions:  $300 \text{ gl}^{-1} \text{ Na}_2\text{S} + 50 \text{ gl}^{-1} \text{ NaOH}$ ,  $T = 95^\circ\text{C}$ , liquid/solid ratio 3.3-6.0 [8.124].

On the basis of these results and alternative flowsheet for the pilot plant investigation has been designed (Fig. 8.37) to test the technology at a greater feed rate. The flowsheet consists of primary mechanochemical leaching in an attritor (Fig. 8.38) and subsequent operations - filtration, cementation, antimony precipitation, crystallization and arsenic precipitation. The pilot plant operation is designed for 500 kg per day feed of tetrahydrate concentrate. For the antimony extraction, electrowinning has also been considered. The residue which is a Cu-Ag-Au concentrate can be used as a feed to a copper smelter.

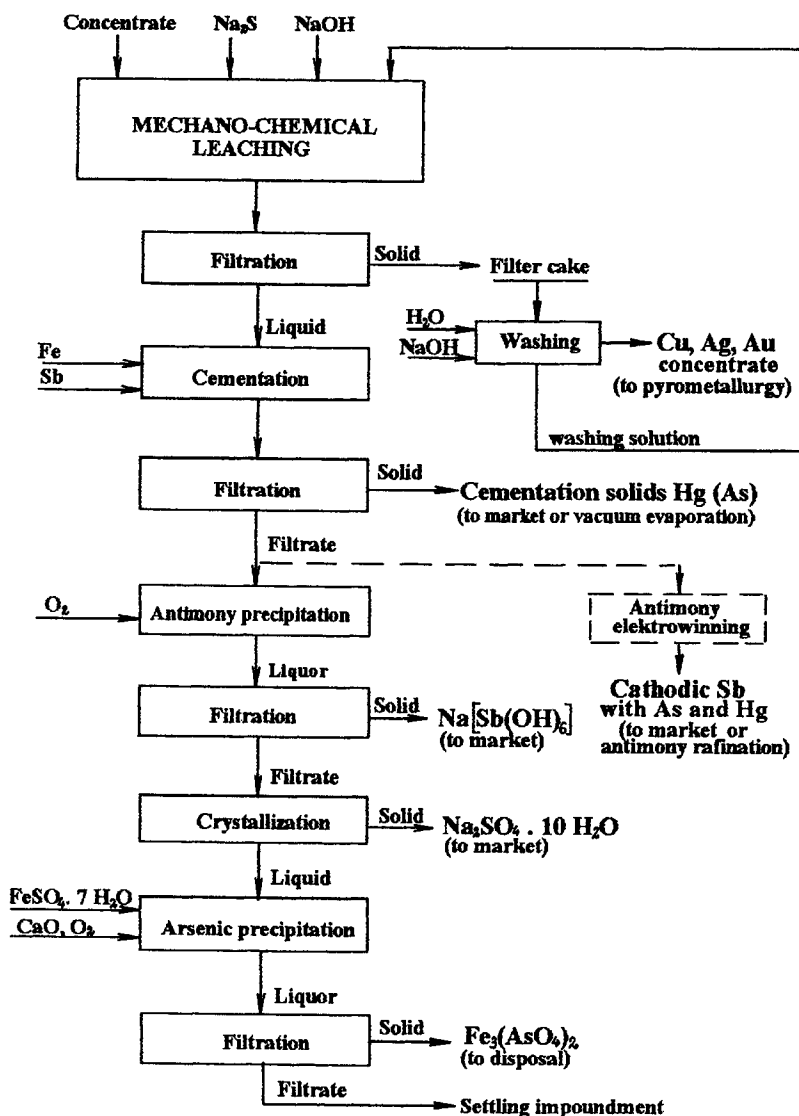


Fig. 8.37 Flowsheet of the MELT process [8.125].

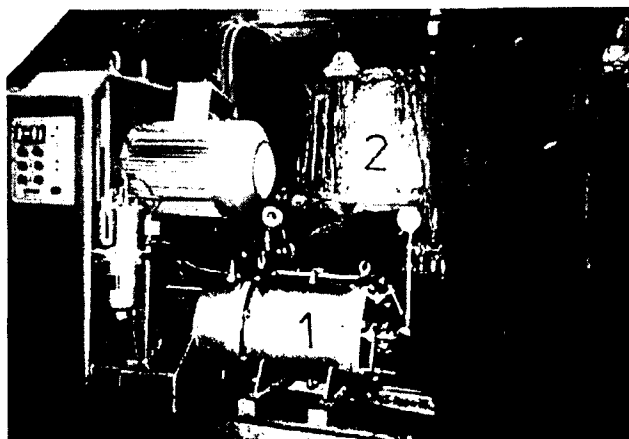


Fig. 8.38 Attritor (1) in combination with chemical reactor (2) in a pilot plant unit at Rudňany (Slovakia).

The potential for using attritor as a chemical reactor was also identified by Liddell [8.90] with batch test work performed in two areas

- initiation of oxidation during grinding in acid solution prior to low temperature low pressure oxidation and
- performing alkaline oxidation simultaneously with ultrafine grinding.

The first area being applicable to gold and base metals, the second area being applicable to the oxidation of FeAsS for gold.

If we compare the results of power input for mechanochemical leaching (ML) with the data for mechanical activation (MA) (Table 8.13) it is evident that ML is from the view-point of energy consumption comparable to the power demands of processes applying ultrafine grinding only as a pretreatment, regardless of any power demands for further hydro- or pyroprocessing.

Table 8.13 Comparison of power input W for mechanical activation (MA) and mechanochemical leaching (ML) of sulfidic concentrates

| Concentrate  | Metallurgical production | W (kWh <sup>t</sup> <sup>-1</sup> ) |         | Reference |
|--------------|--------------------------|-------------------------------------|---------|-----------|
|              |                          | MA                                  | ML      |           |
| Chalcopyrite | Cu                       | 300                                 | -       | 8.61      |
| Chalcopyrite | Cu                       | 224                                 | -       | 8.14      |
| Chalcopyrite | Cu                       | 40                                  | -       | 8.91      |
| Chalcocite   | Cu                       | 100                                 | -       | 8.61      |
| Molybdenite  | Mo                       | 224                                 | -       | 8.14      |
| Sphalerite   | Zn                       | 75                                  | -       | 8.14      |
| Pentlandite  | Ni                       | 80-180                              | -       | 8.65      |
| Pentlandite  | Ni                       | 55-75                               | -       | 8.66      |
| Pyrite       | Au                       | 150                                 | -       | 9.63      |
| Pyrite       | Au                       | 75-150                              | -       | 8.93      |
| Arsenopyrite | Au                       | 87-109                              | -       | 8.90      |
| Telluride    | Au                       | 33-172                              | -       | 8.88      |
| Tetrahedrite | Sb,Cu,Ag                 | -                                   | 120-245 | 8.124     |
| Tetrahedrite | Sb,Cu,Ag                 | -                                   | 82-157  | 8.121     |

## 8.5. Mechanical activation as a way of metallurgical calcine treatment

Oxidative roasting of the major gold-bearing refractory sulfides pyrite and arsenopyrite results in the volatilisation of sulfur and arsenic oxides. The liberated gold particles remain prevailing with the calcine and the subsequent cyanide leaching is improved. Ideally hematite ( $\gamma\text{-Fe}_2\text{O}_3$ ) should be the principal product of roasting [8.127]. However, the generation of sulfur, arsenic and other metals with volatile oxides gives rise to serious environmental concerns [8.128].

### 8.5.1. Pyrite and arsenopyrite calcines

A calcine leach residue with the content of  $28 \text{ gt}^{-1} \text{ Au}$  and having  $P_{90}$  (the size at which 90 % passes) of 82 microns was ground in the METPROTECH mill in the presence of cyanide and lime [8.31]. The  $P_{90}$  after grinding was 4 microns, and 59 % of the gold was dissolved during grinding. A subsequent 24 hour leach of the ground calcine resulted in the gold dissolution increasing to 60 %, indicating that essentially all of the leaching has occurred during grinding.

Arsenopyrite and pyrite residues from the cyanide leaching of calcines were treated using the same type of the mill by Corrans and Angove [8.63]. These residue can often contain appreciable quantities of gold encapsulated within the hematite matrix and can only be liberated by grinding the calcine to sizes below about 10 microns. The results of pyritic and arsenopyritic calcines grinding of Australia origin are shown in Figure 8.39.

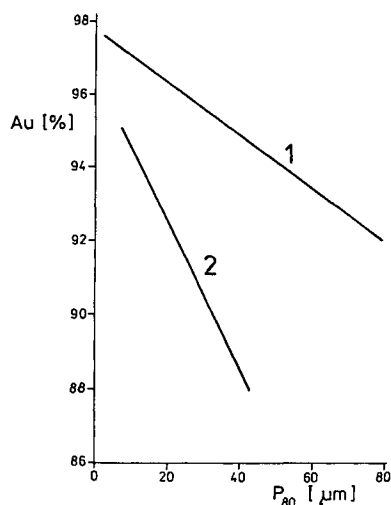


Fig. 8.39 The gold recovery in cyanide leaching from calcines mechanically activated in METPROTECH mill: 1 - pyrite calcine, 2 - arsenopyrite calcine [8.63].

In the case of the arsenopyrite calcine the head grade can approach  $100 \text{ gt}^{-1} \text{ Au}$ , so that regrinding to reduce the value of the cyanidation residue can be economic. In the case of the

pyrite calcine, the curve is flatter whilst the head grade is also lower (50-70  $\text{gt}^{-1}$  Au), so that regrinding is less attractive [8.63].

### 8.5.2. Tetrahedrite calcines

Tetrahedrite concentrate treated in order to remove mercury is the residue(calcine) containing antimony, copper and silver and is an economically interesting source of these metals.

The investigations were carried out on a tetrahedrite calcine from Rudňany (Slovakia). This material is a rich source of copper and silver, but it is not suited for pyrometallurgical processing because of the high content of antimony. The chemical composition of as received calcine is given in Table 8.14.

Table 8.14 Chemical composition of tetrahedrite calcine [8.121]

| Element | Me (%)                |                                 |
|---------|-----------------------|---------------------------------|
|         | As received           | After mechanochemical treatment |
| Cu      | 17.60                 | 16.27                           |
| Sb      | 6.03                  | 0.19                            |
| S       | 19.80                 | 21.82                           |
| Fe      | 24.50                 | 25.63                           |
| Na      | 0.44                  | 2.85                            |
| Bi      | 0.28                  | 0.13                            |
| As      | 0.93                  | 0.14                            |
| Hg      | 0.66                  | <0.01                           |
| Ag      | 1040 $\text{gt}^{-1}$ | 1213 $\text{gt}^{-1}$           |
| Au      | 10.4 $\text{gt}^{-1}$ | 11.5 $\text{gt}^{-1}$           |

The results of mechanochemical leaching of this tetrahedrite calcine are shown in Figure 8.40. The process proceeds in two regimes: mechanochemical (I) and chemical (II). The mill temperature reached 84°C and during subsequent chemical leaching rose to 96°C [8.121].

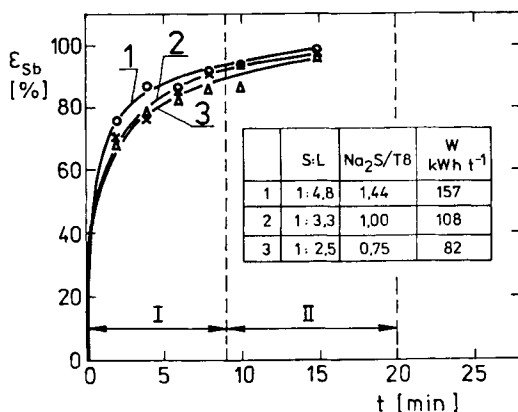


Fig. 8.40 Recovery of antimony into leach,  $\epsilon_{\text{Sb}}$  vs. time of leaching, t. I - mechanochemical leaching, II - chemical leaching. Leaching conditions: 300  $\text{gl}^{-1}$  Na<sub>2</sub>S + 53  $\text{gl}^{-1}$  NaOH, rate of pulp feeding 95-105  $\text{lh}^{-1}$  [8.121].

The liquid/solid ratio in the described experiments was 4.8, 3.3 and 2.5 and resulted in power input of 157, 108 and 82 kWh per metric tone of concentrate, respectively. These examined liquid/solid ratios were acceptable for plant operation. The almost complete extraction of Sb in 15-20 minutes and of As in 20-40 minutes can be achieved, Figure 8.40 (see also Table 8.14). The process is highly selective for Sb and As with only 0.03-0.12 % of the copper dissolving.

The particle size obtained was 100 % -10 microns (Table 8.15). The chemical analysis performed after mechanochemical treatment (Table 8.14) shows that the described process enables us to obtain a Cu-Ag-Au concentrate of high quality. The decrease in antimony content to below 1 % show that this material may be processed by pyrometallurgy.

Table 8.15 Granulometric analysis of tetrahedrite calcine [8.121]

| Range<br>[ $\mu\text{m}$ ] | Recovery (%) |                                 |
|----------------------------|--------------|---------------------------------|
|                            | As received  | After mechanochemical treatment |
| <1.1                       | 5.72         | 40.80                           |
| 1.1-5.0                    | 17.46        | 53.29                           |
| 5.0-10.5                   | 10.76        | 5.91                            |
| 10.5-43.0                  | 31.99        | 0                               |
| 43.0-73.0                  | 18.18        | 0                               |
| 73.0-147.0                 | 15.89        | 0                               |

## 8.6. Economic evaluation of mechanical activation

Johnson et al. [8.93] have performed an economic evaluation of refractory gold processes based on fine grinding pretreatment. From the evaluation it follows

- less oxygen is required by the ACTIVOX<sup>TM</sup> process than by pressure oxidation, biological oxidation or roasting (when coupled with an acid plant for sulfure capture),
- lower reagent consumptions are required for the neutralization step as the extent of oxidation is less,
- the power for fine grinding is not excessive, and accounts for only 15 % of the total power consumed by the process. Considerably more energy is saved by not having to generate the oxygen required to achieve full sulfur oxidation.

Energy consumption is relatively insensitive to the type of media being used (Fig. 8.41), but is affected by pulp density and hardness of activated material [8.63].

Capital and operating costs for ultrafine grinding have been estimated in paper [8.65]. It must be emphasized that the costs are very specific to both size and mineralogy, so that the data in Table 8.16 should be viewed as a guide only.

Table 8.16 Relative economics of different pretreatment processes for FeS<sub>2</sub>/FeAsS concentrate [8.65].

| Costs     | Ultrafine grinding<br>(ACTIVOX <sup>TM</sup> ) | Pressure oxidation | Roasting | Bacterial oxidation |
|-----------|------------------------------------------------|--------------------|----------|---------------------|
| Capital   | 60-80 %                                        | 100 %              | 90 %     | 60 %                |
| Operating | 60-80 %                                        | 100 %              | 75 %     | 90 %                |

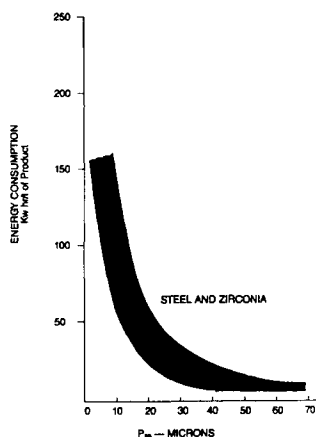


Fig. 8.41 Energy consumption during ultrafine grinding [8.63].

In applying stirred mills the three main operational costs are [8.91]

- energy - minimised by choice of media size, optimization of classification, optimisation of mill design,
- media - minimised by selection of media to provide maximum wear resistance at the lowest initial price and
- wear parts - minimised by selecting the materials that have the best wear characteristics for their particular location in the mill.

A typical operating cost determined for ultrafine grinding of 13 th<sup>-1</sup> copper concentrate from a feed 80 % of 60 microns to a product 80 % of 6 microns in closed circuit classification is given in Table 8.17.

Table 8.17 Operating cost for ultrafine grinding of chalcopyrite/pyrite concentrate to 6  $\mu\text{m}$  [8.91]

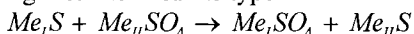
| Operation                                                   | Operating cost Australian dollars (1997) per<br>tonne circuit feed |
|-------------------------------------------------------------|--------------------------------------------------------------------|
| Energy consumption                                          | 2.00                                                               |
| Media consumption                                           | 1.43                                                               |
| Wear parts                                                  | 1.06                                                               |
| Miscellaneous                                               | 0.22                                                               |
| Total operating cost (excluding labour and<br>capital cost) | 4.71                                                               |

To put the operating cost in context with the other unit operations, the ultrafine grinding direct operating cost is 1.02 Australian cents per pound of cathode copper produced. This is approximately only 2.5 % of the total combined crushing, grinding, flotation, ultrafine grinding, oxidation, solvent extraction and electrowinning operating cost [8.91].

## 8.7. Sorption of metals from solutions by mechanically activated minerals

The special properties of fine particles with a high surface area and their significant occurrence as the by-product waste from mixed sulfides processing plants has led to the suggestion that they may be utilized as sorbents for toxic metals [8.129]. Zoubolis studied pyrite fines which are usually stockpiled in the mine area for copper ion separation and arsenic removal from solutions [8.130-8.131].

Exchange reactions of the type



( $Me = Fe, Ni, Cu, Co, Ni$ , platinum metals, etc.) usually take place with sulfides  $Me_I S$  in the presence of excess free acid at increased temperature and pressure. Pentlandite, pyrrhotite, chalcopyrite, pyrite, sphalerite and galena were tested as active sorbents of type  $Me_I S$  [8.132]. The estimation of sorption properties of the mentioned sulfides has shown that mechanically activated pyrrhotite is an exceedingly efficient sorbent and for the sorption of platinum metals a high activity and selectivity can be achieved. According to [8.132] the capacity of mechanically activated pyrrhotite for platinum metals is as follows ( $mgg^{-1}$ ): Os - 3000; Pd - 2300; Pt - 23.2; Rh - 14.0; Ru - 5.0; Ir - 2.2.

A pyrrhotite concentrate was effectively used for copper sorption from solutions using the unique sorption properties of activated pyrrhotite in the two stage counter-current flowsheet shown in Fig. 8.42 [8.132].

When nickel powder is in contact with the copper ions the cementation reaction proceeds by the equation



The application of nickel concentrate (from which the nickel is produced) instead of nickel powder has been developed by Kulebakin [8.132]. The as received concentrate is composed mainly of  $Ni_3S_2$  and  $NiO$ . After mechanical activation the new phase  $NiS$  is formed. The observed changes in surface area and amorphization depend on regime of the mechanical activation. The activated concentrate has a positive effect on copper sorption (Fig. 8.43).

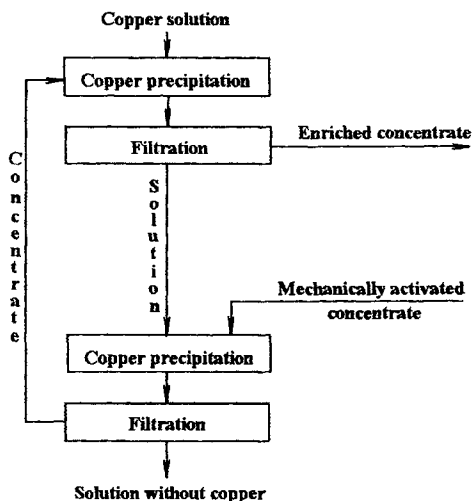


Fig. 8.42 The counter-current flowsheet of copper sorption by mechanically activated pyrrhotite concentrate [8.132].

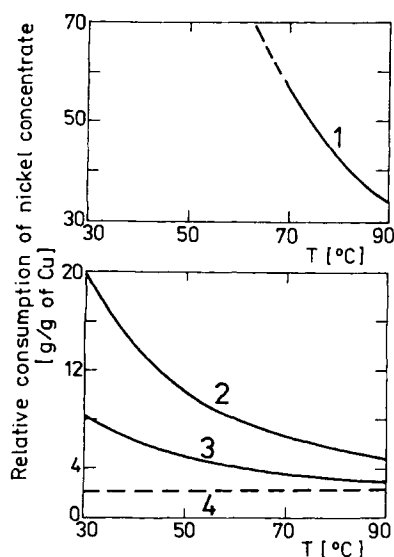


Fig. 8.43 The influence of mechanical activation and temperature on relative consumption of nickel concentrate [8.132], 1 - as received concentrate; 2,3 - concentrate mechanically activated in a planetary mill for 2 and 7 minutes, respectively; 4 - theoretical calculation based on the equation:  $\text{Cu}^{2+} + \text{NiS} \rightleftharpoons \text{Ni}^{2+} + \text{CuS}$ .

Mechanical activation for 2 minutes has reduced the consumption of nickel concentrate from 34 to 4.7  $\text{gg}^{-1}$  Cu at 90 $^{\circ}\text{C}$  and from 57 to 7.1  $\text{gg}^{-1}$  Cu at 70 $^{\circ}\text{C}$ . The activity of as received concentrate at low temperatures is low, whereas the activated concentrate has considerable activity even at 30 $^{\circ}\text{C}$ . The mechanical activation of nickel concentrate brings about the changes of surface microstructure. XRD analysis of copper sorption products has shown the occurrence of new phases  $\text{Cu}_7\text{S}_4$ ,  $\text{Cu}_9\text{S}_5$  and  $\text{NiS}$ .

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## SUMMARY

The intention of this book has been critically review the global progress in the area of mechanical activation of minerals and to illustrate the technological application to extractive metallurgy and mineral processing.

Mechanochemistry as a branch of solid state chemistry which enquires into processes which proceed in solids due to the application of mechanical energy. The central problem of the solid state chemistry is the relationship between structure and reactivity of solids. Mechanochemistry helps us to solve this problem by the intentional formation of defects in the structure of solid substances by the application of mechanical forces using intensive grinding equipments.

This book aims to be the collection of the knowledge obtained by mechanical activation of minerals which contribute to the theoretical elucidation of the corresponding structural transformations. It is a matter of

- identification of new compounds formed at the surface of minerals due to mechanochemical oxidation,
- quantification of the relationship between new surface formation and structural disordering in the course of activation and
- elucidation of the relationship between changes in hyperfine structure of the minerals and their lattice parameters.

Identification of the transformations in mechanically activated sulfide minerals has enabled us to evaluate the sensitivity of subsequent reactivity to structural changes during activation. The publication presents examples illustrating that many solid phase reactions are structure-sensitive processes. The factors influencing this structural sensitivity are identified.

It is clear extractive metallurgy, aimed at the production of metals from sulfidic ores, is an area of industry suitable for the successful verification of the theoretical knowledge of mechanical activation. Several commercially operating processes are examined and their flowsheets are presented as successful of activation. In these processes, the introduction of a mechanical activation step into the technological cycle significantly modifies the subsequent processing steps.

More specifically, activation leads to

- a decrease in temperature of roasting and improvement in retention of gold in the processes of pyrometallurgical processing of concentrates with precious metal content,
- manifold increase in extraction rate and reduction of extraction temperature in the the hydrometallurgical processing of non-ferrous metals concentrates and
- possible modification of biohydrometallurgical processes, especially from the view-point of the toxicity of solutions containing metals towards bacteria.

Special attention deserves to be given to the chapter dealing with the mechanochemical leaching of tetrahedrite raw materials which represent a rich deposit of Cu, Ag and Au ores in ore deposits globally. This process was developed in the author's Institute to the point where the extraction is many times more effective than the established technologies used by Equity Silver in Canada and Sunshine Mining and Refining Company in USA. This process, together with application of mechanical activation as a physical pretreatment of precious metal concentrates in Australia, New Zealand and South Africa represents an outstanding example of the development from theoretical knowledge to the stage of industrial application.

The author of this monograph devoted many-years of effort to the collection and review of the literature, in addition to running a substantial experimental programme in this area. However, the presented view of the problems and achievements cannot be complete due to a large international effort in mechanical activation. After successful application to mineral processing and extractive metallurgy of minerals, mechanical activation is heading for new fields of study such as preparation of alloys, composites, nanocrystalline and amorphous substances, intermetallic compounds and smart materials for the 21st century.

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