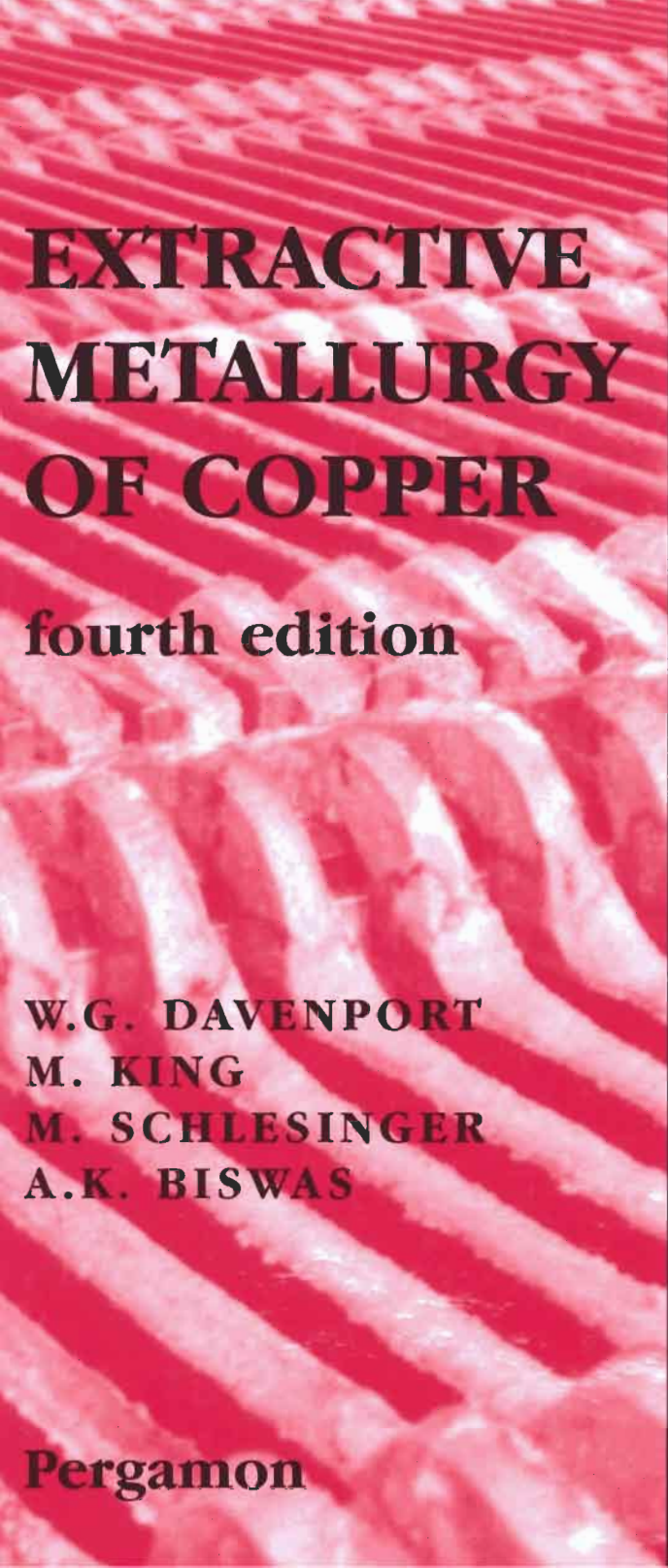


The background of the cover features a close-up, high-contrast photograph of copper coils, likely from a heat exchanger, showing the metallic texture and the curved shape of the tubes.

EXTRACTIVE METALLURGY OF COPPER

fourth edition

**W.G. DAVENPORT
M. KING
M. SCHLESINGER
A.K. BISWAS**

Pergamon

**C
O
P
P
E
R**

PERIOD

	1 (IA)																		2 (IIA)																		
1	1	H 1.0079 Hydrogen																																			
2	3	Li 6.94 ₁ Lithium	4	Be 9.01218 Beryllium																																	
3	11	Na 22.98977 Sodium	12	Mg 24.305 Magnesium	3 (IIIA)		4 (IVA)		5 (VA)		6 (VIA)		7 (VIIA)		8		9 (VIIIA)																				
4	19	K 39.098 ₃ Potassium	20	Ca 40.08 Calcium	21	Sc 44.9559 Scandium	22	Ti 47.9 ₀ Titanium	23	V 50.9415 Vanadium	24	Cr 51.996 Chromium	25	Mn 54.9380 Manganese	26	Fe 55.84 ₇ Iron	27	Co 58.9332 Cobalt																			
5	37	Rb 85.467 ₈ Rubidium	38	Sr 87.62 Strontium	39	Y 88.9059 Yttrium	40	Zr 91.22 Zirconium	41	Nb 92.9064 Niobium	42	Mo 95.94 Molybdenum	43	Tc (98) Technetium	44	Ru 101.0 ₇ Ruthenium	45	Rh 102.9055 Rhodium																			
6	55	Cs 132.9054 Cesium	56	Ba 137.33 Barium	57	La 138.905 ₅ Lanthanum	72	Hf 178.4 ₉ Hafnium	73	Ta 180.947 ₉ Tantalum	74	W 183.8 ₅ Wolfram	75	Re 186.207 Rhenium	76	Os 190.2 Osmium	77	Ir 192.2 ₂ Iridium																			
7	87	Fr (223) Francium	88	Ra 226.0254 Radium	89	Ac 227.0278 Actinium	Lanthanide Metals																														
	Actinide Metals																																				
							58	Ce 140.12 Cerium	59	Pr 140.9077 Praseodymium	60	Nd 144.2 ₄ Neodymium	61	Pm (145) Promethium	62	Sm 150.4 Samarium																					
							90	Th 232.0381 Thorium	91	Pa 231.0359 Protactinium	92	U 238.029 Uranium	93	Np 237.0482 Neptunium	94	Pu (244) Plutonium																					

18 (VIII B)

										2 He 4.00260 Helium
			13 (IIIB)	14 (IVB)	15 (VB)	16 (VIB)	17 (VIIB)			
			5 B 10.81 Boron	6 C 12.011 Carbon	7 N 14.0067 Nitrogen	8 O 15.999 ₄ Oxygen	9 F 18.998403 Fluorine	10 Ne 20.17 ₉ Neon		
			13 Al 26.98154 Boron	14 Si 28.085 ₅ Silicon	15 P 30.97376 Phosphorous	16 S 32.06 Sulphur	17 Cl 35.453 Chlorine	18 Ar 39.94 ₈ Argon		
10	11 (IB)	12 (IIB)								
28 Ni 58.70 Nickel	29 Cu 63.54 ₆ Copper	30 Zn 65.38 Zinc	31 Ga 69.72 Gallium	32 Ge 72.5 ₉ Germanium	33 As 74.9216 Arsenic	34 Se 78.9 ₆ Selenium	35 Br 79.904 Bromine	36 Kr 83.80 Krypton		
46 Pd 106.4 Palladium	47 Ag 107.868 Silver	48 Cd 112.41 Cadmium	49 In 114.82 Indium	50 Sn 118.6 ₉ Tin	51 Sb 121.7 ₅ Antimony	52 Te 127.6 ₀ Tellurium	53 I 126.9045 Iodine	54 Xe 131.30 Xenon		
78 Pt 195.0 ₉ Platinum	79 Au 196.9665 Gold	80 Hg 200.5 ₉ Mercury	81 Tl 204.3 ₇ Thallium	82 Pb 207.2 Lead	83 Bi 208.9804 Bismuth	84 Po (209) Polonium	85 At (210) Astatine	86 Rn (222) Radon		

63 Eu 151.96 Europium	64 Gd 157.2 ₅ Gadolinium	65 Tb 158.9254 Terbium	66 Dy 162.5 ₀ Dysprosium	67 Ho 164.9304 Holmium	68 Er 167.2 ₆ Erbium	69 Tm 168.9342 Thulium	70 Yb 173.0 ₄ Ytterbium	71 Lu 174.96 ₇ Lutetium
95 Am (243) Americium	96 Cm (247) Curium	97 Bk (247) Berkelium	98 Cf (251) Californium	99 Es (252) Einsteinium	100 Fm (257) Fermium	101 Md (258) Mendelevium	102 No (259) Nobelium	103 Lr (260) Lawrencium

Extractive Metallurgy of Copper

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Extractive Metallurgy of Copper

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FOURTH EDITION

PERGAMON



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CONTENTS

Preface	xiii
Preface to the Third Edition	xv
Preface to the Second Edition	xvii
Preface to the First Edition	xix
1 Overview	1
1.1 Introduction	1
1.2 Extracting Copper from Copper-Iron-Sulfide Ores	1
1.3 Hydrometallurgical Extraction of Copper	11
1.4 Melting and Casting Cathode Copper	13
1.5 Recycle of Copper and Copper-Alloy Scrap	15
1.6 Summary	15
Suggested Reading	16
References	16
2 Production and Use	17
2.1 Locations of Copper Deposits	18
2.2 Location of Extraction Plants	18
2.3 Copper Minerals and 'Cut-Off' Grades	19
2.4 Price of Copper	28
2.5 Summary	29
References	29
3 Concentrating Copper Ores	31
3.1 Concentration Flowsheet	31
3.2 Crushing and Grinding (Comminution)	33
3.3 Flotation Feed Particle Size	38
3.4 Froth Flotation	42
3.5 Specific Flotation Procedures for Cu Ores	46
3.6 Flotation Cells	49
3.7 Sensors, Operation and Control	50

3.8	The Flotation Product	52
3.9	Other Flotation Separations	53
3.10	Summary	53
	Suggested Reading	54
	References	54
4	Matte Smelting Fundamentals	57
4.1	Why Smelting?	57
4.2	Matte and Slag	59
4.3	Reactions During Matte Smelting	65
4.4	The Smelting Process: General Considerations	66
4.5	Smelting Products: Matte, Slag and Offgas	67
4.6	Summary	70
	Suggested Reading	70
	References	70
5	Flash Smelting – Outokumpu Process	73
5.1	Outokumpu Flash Furnace	74
5.2	Peripheral Equipment	77
5.3	Furnace Operation	82
5.4	Control	83
5.5	Impurity Behavior	86
5.6	Future Trends	87
5.7	Summary	87
	Suggested Reading	88
	References	88
6	Inco Flash Smelting	91
6.1	Furnace Details	91
6.2	Auxiliary Equipment	96
6.3	Operation	97
6.4	Control Strategy	98
6.5	Cu-in-Slag and Molten Converter Slag Recycle	100
6.6	Inco vs. Outokumpu Flash Smelting	101
6.7	Summary	101
	Suggested Reading	101
	References	102

7	Noranda and Teniente Smelting	103
7.1	Noranda Process	104
7.2	Reaction Mechanisms	106
7.3	Operation and Control	108
7.4	Production Rate Enhancement	109
7.5	Noranda Future	110
7.6	Teniente Smelting	110
7.7	Process Description	111
7.8	Operation	111
7.9	Control	113
7.10	Impurity Distribution	114
7.11	Teniente Future	115
7.12	Discussion	115
7.13	Summary	116
	Suggested Reading	117
	References	117
8	Ausmelt/Isasmelt Matte Smelting	119
8.1	Basic Operations	119
8.2	Feed Materials	120
8.3	The Isasmelt Furnace and Lance	120
8.4	Smelting Mechanisms	125
8.5	Startup and Shutdown	126
8.6	Current Installations	126
8.7	Other Coppermaking Uses of Ausmelt/Isasmelt Technology	127
8.8	Summary	127
	Suggested Reading	128
	References	129
9	Batch Converting of Cu Matte	131
9.1	Chemistry	131
9.2	Industrial Peirce-Smith Converting Operations	137
9.3	Oxygen Enrichment of Peirce-Smith Converter Blast	144
9.4	Maximizing Converter Productivity	145
9.5	Recent Developments in Converting – Shrouded Blast Injection	148
9.6	Alternatives to Peirce-Smith Converting	148
9.7	Summary	150
	Suggested Reading	151
	References	151

10	Continuous Converting	155
10.1	Common Features of Continuous Converting	155
10.2	Downward Lance Mitsubishi Continuous Converting	157
10.3	Solid Matte Outokumpu Flash Converting	162
10.4	Submerged-Tuyere Noranda Continuous Converting	166
10.5	% Cu-in-Slag	170
10.6	Summary	170
	Suggested Reading	171
	References	171
11	Copper Loss in Slag	173
11.1	Copper in Slags	173
11.2	Decreasing Copper in Slag I: Minimizing Slag Generation	175
11.3	Decreasing Copper in Slag II: Minimizing Cu Concentration in Slag	176
11.4	Decreasing Copper in Slag III: Pyrometallurgical Slag Settling/Reduction	176
11.5	Decreasing Copper in Slag IV: Slag Minerals Processing	181
11.6	Summary	181
	Suggested Reading	183
	References	183
12	Direct-To-Copper Flash Smelting	187
12.1	The Ideal Direct-to-Copper Process	187
12.2	Industrial Single Furnace Direct-to-Copper Smelting	188
12.3	Chemistry	189
12.4	Industrial Details	190
12.5	Control	190
12.6	Cu-in-Slag: Comparison with Conventional Matte Smelting/Converting	193
12.7	Cu-in-Slag Limitation of Direct-to-Copper Smelting	194
12.8	Direct-to-Copper Impurities	195
12.9	Summary	195
	Suggested Reading	196
	References	196
13	Mitsubishi Continuous Smelting/Converting	199
13.1	The Mitsubishi Process	201
13.2	Smelting Furnace Details	201

13.3	Electric Slag Cleaning Furnace Details	203
13.4	Converting Furnace Details	203
13.5	Recent Mitsubishi Process Developments	207
13.6	Reaction Mechanisms in Mitsubishi Smelting	208
13.7	Optimum Matte Grade	210
13.8	Impurity Behavior in Mitsubishi Smelting/Converting	210
13.9	Process Control in Mitsubishi Smelting/Converting	211
13.10	Summary	212
	Suggested Reading	214
	References	215
14	Capture and Fixation of Sulfur	217
14.1	Offgases from Smelting and Converting Processes	217
14.2	Sulfuric Acid Manufacture	218
14.3	Smelter Offgas Treatment	222
14.4	Gas Drying	224
14.5	Acid Plant Chemical Reactions	227
14.6	Industrial Sulfuric Acid Manufacture	231
14.7	Recent and Future Developments in Sulfuric Acid Manufacture	240
14.8	Alternative Sulfur Products	241
14.9	Future Improvements in Sulfur Capture	241
14.10	Summary	242
	Suggested Reading	243
	References	243
15	Fire Refining and Casting of Anodes: Sulfur and Oxygen Removal	247
15.1	Industrial Methods of Fire Refining	247
15.2	Chemistry of Fire Refining	252
15.3	Choice of Hydrocarbon for Deoxidation	253
15.4	Casting Anodes	253
15.5	Continuous Anode Casting	256
15.6	New Anodes from Rejects and Anode Scrap	260
15.7	Removal of Impurities During Fire Refining	260
15.8	Summary	261
	Suggested Reading	261
	References	262
16	Electrolytic Refining	265
16.1	Principles	265

16.2	Behavior of Anode Impurities During Electrowinning	269
16.3	Industrial Electrowinning	272
16.4	Cathodes	273
16.5	Electrolyte	273
16.6	Cells and Electrical Connections	278
16.7	Typical Refining Cycle	279
16.8	Refining Objectives	280
16.9	Maximizing Cathode Copper Purity	280
16.10	Optimum Physical Arrangements	280
16.11	Optimum Chemical Arrangements	281
16.12	Optimum Electrical Arrangements	282
16.13	Minimizing Energy Consumption	283
16.14	Recent Developments in Electrowinning	283
16.15	Summary	284
	Suggested Reading	284
	References	285
17	Hydrometallurgical Copper Extraction: Introduction and Leaching	289
17.1	Heap Leaching	289
17.2	Industrial Heap Leaching	293
17.3	Steady-State Leaching	299
17.4	Leaching of Chalcopyrite Concentrates	300
17.5	Other Leaching Processes	301
17.6	Future Developments	301
17.7	Summary	301
	Suggested Reading	303
	References	303
18	Solvent Extraction Transfer of Cu from Leach Solution to Electrolyte	307
18.1	The Solvent Extraction Process	307
18.2	Chemistry	309
18.3	Extractants	310
18.4	Industrial Solvent Extraction Plants	312
18.5	Quantitative Design of Series Circuit	317
18.6	Stability of Operation	321
18.7	'Crud'	322
18.8	Summary	323
	Suggested Reading	324
	References	324

19	Electrowinning	327
19.1	Electrowinning Reactions	328
19.2	Electrowinning Tankhouse Practice	329
19.3	Maximizing Copper Purity	335
19.4	Maximizing Current Efficiency	335
19.5	Future Developments	337
19.6	Summary	337
	Suggested Reading	338
	References	338
20	Collection and Processing of Recycled Copper	341
20.1	The Materials Cycle	341
20.2	Secondary Copper Grades and Definitions	344
20.3	Scrap Processing and Beneficiation	346
20.4	Summary	351
	Suggested Reading	351
	References	352
21	Chemical Metallurgy of Copper Recycling	355
21.1	The Secondary Copper Smelter	355
21.2	Scrap Processing in Primary Copper Smelters	360
21.3	Summary	363
	Suggested Reading	363
	References	364
22	Melting and Casting	367
22.1	Product Grades and Quality	367
22.2	Melting Technology	370
22.3	Casting Machines	374
22.4	Summary	380
	Suggested Reading	381
	References	381
23	Costs of Copper Production	385
23.1	Overall Investment Costs: Mine through Refinery	386
23.2	Overall Direct Operating Costs: Mine through Refinery	389
23.3	Total Production Costs, Selling Prices, Profitability	389

23.4	Concentrating Costs	391
23.5	Smelting Costs	393
23.6	Electrorefining Costs	395
23.7	Production of Copper from Scrap	397
23.8	Leach/Solvent Extraction/Electrowinning Costs	397
23.9	Profitability	398
23.10	Summary	399
	References	399

Appendices **401**

A	Stoichiometric Data for Copper Extraction	401
B	Lesser-Used Smelting Processes	403
C	Copper Recovery from Anode Slimes	413
D	Sketch of Series-Parallel Solvent Extraction Circuit	415
E	Extended List of Chinese Copper Refineries and their Capacities	416

Index **417**

Preface

This edition contains more-than-ever industrial information, all of it provided generously by our industrial friends and colleagues. We thank them profusely for their help and generosity over the years.

The publication we consulted most for this edition was *Copper 99/Cobre99* (TMS, Warrendale, PA [six volumes]). For a near-future update, we direct the reader to *Copper 03/Cobre 03* being held in Santiago, Chile, November 30, 2003 (www.cu2003.cl).

As with previous editions, Margaret Davenport read every word of our manuscript. After 27 years of proofreading, she may well know more than the authors.

Dedication

It is with great sadness that we report the death of Anil Biswas – friend, colleague and inspiration. Co-author of all previous editions, Anil was at the Department of Mining and Metallurgical Engineering, University of Queensland, St Lucia, Brisbane, Australia.

Anil's objectives for this book were to (i) describe how copper metal is extracted from ore and scrap, and (ii) indicate how the extraction could be made more efficient. We are proud to continue with his original plan.

March 31, 2002

W.G. Davenport, Cambridge, England
M.J. King, Phoenix, Arizona
M.E. Schlesinger, Rolla, Missouri

Preface to the Third Edition

This edition chronicles the changes which have taken place in copper extraction over the last 20 years. The major changes have been the shrinkage of reverberatory smelting, the continued growth of flash smelting and the remarkable (and continuing) growth of solvent extraction/electrowinning. The use of stainless steel cathodes (instead of copper starting sheets) in electrorefining and electrowinning has also been a significant development.

These industrial growth areas receive considerable attention in this edition as do SO_2 collection and sulphuric acid manufacture. SO_2 capture has continued to grow in importance – only a few smelters now emit their SO_2 to the atmosphere.

Several important volumes on copper extraction have appeared recently, namely: *Copper 91/Cobre 91* (Pergamon Press, New York [four volumes]) and *Extractive Metallurgy of Copper, Nickel and Cobalt* (TMS, Warrendale, Pennsylvania [two volumes]). A volume on *Converting, Fire-refining and Casting* is scheduled to appear in 1994 (TMS) and the proceedings of *Cobre95/Copper 95* will appear in 1995. The reader is directed to these publications for updated information.

We wish to thank our colleagues in the copper industry for their many contributions to this edition. They have responded to our questions, encouraged us to visit their plants and engaged us in rigorous debate regarding extraction optimization. We would particularly like to thank Brian Felske (Felske and Associates), David Jones (Magma Copper Company) and Eric Partelpoeg (Phelps Dodge Mining Company). Without them this edition would not have been possible.

The manuscript was prepared and proofed by Patricia Davenport and Margaret Davenport. Their perseverance, skill and enthusiasm are happily acknowledged.

Preface to the Second Edition

For this edition we have concentrated mainly on bringing the operating data and process descriptions of the first edition up to date. Typographical errors have been corrected and several passages have been rewritten to avoid misinterpretation. Since most of the new data have come directly from operating plants, very few new references have been added. For collections of recent published information, the reader is directed to the excellent symposium publications: Extractive Metallurgy of Copper, Volumes I and II, Yannopoulos, J. C. and Agarwal, J. C. editors, A.I.M.E., New York, 1976, Copper and Nickel Converters, Johnson, R.E., A.I.M.E., New York, 1979, and to the reviews of copper technology and extractive metallurgy published annually in the *Journal of Metals* (A.I.M.E., New York). Most of the credit for this edition should go to the many industrial engineers and scientists who almost without exception responded to our requests for new information on their processes. We would like in particular to single out Jan Matousek of INCO, Keith Murden of Outokumpu Oy and John Schloen of Canadian Copper Refiners (now a metallurgical consultant) for their help.

September 1979

A. K. Biswas
W. G. Davenport

Preface to the First Edition

This book describes the extraction of copper from its ores. The starting point is with copper ores and minerals and the finishing point is the casting and quality control of electrical grade copper. Techniques for recovering copper from recycled scrap are also discussed.

The main objectives of the book are to describe the extractive metallurgy of copper as it is today and to discuss (qualitatively and quantitatively) the reasons for using each particular process. Arising from these descriptions and discussions are indications as to how copper-extraction methods will develop in the future. Control of air and water pollution is of tremendous importance when considering future developments and these are discussed in detail for each process. Likewise, the energy demands of each process are dealt with in detail. Costs are mentioned throughout the text and they are considered in depth in the final chapter.

The book begins with an introductory synopsis (for the generalist reader) of the major copper-extraction processes. It then follows copper extraction in a step-wise fashion beginning with mineral beneficiation and advancing through roasting, smelting, converting, refining, casting and quality control. Hydrometallurgy and its associated processes are introduced just before electrowinning so that electrowinning and electrorefining can be discussed side by side and the final products of each method compared. The last two chapters are not in sequence – they are devoted to the sulphur pollution problem and to economics.

As far as possible, the length of each chapter is commensurate with the relative importance of the process it describes. Blast-furnace copper smelting is, for example, given a rather brief treatment because it is a dying process while newer techniques such as continuous copper-making and solvent extraction are given extensive coverage because they may assume considerable importance in the near future.

A word about units: the book is metric throughout, the only major exception to the Standard International Unit System being that energy is reported in terms of kilocalories and kilowatt-hours. The principal units of the book are metric tons (always written tonnes in the text), kilograms and metres. A conversion table is provided in Appendix I. A knowledge of thermodynamics is assumed in parts of the book, particularly with respect to equilibrium constants. For concise information on the thermodynamic method as applied to metallurgy, the reader is

directed to *Metallurgical Thermochemistry* by O. Kubaschewski, E. L. Evans and C. B. Alcock, an earlier volume in this series.

The text of the book is followed by four appendixes which contain units and conversion factors: stoichiometric data; enthalpy and free energy data; and a summary of the properties of electrolytic tough pitch copper.

Copper is one of man's most beautiful and useful materials. It has given us great satisfaction to describe and discuss the methods by which it is obtained. Both of our universities have had a long association with the copper industries of our countries, and it is hoped that, through this book, this association will continue.

A. K. Biswas
University of Queensland

W. G. Davenport
McGill University

CHAPTER 1

Overview

1.1 Introduction

Copper is most commonly present in the earth's crust as copper-iron-sulfide and copper sulfide minerals, e.g. chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4) and chalcocite (Cu_2S). The concentration of these minerals in an ore body is low. Typical copper ores contain from 0.5% Cu (open pit mines) to 1 or 2% Cu (underground mines). Pure copper metal is produced from these ores by concentration, smelting and refining, Fig. 1.1.

Copper also occurs in oxidized minerals (carbonates, oxides, hydroxy-silicates, sulfates), but to a lesser extent. Copper metal is usually produced from these minerals by hydrometallurgical methods, Fig. 1.2. Hydrometallurgy is also used to produce copper metal from chalcocite, Cu_2S .

A third major source of copper is scrap copper and copper alloys. Production of copper from recycled used objects is 10 or 15% of mine production. In addition, there is considerable re-melting/re-refining of scrap generated during fabrication and manufacture.

This chapter introduces the principal processes by which copper is extracted from ore and scrap. It also indicates the relative industrial importance of each.

1.2 Extracting Copper from Copper-Iron-Sulfide Ores

About 80% of the world's copper-from-ore originates in Cu-Fe-S ores. Cu-Fe-S minerals are not easily dissolved by aqueous solutions, so the vast majority of copper extraction from these minerals is pyrometallurgical. The extraction entails:

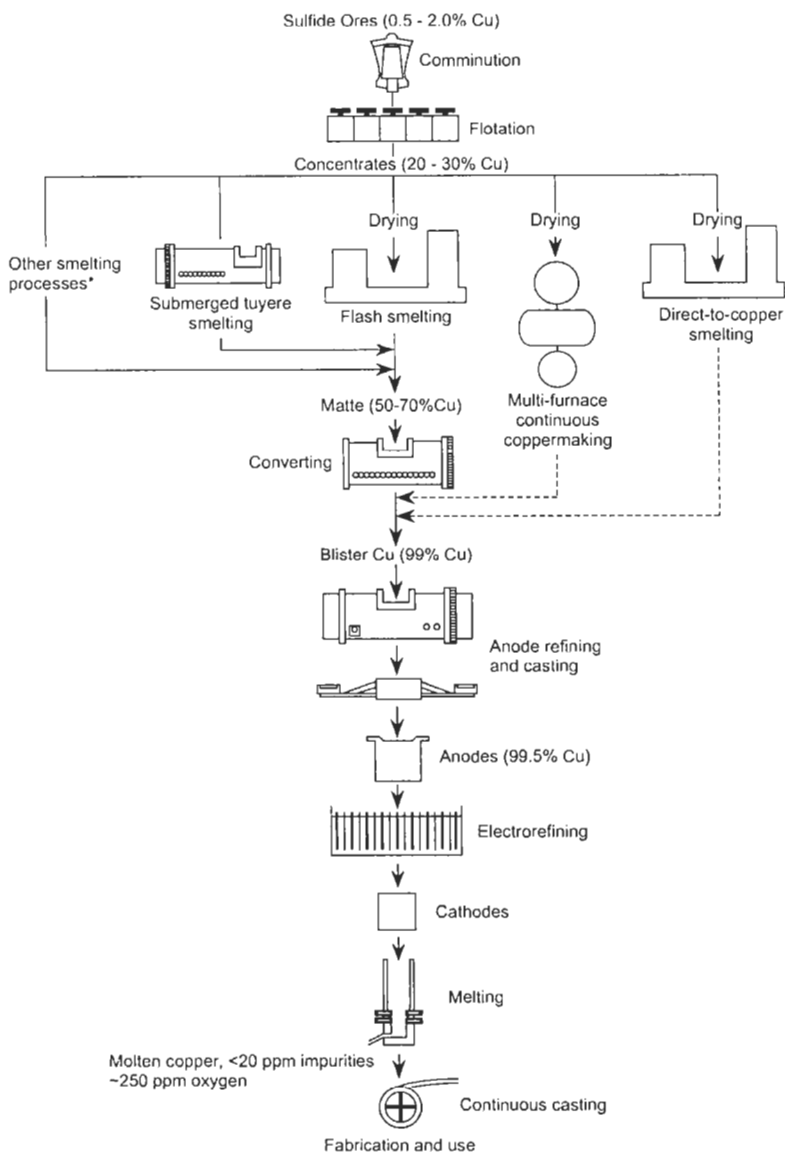


Fig. 1.1. Principal processes for extracting copper from sulfide ores. Parallel lines indicate alternative processes. *Primarily Isasmelt/Ausmelt, reverberatory, shaft, electric, and Vanyukov smelting. -----Two furnaces, worldwide.

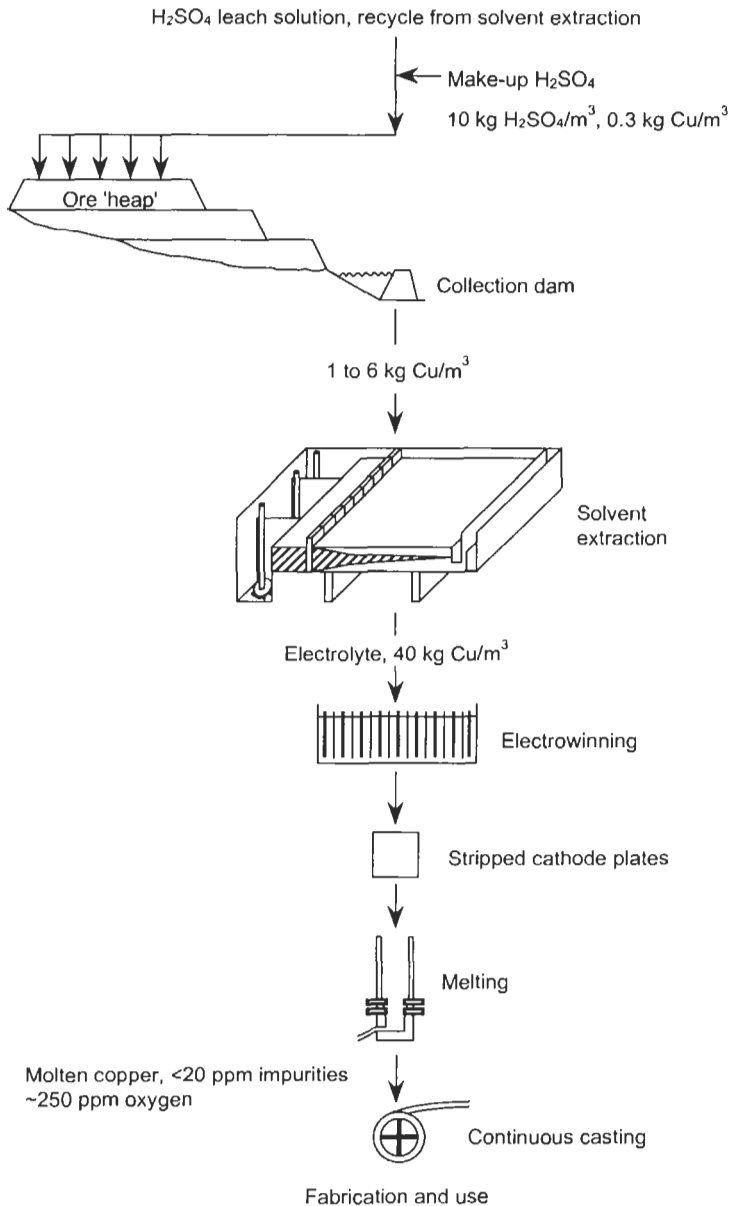


Fig. 1.2. Hydrometallurgical heap leach copper extraction flowsheet for 'oxide' and chalcocite ores.

- (a) isolating an ore's Cu-Fe-S (and Cu-S) mineral particles into a concentrate by froth flotation
- (b) smelting this concentrate to molten high-Cu matte
- (c) converting the molten matte to impure molten copper
- (d) fire- and electrorefining this impure copper to ultra-pure copper.

1.2.1 Concentration by froth flotation (Chapter 3)

The copper ores being mined in 2002 are too lean in copper (0.5 – 2% Cu) to be smelted directly. Heating and melting their huge quantity of waste rock (e.g. granite) would require prohibitive amounts of hydrocarbon fuel. Fortunately, the Cu-Fe-S and Cu-S minerals in an ore can be isolated by physical means into high-Cu 'concentrate' which can be smelted economically.

The most effective method of isolating the Cu minerals is froth flotation. This process causes the Cu minerals to become selectively attached to air bubbles rising through a water-finely ground ore mixture, Fig. 1.3.

Selectivity of flotation is created by using reagents which make Cu minerals water repellent while leaving waste minerals 'wetted'. These reagents cause Cu

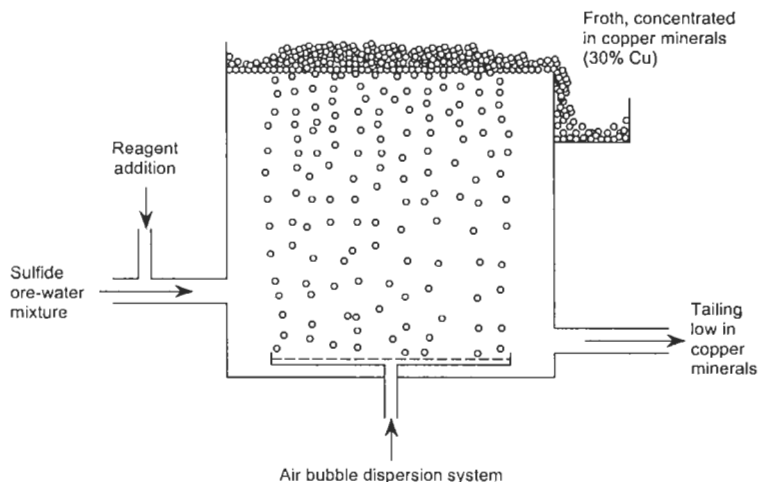


Fig. 1.3. Schematic view of flotation cell. Reagents cause Cu-Fe sulfide and Cu sulfide minerals in the ore to attach to rising air bubbles, which are then collected in a short-lived froth. This froth is de-watered to become concentrate. The un-floated waste passes through several cells before being discarded as a final tailing. Many types and sizes (up to 100 m³) of cell are used, Chapter 3.

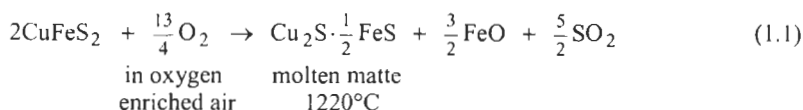
minerals to 'float' on rising bubbles while the other minerals remain unfloated. The 'floated' Cu-mineral particles overflow the flotation cell in a froth to become concentrate ~30% Cu.

Flotation is preceded by crushing and grinding copper ore into fines. Its use has led to adoption of smelting processes which are effective at treating finely ground material.

1.2.2 Matte smelting (Chapter 4)

Matte smelting oxidizes and melts flotation concentrate in a large, hot (1250°C) furnace, Fig. 1.1. The objective of the smelting is to oxidize S and Fe from the Cu-Fe-S concentrate to produce a Cu-enriched molten sulfide phase (matte). The oxidant is almost always oxygen-enriched air.

Example reactions are:



$$\Delta H_{25^\circ\text{C}}^\circ = -450 \text{ MJ/kg mol CuFeS}_2$$



$$\Delta H_{25^\circ\text{C}}^\circ = -20 \text{ MJ/kg mole FeO.}$$

The products of smelting are (i) molten sulfide matte (45-75% Cu) containing most of the Cu-in-concentrate and (ii) molten oxide slag as free of Cu as possible. The molten matte is subsequently converted (oxidized) in a converting furnace to form impure molten copper. The slag is treated for Cu recovery then sold or discarded, Chapter 11.

SO₂-bearing offgas (10 to 60% SO₂) is also generated. SO₂ is harmful to the environment so it must be removed before the offgas is released to the atmosphere. This is almost always done by capturing the SO₂ as sulfuric acid, Chapter 14.

An important objective of matte smelting is to produce a slag which contains as little Cu as possible. This is done by:

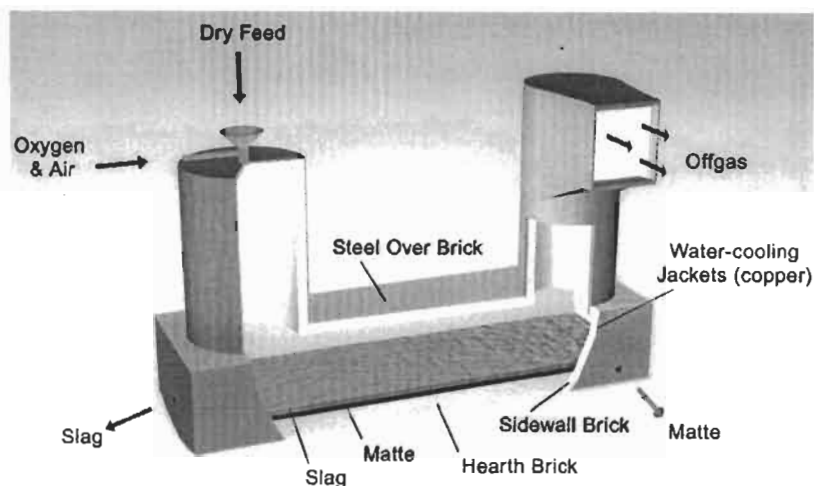


Fig. 1.4. Outokumpu oxygen-enriched air flash furnace. Flash furnaces are typically 20 m long and 7m wide. They smelt 1000 to 3000 tonnes of concentrate per day.

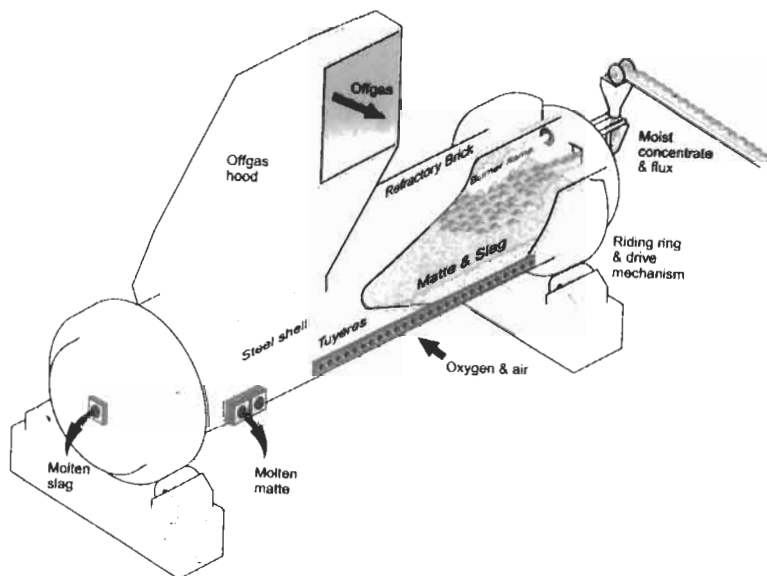


Fig. 1.5. Noranda submerged tuyere smelting furnace. Noranda furnaces are typically 20 to 25 m long and 5 m diameter. They smelt 1500 to 3000 tonnes of concentrate per day. Teniente smelting furnaces are similar.

- (a) including SiO_2 flux in the furnace charge to promote matte-slag immiscibility
- (b) keeping the furnace hot so that the slag is molten and fluid.

Matte smelting is most often done in flash and submerged tuyere furnaces (Figs. 1.4 and 1.5). It is carried out to a lesser extent in top lance furnaces (Mitsubishi, Isasmelt, Ausmelt), shaft furnaces, reverberatory furnaces, and electric furnaces. In two cases, concentrate is flash smelted directly to molten copper, Chapter 12.

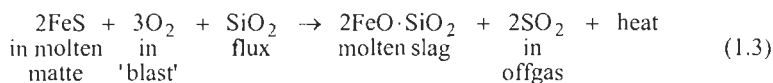
1.2.3 Converting (Chapters 9 and 10)

Copper converting is oxygen enriched-air or air oxidation of the molten matte from smelting. It removes Fe and S from the matte to produce crude (99% Cu) molten copper. This copper is then sent to fire- and electrorefining. Converting is mostly carried out in the cylindrical Peirce-Smith converter, Fig. 1.6.

Liquid matte (1200°C) is transferred from the smelting furnace in large ladles and poured into the converter through a large central mouth, Fig. 1.6b. The oxidizing 'blast' is then started and the converter is rotated – forcing oxygen enriched-air or air into the matte through a line of tuyeres along the length of the vessel. The heat generated in the converter by Fe and S oxidation is sufficient to make the process autothermal.

The converting takes place in two sequential stages:

- (a) the FeS elimination or slag forming stage:



- (b) the blister copper forming stage:



Coppermaking (b) doesn't occur until the matte contains less than about 1% Fe so that most of the Fe can be removed from the converter (as slag) before copper production begins. Likewise, significant oxidation of copper does not occur until the sulfur content of the copper falls below ~0.02%. Blowing is terminated near this sulfur end point. The resulting molten 'blister' copper (1200°C) is sent to refining.

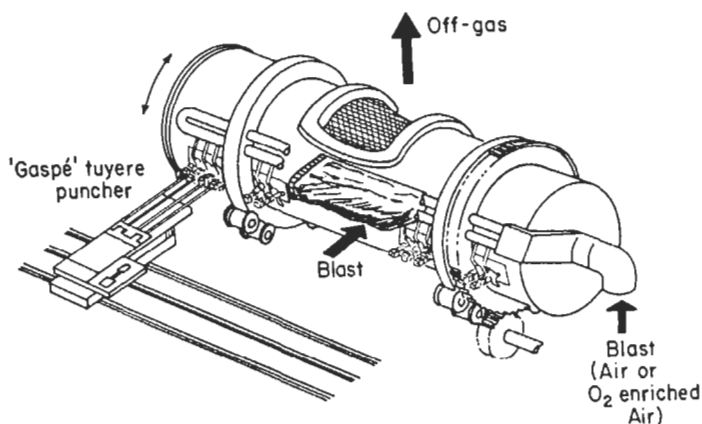


Fig. 1.6a. Peirce-Smith converter for producing molten 'blister' copper from molten Cu-Fc-S matte, typical production rate 200-600 tonnes of copper per day. Oxygen-enriched air or air 'blast' is blown into the matte through submerged tuyeres. Silica flux is added through the converter mouth or by air gun through an endwall. Offgas is collected by means of a hood above the converter mouth. (After Boldt and Queneau, 1967 courtesy Inco Limited)

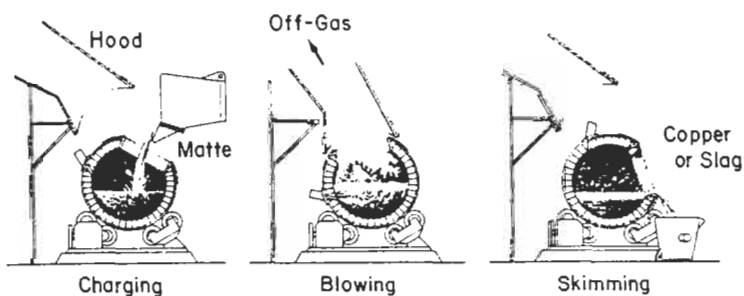


Fig. 1.6b. Positions of Peirce-Smith converter for charging, blowing and skimming (Boldt and Queneau, 1967 courtesy Inco Limited). SO_2 offgas escapes the system unless the hooding is tight. A converter is typically 4 or 4.5 m diameter. Hoboken converters are similar but with axial offgas removal, Chapter 9

Because conditions in the converter are strongly oxidizing and agitated, converter slag inevitably contains 4 to 8% Cu. This Cu is recovered by settling or solidification/froth flotation then sold or discarded, Chapter 11.

SO₂, 8 to 12 volume% in converter offgas, is a byproduct of both converting reactions. It is combined with smelting furnace gas and captured as sulfuric acid. There is, however, some leakage of SO₂ into the atmosphere during charging and pouring, Fig. 1.6b. This problem is encouraging development of continuous converting processes, Chapter 10.

1.2.4 Direct-to-copper smelting (Chapter 12)

Smelting and converting are separate steps in oxidizing Cu-Fe-S concentrates to metallic copper. It would seem natural that these two steps should be combined to produce copper directly in one furnace. It would also seem natural that this should be done continuously rather than by batchwise Peirce-Smith converting.

In 2002, copper is made in a single furnace at only two places; Glogow, Poland and Olympic Dam, Australia – both using a flash furnace.

The strongly oxidizing conditions in a direct-to-copper furnace give 14 to 24% oxidized Cu in slag. The expense of reducing this Cu back to metallic copper has so far restricted the process to concentrates which produce little slag.

Continuous smelting/converting, even in more than one furnace, has energy, SO₂ collection and cost advantages. Mitsubishi lance, Outokumpu flash and Noranda submerged tuyere smelting/converting all use this approach, Chapters 10 and 13.

1.2.5 Fire refining and electrorefining of 'blister' copper (Chapters 15 and 16)

The copper from the above processing is electrochemically refined to high purity cathode copper. This final copper contains less than 20 parts per million (ppm) undesirable impurities. It is suitable for electrical and all other uses.

Electrorefining requires strong, flat thin anodes to interleave with cathodes in the refining cell, Fig. 1.7. These anodes are produced by removing S and O from molten converter 'blister' copper then casting the resulting 'fire refined' copper in open, anode shape molds (occasionally in a continuous strip caster).

Copper electrorefining entails:

- (a) electrochemically dissolving copper from impure anodes into CuSO₄-H₂SO₄-H₂O electrolyte
- (b) electrochemically plating pure copper (without the anode impurities) from the electrolyte onto stainless steel or copper cathodes.

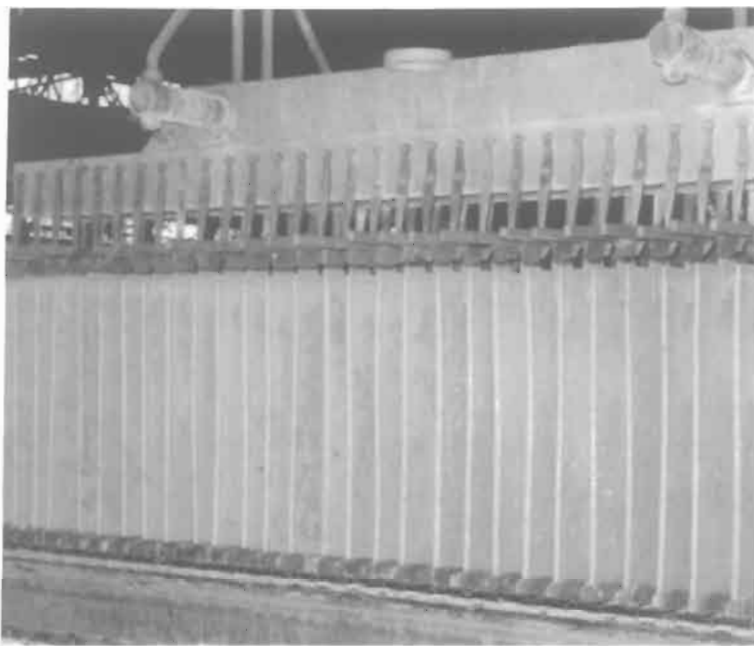


Fig. 1.7. Electrolytic refinery showing copper-laden cathodes being removed from an electrolytic cell. The cathodes are roughly $1\text{ m} \times 1\text{ m}$. The anodes remain in the cell (bottom). (Photograph courtesy R. Douglas Stern, Phelps Dodge Mining Company)

Copper is deposited on the cathodes for 7 to 14 days. The cathodes are then removed from the cell. Their copper is washed and sold or melted and cast into useful products, Chapter 22.

The electrolyte is an aqueous solution of H_2SO_4 (150 to 200 kg/m^3) and CuSO_4 (40 – 50 kg Cu/m^3). It also contains impurities and trace amounts of chlorine and organic ‘addition agents’.

Many anode impurities are insoluble in this electrolyte (Au, Pb, Pt metals, Sn). They do not interfere with the electrorefining. They are collected as ‘slimes’ and treated for Cu and byproduct recovery.

Other impurities such as As, Bi, Fe, Ni and Sb are partially or fully soluble. Fortunately, they do not plate with the copper at the low voltage of the electrorefining cell (~ 0.3 volt). They must, however, be kept from accumulating in the electrolyte to avoid physical contamination of the cathode copper. This is done by continuously bleeding part of the electrolyte through a purification circuit.

1.3 Hydrometallurgical Extraction of Copper

About 80% of copper-from-ore is obtained by flotation, smelting and refining. The other 20% is obtained hydrometallurgically. Hydrometallurgical extraction entails:

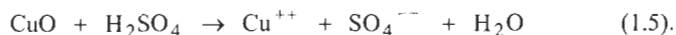
- sulfuric acid leaching of Cu from broken or crushed ore to produce impure Cu-bearing aqueous solution
- transfer of Cu from this impure solution to pure, high-Cu electrolyte via solvent extraction
- electroplating pure cathode copper from this pure electrolyte.

The ores most commonly treated this way are:

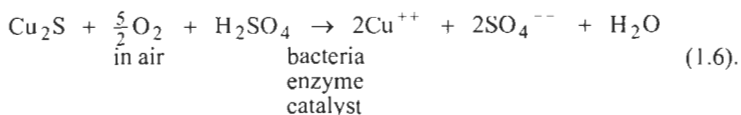
- 'oxide' copper minerals, e.g. carbonates, hydroxy-silicates, sulfates, hydroxy-chlorides
- chalcocite, Cu_2S .

The leaching is mostly done by sprinkling dilute sulfuric acid on top of heaps of broken or crushed ore (~0.5% Cu) and allowing the acid to trickle through to collection ponds, Fig. 1.2. Several months of leaching are required for efficient Cu extraction.

Oxidized minerals are rapidly dissolved by sulfuric acid by reactions like:



Sulfide minerals, on the other hand, require oxidation, schematically:



As shown, sulfide leaching is greatly speeded up by bacterial action, Chapter 17.

Leaching is occasionally applied to Cu-bearing flotation tailings, mine wastes, old mines and fractured orebodies. Leaching of ore heaps is, however, by far the most important process.

1.3.1 Solvent extraction (Chapter 18)

The solutions from heap leaching contain 1 to 6 kg Cu/m^3 and 0.5 to 5 kg

$\text{H}_2\text{SO}_4/\text{m}^3$ plus impurities, e.g. Fe and Mn. These solutions are too dilute in Cu and too impure for direct electroplating of pure copper metal. Their Cu must be transferred to pure, high-Cu electrolyte.

The transfer is done by:

- extracting Cu from an impure leach solution into a Cu-specific organic extractant
- separating the Cu-loaded extractant from the Cu-depleted leach solution
- stripping Cu from the loaded extractant into $185 \text{ kg H}_2\text{SO}_4/\text{m}^3$ electrolyte.

Extraction and stripping are carried out in large mixer-settlers, Fig. 1.8.

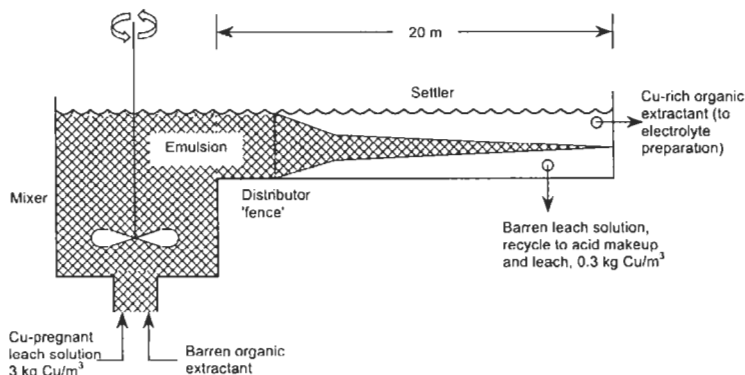
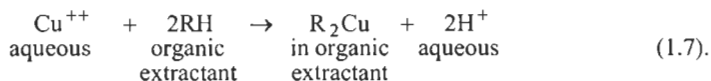


Fig. 1.8. Schematic view of solvent extraction mixer/settler for extracting Cu from pregnant leach solution into organic extractant. The Cu-loaded organic phase goes forward to another mixer/settler ('stripper') where Cu is stripped from the organic into pure, strongly acidic, high-Cu electrolyte for electrowinning.

The solvent extraction process is represented by the reaction:



It shows that a low-acid aqueous phase causes the organic extractant to 'load' with Cu (as R_2Cu). It also shows that a high acid solution causes the organic to unload ('strip').

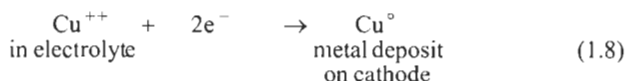
Thus, when organic extractant is contacted with weak acid pregnant leach solution [step (a) above], Cu is loaded into the organic phase. Then when the organic phase is subsequently put into contact with high acid electrolyte [step (c) above], the Cu is stripped from the organic into the electrolyte at high Cu^{++} concentration, suitable for electrowinning.

The extractants absorb considerable Cu but almost no impurities. They give electrolytes which are strong in Cu but dilute in impurities.

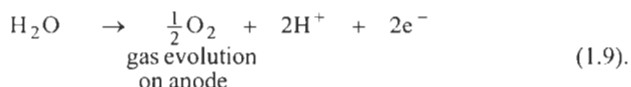
1.3.2 Electrowinning (Chapter 19)

The Cu in the above electrolytes is universally recovered by electroplating pure metallic cathode copper. This electrowinning is similar to electrorrefining except that the anode is an inert lead alloy.

The cathode reaction is:



The anode reaction is:



About 2 volts are required.

Pure metallic copper (less than 20 ppm undesirable impurities) is produced at the cathode and gaseous O_2 at the anode.

1.4 Melting and Casting Cathode Copper

The first steps in making products from electrorefined and electrowon copper are melting and casting. The melting is mostly done in vertical shaft furnaces in which descending cathode sheets are melted by ascending hot combustion gases. Low-sulfur fuels prevent sulfur pickup. Reducing flames prevent excessive oxygen pickup.

The molten copper is cast in continuous or semi-continuous casting machines from where it goes to rolling, extrusion and manufacturing. An especially significant combination is continuous bar casting/rod rolling, Chapter 22. The product of this process is 1 cm diameter rod for drawing to wire.

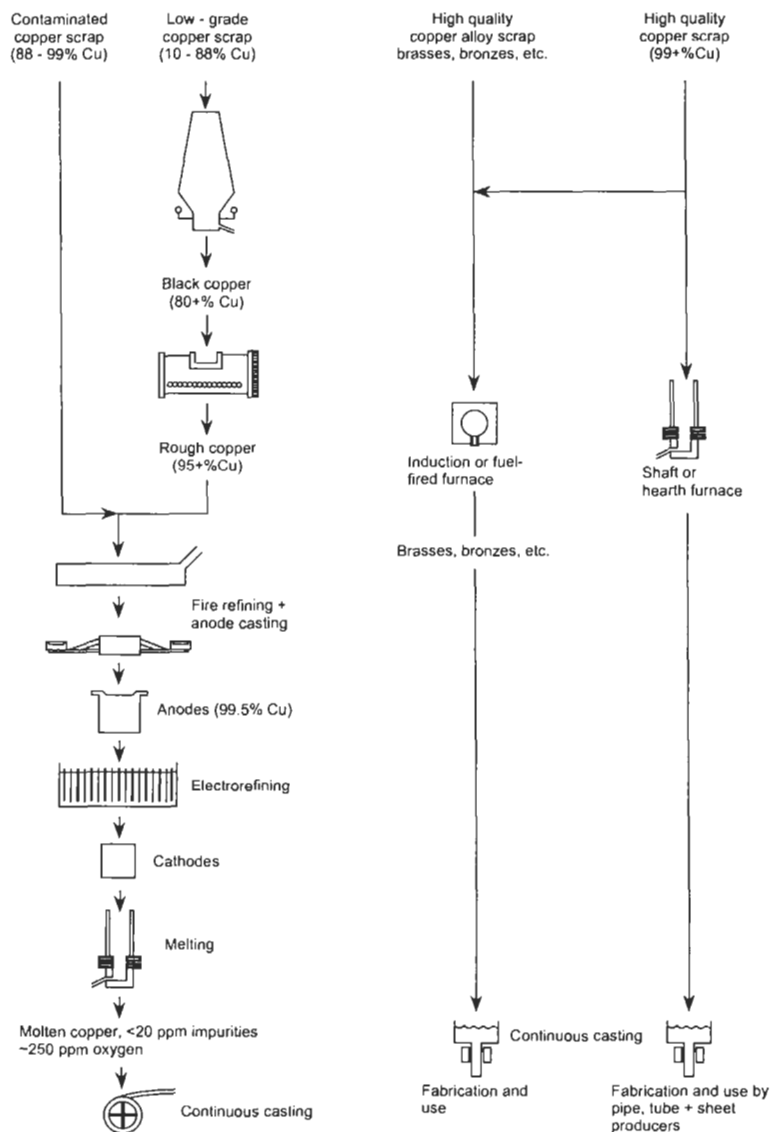


Fig. 1.9. Flowsheet of processes for recovering copper and copper alloys from scrap. Low grade scrap is usually smelted in shaft furnaces but other furnaces (e.g. electric) are also used.

1.4.1 Types of copper product

The copper described above is 'electrolytic tough pitch' copper. It contains ~0.025% oxygen and less than 20 parts per million unwanted impurities. It is far and away the most common type of copper. A second type is oxygen-free copper (<5 ppm O). It is used for highly demanding applications (e.g. for wrapping optical fiber bundles). It accounts for about 1% of copper production. About 20% of copper production is used in alloy form as brasses, bronzes, etc. The copper for these materials comes mainly from recycle scrap.

1.5 Recycle of Copper and Copper-Alloy Scrap (Chapters 20 and 21)

Recycle of copper and copper-alloy scrap used objects (old scrap) accounts for 10-15% of pre-manufacture copper production. Recycle of manufacturing wastes (new scrap) accounts for another 25 or 35%.

Production of copper from scrap has the advantages that:

- (a) it requires considerably less energy than mining and processing copper ore
- (b) it avoids mine, concentrator, leach and smelter wastes
- (c) it is helping to ensure the availability of copper for future generations.

The treatment given to copper scrap depends on its purity, Fig. 1.9. The lowest grade scrap is smelted and refined like concentrate in a primary or secondary (scrap) smelter/refinery. Higher-grade scrap is fire refined then electrorefined. The highest-grade scrap (mainly manufacturing waste) is often melted and cast without refining. Its copper is used for non-electrical products, e.g. tube, sheet and alloys.

Alloy scrap (brass, bronze) is melted and cast as alloy. There is no advantage to smelting/refining it to pure copper. Some slagging is done during melting to remove dirt and other contaminants.

1.6 Summary

About 80% of the world's copper-from ore is produced by concentration/smelting/refining of sulfide ores. The other 20% is produced by heap leaching/solvent extraction/electrowinning of 'oxide' and chalcocite ores.

An important source of copper is recycled copper and copper alloy scrap. It accounts for 40 or 50% of pre-manufacture copper production. This copper is recovered by simple melting of high-purity scrap and smelting/refining of impure scrap.

Electrochemical processing is always used in producing high-purity copper: electrorefining in the case of pyrometallurgical extraction and electrowinning in the case of hydrometallurgical extraction. The principal final copper product is electrolytic tough pitch copper (~250 ppm oxygen and 20 ppm unwanted impurities). It is suitable for virtually all applications.

The tendency in copper extraction is towards processes which do not harm the environment and which consume little energy. This has led to energy- and pollution-efficient oxygen-enriched air smelting; to solvent extraction/electrowinning of copper from leach solutions and to increased recycle of copper scrap.

Suggested Reading

Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vols. I-VI, TMS, Warrendale, PA.

Davenport, W. G., Jones, D. M., King, M. J. and Partelpoeg, E. H. (2001) *Flash Smelting, Analysis, Control and Optimization*, TMS, Warrendale, PA.

References

Boldt, J. R. and Queneau, P. (1967) *The Winning of Nickel*, Longmans Canada Ltd., Toronto, Canada.

CHAPTER 2

Production And Use

Metallic copper occurs occasionally in nature. For this reason, it was known to man about 7000 B.C (Killick, 2002). Its early uses were in jewelry, utensils, tools and weapons. Its use increased gradually over the years then dramatically in the 20th century with mass adoption of electricity (Fig. 2.1).

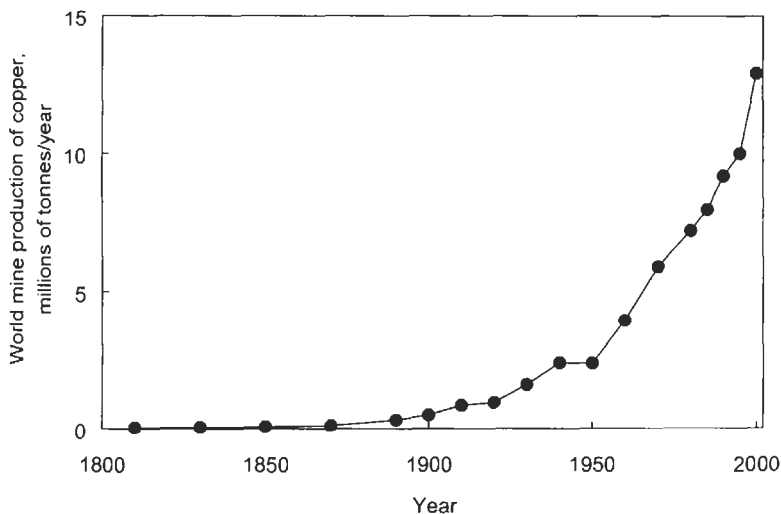


Fig. 2.1. World mine production of copper in the 19th and 20th centuries (Butts, 1954; USGS, 2002b).

Copper is an excellent conductor of electricity and heat. It resists corrosion. It is easily fabricated into wire, pipe, sheet etc. and easily joined. Electrical conductivity, thermal conductivity and corrosion resistance are its most exploited properties, Table 2.1.

Table 2.1. Usage of copper by exploited property (Copper Development Association, 2002) and by application (Noranda, 2002). Electrical conductivity is the property most exploited. Building construction and electrical/electronic products are the largest applications.

Exploited property	% of total use
Electrical conductivity	61
Corrosion resistance	20
Thermal conductivity	11
Mechanical and structural properties	6
Aesthetics	2

Application	% of total use
Building construction	40
Electrical and electronic products	25
Industrial machinery and equipment	14
Transportation equipment	11
Consumer goods	10

This chapter discusses production and use of copper around the world. It gives production, use and price statistics – and identifies and locates the world's principal copper-producing plants. It shows that Chile is by far the world's largest producer of copper, Table 2.3.

2.1 Locations of Copper Deposits

World mine production of copper is dominated by the western mountain region of South America. Nearly half of the world's mined copper originates in this region. The remaining production is scattered around the world, Table 2.3.

2.2 Location of Extraction Plants

The usual first stage of copper extraction is beneficiation of ore (~1% Cu) to high-grade (30% Cu) concentrate. This is always done at or near the mine site to avoid transporting worthless rock.

The resulting concentrate is smelted near the mine or in seacoast smelters around the world. The trend in recent years has been towards the latter. Seacoast smelters have the advantage that they can conveniently receive concentrates from around the world, rather than being tied to a single, depleting concentrate source (mine). The world's smelters are listed in Table 2.4 and plotted in Fig. 2.2.

Copper electrorefineries are usually built adjacent to the smelter that supplies them with anodes. The world's major electrorefineries are listed in Table 2.5 and plotted in Fig. 2.3.

Leach/solvent extraction/electrowinning operations are located next to their mines. This is because leach ores are dilute in copper, hence uneconomic to transport. The world's main copper leach/solvent extraction/electrowinning plants are listed in Table 2.6 and plotted in Fig. 2.4. Chile dominates.

2.3 Copper Minerals and 'Cut-Off' Grades

Table 2.2 lists copper's main minerals. These minerals occur at low concentrations in ores, the remainder being 'waste' minerals such as andesite and granite. It is now rare to find a large copper deposit averaging more than 1 or 2% Cu. Copper ores containing down to 0.5% Cu (average) are being mined from open pits while ores down to 1% (average) are being taken from underground mines.

Table 2.2. Principal commercial copper minerals. Chalcopyrite is by far the biggest copper source. Sulfide minerals are treated by the Fig. 1.1 flowsheet, i.e. pyrometallurgically. Carbonates, chlorides, oxides, silicates and sulfates are treated by the Fig. 1.2 flowsheet, i.e. hydrometallurgically. Chalcocite is treated both ways.

Type	Common minerals	Chemical formulae	Theoretical % Cu
<u>Primary sulfide minerals</u>	chalcopyrite	CuFeS_2	34.6
(hypogene sulfides)	bornite	Cu_5FeS_4	63.3
<u>Secondary minerals</u>			
supergene sulfides	chalcocite	Cu_2S	79.9
	covellite	CuS	66.5
native copper	metal	Cu^0	100.0
carbonates	malachite	$\text{CuCO}_3 \cdot \text{Cu(OH)}_2$	57.5
	azurite	$2\text{CuCO}_3 \cdot \text{Cu(OH)}_2$	55.3
hydroxy-silicates	chrysocolla	$\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$	36.2
hydroxy-chlorides	atacamite	$\text{Cu}_2\text{Cl(OH)}_3$	59.5
oxides	cuprite	Cu_2O	88.8
	tenorite	CuO	79.9
sulfates	antlerite	$\text{CuSO}_4 \cdot 2\text{Cu(OH)}_2$	53.7
	brochantite	$\text{CuSO}_4 \cdot 3\text{Cu(OH)}_2$	56.2

Table 2.3. World production of copper in 1999, kilotonnes of contained copper (USGS, 2002a). Smelting and refining include primary (concentrate) and secondary (scrap) smelting and refining. Electrowon production accounted for about 20% of total mine production.

Country	Mine production	Smelter production	Refinery production	Electrowon production
Argentina	145		16	
Armenia	7			
Australia	829	393	487	78
Austria		78	79	
Belgium		165	423	
Botswana	38	21		
Brazil	32	195	185	
Bulgaria	75	166	31	
Burma	27			27
Canada	634	604	551	
Chile	4602	1457	1296	1373
China	590	1190	1400	
Congo	21			21
Cyprus	11			11
Egypt			5	
Finland	12	157	114	
France			2	
Georgia	8			
Germany		350	710	
Hungary			12	
India	36	226	243	
Indonesia	1012	174	174	
Iran	145	154	130	14
Italy			70	
Japan	1	1481	1437	
Kazakhstan	430	400	395	

Korea, North	14	25	25	
Korea, South		410	475	
Macedonia	10			
Mexico	365	328	355	45
Mongolia	125			1
Morocco	7			
Namibia	5	13		
Norway		27	27	
Oman		24	24	
Papua New Guinea	201			
Peru	554	340	324	127
Philippines	32	140	135	
Poland	456	518	486	
Portugal	76			
Romania	16	19	18	
Russia	570	780	840	
Saudi Arabia	1			
Serbia & Montenegro	41	90	86	
Slovakia		10	20	
South Africa	137	126	101	
Spain	23	330	316	
Sweden	76	130	130	
Taiwan			4	
Turkey	76	37	72	
United Kingdom			50	
United States	1440	1000	1238	557
Uzbekistan	65	80	80	
Zambia	241	170	170	55
Zimbabwe	2	10	7	2
Total	13200	11800	12700	2300

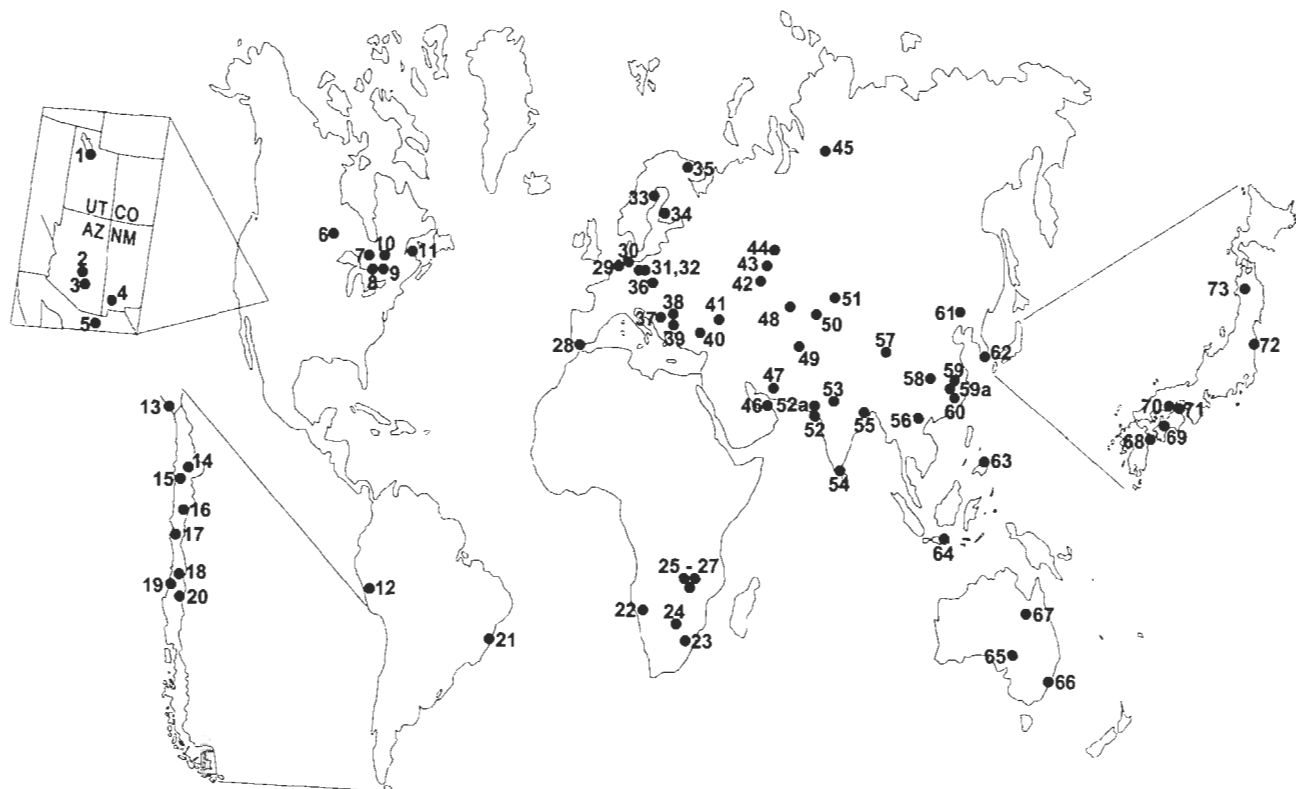


Fig. 2.2. Primary (concentrate) smelters of the world. Capacity and type of smelter are shown in Table 2.4.

Table 2.4. Principal primary smelters of the world. The numbers correspond to those in Fig. 2.2. The type of smelting furnace is: F: Outokumpu flash furnace; T: Teniente furnace; N: Noranda Furnace; M: Mitsubishi system; IF: Inco flash furnace; IS: Isasmelt furnace; R: reverberatory furnace; S; shaft furnace; E: electric furnace; V: Vanyukov furnace; K: Kivcet furnace. (s: smelting; c: converting; cu: direct to copper furnace). *Annual production, kilotonnes of copper per year.

Location	Furnace	*	Location	Furnace	*
1 Kennecott, Utah	Fs, Fe	280	38 Baia Mare, Romania	F	50
2 Miami, Arizona	IS	200	39 Pirdop, Bulgaria	F	45
3 Hayden, Arizona	IF	180	40 Samsun, Turkey	F	30
4 Chino, New Mexico	IF	shut	41 Mednogorsk, Russia	R	40
5 La Caridad, Sonora	F, T	320	42 Sredneuralsk, Russia	R	70
6 Flin Flon, Manitoba	R	60	43 Kirovgrad, Russia	R	70
7 Timmins, Ontario	M	130	44 Krasnouralsk, Russia	R	40
8 Sudbury, Ontario	IF	170	45 Norilsk, Russia	F,V	300
9 Falconbridge, Ont.	E	30	46 Oman	R	25
10 Noranda, Québec	Ns,Nc	220	47 Sar Chesma, Iran	R	150
11 Gaspé, Québec	R	shut	48 Dzhezkasgan, Kazak	E	200
12 La Oroya, Peru	R	70	49 Almalyk, Uzbekistan	IF	120
13 Ilo, Peru	R, T	285	50 Balkash, Kazakstan	R, V	300
14 Chuquicamata, Chile	F,R,T	535	51 Irtysk, Kazakstan	K	30
15 Altonorte, Chile	N, R	160	52 Birla, India	F	150
16 Potrerillos, Chile	T, R	160	52a Swil, India		50
17 Paipote, Chile	T	80	53 Khetri, India	F	30
18 Chagres, Chile	F	150	54 Tuticorin, India	IS	165
19 Las Ventanas, Chile	T	115	55 Ghatsila, India	F	30
20 Caletones, Chile	T	380	56 Kunming, China	IS	170
21 Caraiba, Brazil	F	200	57 Bayin, China		60
22 Tsumeb, Namibia	R	20	58 Daye, China	N	100
23 Palabora, S. Africa	R	140	59 Tonling, China	F	100
24 Selebi-Phikwe, Botswana	F	20	59a Jinlong, China		130
25 Mufulira, Zambia	E	230	60 Guixi, China	F	200
26 Nkana, Zambia	R,T	240	61 Shengyang, China	S to N	100
27 Luanshya, Zambia	R	50	62 Onsan, Korea	F, M	400
28 Huelva, Spain	F	290	63 Leyte, Philippines	F	180
29 Hoboken, Belgium	IS	75	64 Gresik, Indonesia	M	240
30 Hamburg, Germany	F	370	65 Olympic Dam, Aus.	Fcu	250
31 Glogow, Poland	SF,Fcu	350	66 Port Kembla, Aus.	Ns, Mc	150
32 Legnica, Poland	SF	120	67 Mount Isa, Australia	IS	260
33 Ronnskar, Sweden	E, F, TBRC	140	68 Saganoseki, Japan	F	450
34 Harjavalta, Finland	F	150	69 Toyo, Japan	F	250
35 Monchegorsk, Russ.	E	80	70 Tamano, Japan	F	220
36 Krompachy, Slovakia	R	20	71 Naoshima, Japan	M	270
37 Bor, Serbia	R	165	72 Onahama, Japan	R	260
			73 Kosaka, Japan	F	70

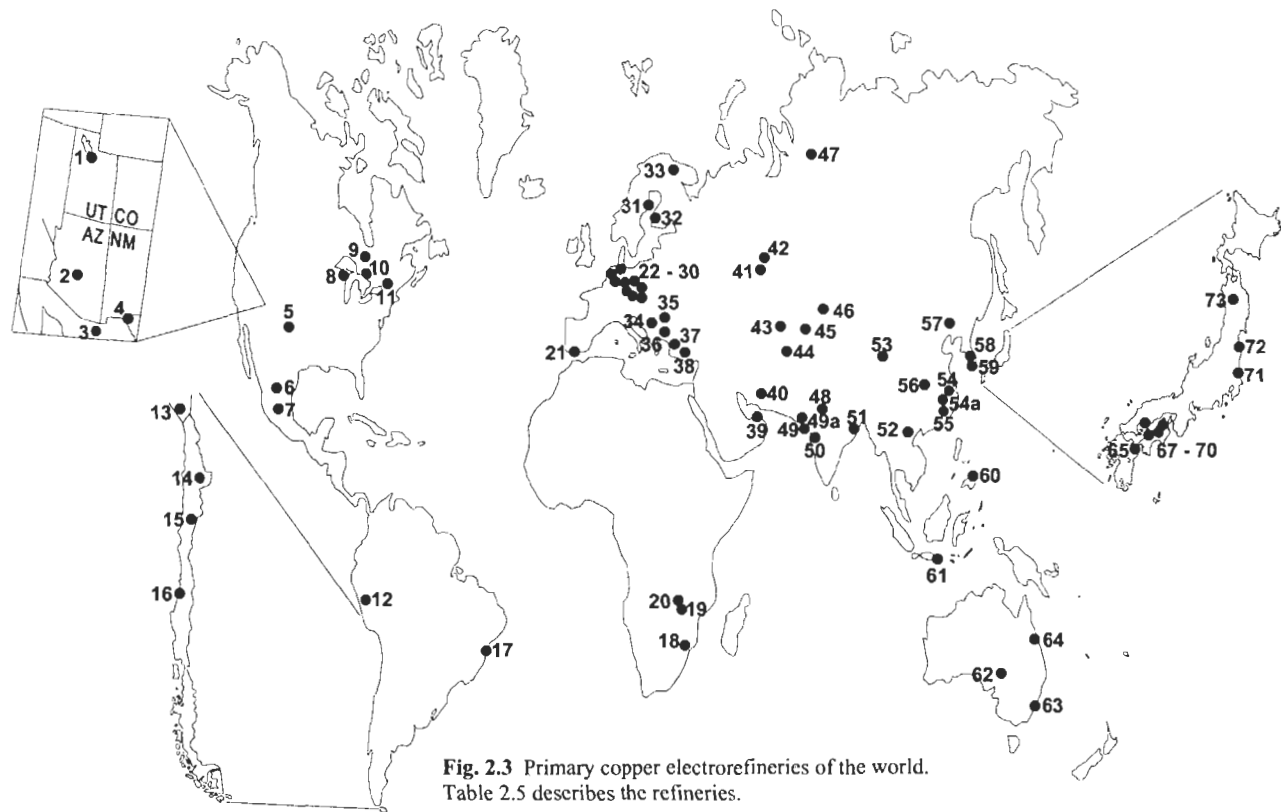


Fig. 2.3 Primary copper electrorefineries of the world.
Table 2.5 describes the refineries.

Table 2.5. Copper electrorefineries around the world. The numbers correspond to those in Fig. 2.3. PC = polymer concrete cells. SS = stainless steel cathodes. y = yes. Prod = production capacity kilotonnes of cathode copper per year. See Appendix E for more details on Chinese refineries.

Location	PC	SS	Prod.	Location	PC	SS	Prod.
1 Kennecott, Utah	y	y	281	38 Denizil, Turkey			40
2 Miami, Arizona	y	y	shut	38a Egypt			12
3 La Caridad, Mexico	y	y	300	39 Oman			20
4 El Paso, Texas	y		426	40 Sar Chesma, Iran			158
5 Amarillo, Texas			500	41 Pyshma, Russia			300
6 Jocotitlan, Mexico			66	42 Kyskhtym, Russia			75
7 Mexico City, Mexico	y		120	44 Almalyk, Uzbekistan			120
8 White Pine, Michigan		y	70	43 Dzhezkasgan, Kazakstan			207
9 Timmins, Ontario	y	y	130	45 Balkash, Kazakstan			300
10 Sudbury, Ontario			170	47 Norilsk, Russia			300
11 Montreal East, Quebec	y	y	360	48 Khetri, India			31
12 La Oroya, Peru			70	49 Birla, India	y	y	150
13 Ilo, Peru	y		280	49a Swil, India			50
14 Chuquicamata, Chile	y		653	50 Silvassa, India	y	y	165
15 Potrerillos, Chile	y		134	51 Ghatsila, India			17
16 Las Ventanas, Chile	y		300	52 Kunming, China			170
17 Caraiiba, Brazil			180	53 Bayin, China			60
18 Palabora, South Africa			140	54 Tonling, China			250
19 Kitwe, Zambia	y		220	54a Jinlong, China			130
20 Mufilira, Zambia			270	55 Guixi, China	y		200
21 Huelva, Spain	y	y	250	56 Daye, China			100
22 Olen, Belgium	y	y	350	57 Shengyang, China			100
23 Beerse, Belgium	y		37	58 Cheung Hang, Korea			60
24 Hamburg, Germany		y	370	59 Onsan, Korea, 2 refs.	y	y	365
25 Hettstedt, Germany			60	60 Leyte, Philippines			173
26 Lunen, Germany		y	180	61 Gresik, Indonesia	y	y	200
27 Brixlegg, Austria	y	y	75	62 Olympic Dam, Austral.	y	y	210
28 Krompachy, Slovakia			20	63 Port Kembla, Australia	y	y	120
29 Glogow, Poland, 2 refs.	y		390	64 Townsville, Australia	y	y	270
30 Legnica, Poland			80	65 Saganoseki, Japan	y		270
31 Ronnskar, Sweden	y	y	140	67 Toyo, Japan	y		105
32 Pori, Finland			125	68 Nishibara, Japan	y		145
33 Pechenga, Russia	y		75	69 Naoshima, Japan			220
34 Bor, Serbia			165	70 Tamano, Japan	y		220
35 Baia Mare, Romania			50	71 Hitachi, Japan	y	y*	180
36 Pirdop, Bulgaria	y		45	72 Onahama, Japan			260
37 Sarkuysan, Turkey			70	73 Kosaka, Japan	y		70

* under contract



Fig. 2.4a. Principal leach-solvent extraction-electrowinning plants of the world. Fig. 2.4b shows the Chilean operations.

Table 2.6. Solvent extraction/electrowinning plants around the world. The numbers correspond to those on Figs. 2.4a and 2.4b.

Location	Cathode*	Location	Cathode*
1 Gibraltar, BC	5	28 Mantos Blancos, Chile	45
2 Bagdad, AZ	10	29 Chiquicamata, Chile, 2	115
3 Pinto Valley, AZ	7	30 Zaldivar, Chile	145
4 Miami (BHP), AZ	12	31 Escondida Oxidos, Ch.	130
5 Miami (PD), AZ	73	32 El Salvador, Chile	12
6 Ray, AZ	46	33 Bio Cobre, Chile	10
7 Silver Bell, AZ	23	34 Manto Verde, Chile	42
8 Sierrita, AZ	23	35 Dos Amigos, Chile	3
9 San Manuel, AZ	23	36 Andacollo, Chile	20
10 Morenci AZ 4SX, 3EW	420	37 El Soldado, Chile	8
11 Tyrone, NM	74	38 Los Bronces, Chile, 2	30
12 Chino, NM	68	39 Pudahuel, Chile	18
13 Cananea, Mexico	55	40 El Teniente, Chile	8
14 La Caridad, Mexico	22	41 Chingola, Zambia	110
15 Tintaya, Peru	34	42 Nkana, Zambia	14
17 Toquepala, Peru	56	43 Chambishi, Zambia	15
18 Cerro Verde, Peru	60	43a Bwana Mkubwa	25
19 Cerro Colorado, Ch.	130	44 Hellenic Cu, Cyprus	5
20 Collahuasi, Chile	50	45 Kokkola, Finland	21
21 Quebrada Blanca, Ch	83	46 Nifty, Australia	21
22 Tocopilla, Chile	5	47 Mt Gordon, Australia	50
22a El Tesoro	75	48 Mt Cuthbert, Australia	4
23 El Abra, Chile	225	49 Cloncurry, Australia	6
24 Lomas Bayas, Chile	60	50 Port Pirie, Australia	5
25 Michilla, Chile	60	51 Olympic Dam, Aus.	20
26 Radomiro Tomic, Ch	256	52 Girilambone, Australia	18
27 Ivan Zar, Chile	10		

* kilotonnes of cathode copper per year

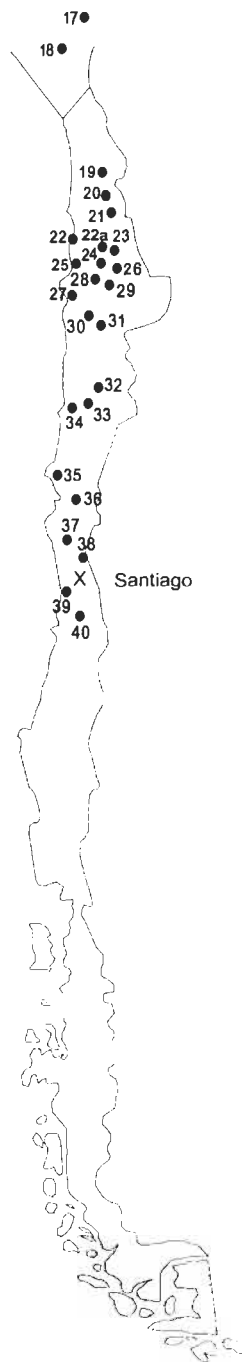


Fig. 2.4b. Leach-solvent extraction-electrowinning plants in Chile. They are mainly in the northern desert.

The average grade of ore being extracted from any given mine is determined by the 'cut-off' grade (% Cu) which separates 'ore' from 'waste'. Material with less than the 'cut-off' grade (when combined with all the ore being extracted) cannot be profitably treated for copper recovery. It is 'waste'. It is sent to waste dumps rather than to concentrating or leaching.

'Cut-off' grade depends on mining and extraction costs and copper selling price. If, for example, copper price rises and costs are constant, it may become profitable to treat lower grade material – in which case 'cut-off' grade (and average ore grade) decrease. Lower copper prices and increased costs have the opposite effect.

2.4 Price of Copper

The selling price of copper through the 20th century is shown in Fig. 2.5. In actual dollars, the price has moved upwards. In constant dollars, however, the price has fallen precipitously. At the start of 2002, it is near a 50-year low.

The low price is caused by an excess of supply over demand. It is difficult for producers but beneficial to users.

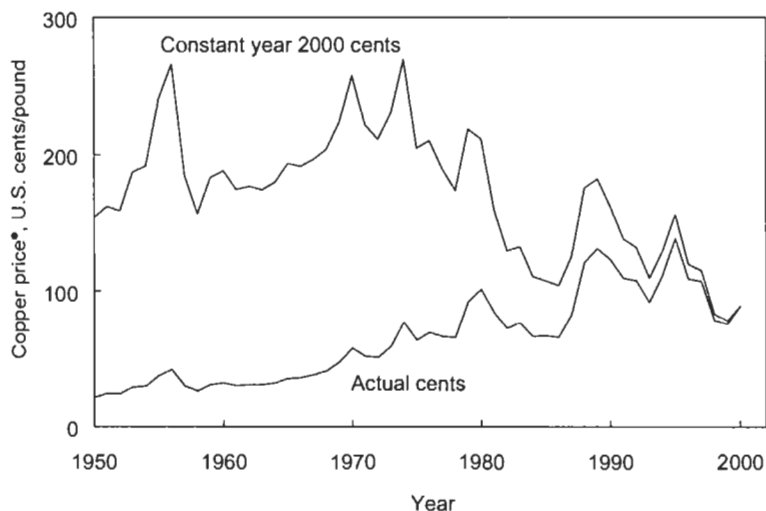


Fig. 2.5. Price of copper since 1950 (U.S.G.S., 2002b). (*U.S. producer price for cathode, 99.99% Cu)

2.5 Summary

Copper is produced around the world. Nearly half, however, is mined in the western mountain region of South America.

Concentrators and leach/solvent extraction/electrowinning plants are located near their mines. Smelters and refineries, on the other hand, are increasingly being located on seacoasts so that they can receive concentrates from all the world's mines.

Copper's most exploited property is its high electrical conductivity – in conjunction with its excellent corrosion resistance, formability and joinability. Its high thermal conductivity and corrosion resistance are also exploited in many heat transfer applications.

Worldwide, about 14 million tonnes of copper come into use per year. 85 to 90% of this comes from new mine production and 10 to 15% from recycled used objects.

References

Butts, A. (1954) *Copper, The Science and Technology of the Metal, Its Alloys and Compounds*, Reinhold Publishing Corp., New York, NY.

Copper Development Association (2002) Copper and copper alloy consumption in the United States by functional use – 1997. www.copper.org (Market data)

Killick, D. (2002) Personal communication. Department of Materials Science and Engineering, University of Arizona, Tucson, AZ 85721, U.S.A.

Noranda Inc. (2002) Copper end uses. www.noranda.com (Our business, Copper. Copper end uses)

USGS (2002a) United States Geological Survey, Commodity statistics and information – copper. Tabulated by Edelstein, D.L., Coleman, R.R., Roberts, L. and Wallace, G.J. <http://minerals.usgs.gov> (Commodity statistics and information, Copper, Minerals Yearbook, Copper 2000)

USGS (2002b) United States Geological Survey, Historical statistics for mineral commodities – copper. Tabulated by Porter, K.E. and Edelstein, D.L. <http://minerals.usgs.gov>

CHAPTER 3

Concentrating Copper Ores

Copper minerals are too dilute in ore (0.5 to 2% Cu) for economic direct smelting. Heating and melting the huge quantity of worthless rock would require too much energy and too much furnace capacity. For this reason, all ores destined for pyrometallurgical processing are physically concentrated before smelting. The product is concentrate containing ~30% Cu (virtually all in sulfide minerals).

Ores destined for hydrometallurgical extraction are almost never concentrated. Cu is usually extracted from these ores by leaching broken or crushed ore.

This chapter describes concentrating Cu ores. It emphasizes sulfide minerals because they account for almost all Cu concentration.

3.1 Concentration Flowsheet

Concentration of Cu ores consists of isolating an ore's Cu minerals into a high-Cu concentrate. It entails:

- (a) crushing and grinding the ore to a size where its Cu mineral grains are divided from its non-Cu-mineral grains
- (b) physical separation of Cu minerals from non-Cu minerals by froth flotation to form Cu rich concentrate and Cu barren 'tailing'.

Fig. 3.1 shows a typical concentrator flowsheet with the above steps. Tables 3.1 and 3.3 give industrial data. Copper concentrators typically treat 10 000 to 100 000 tonnes of ore per day, depending on the rate their mines produce ore.

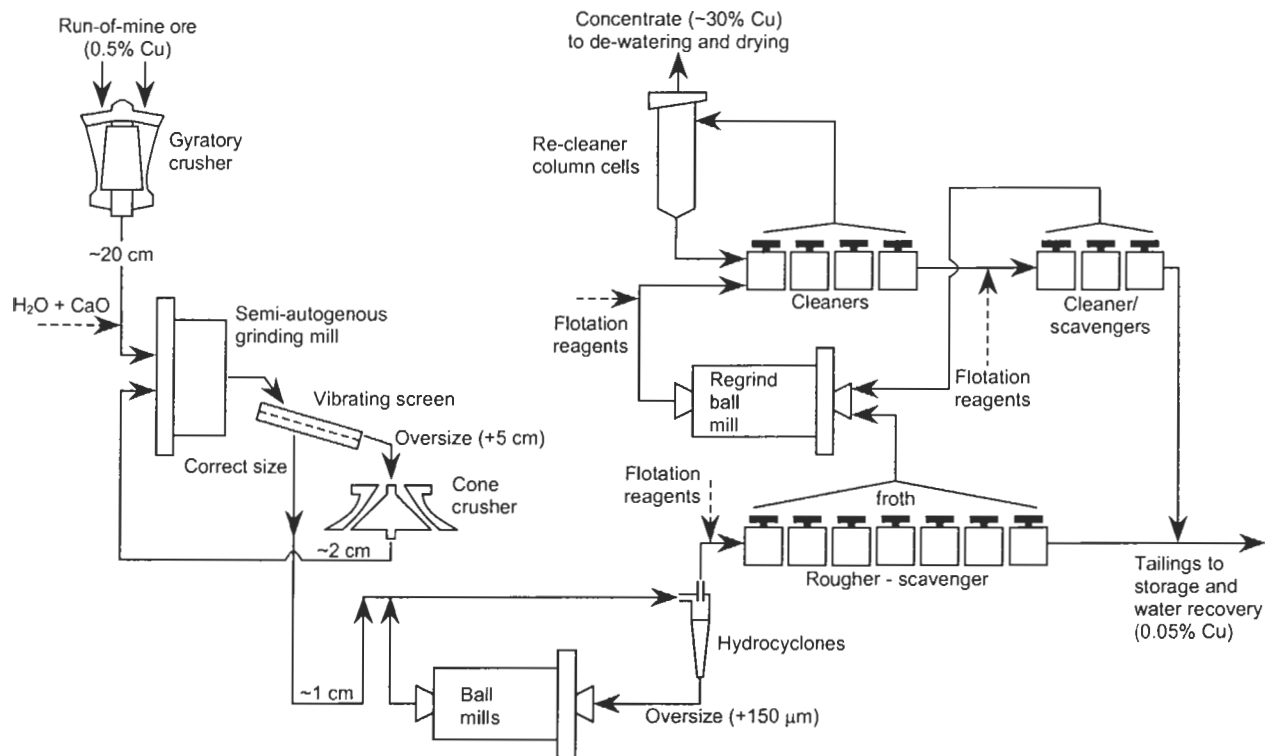


Fig. 3.1. Generalized flowsheet for producing Cu concentrates (~30% Cu) from Cu-Fe-S and Cu-S ores.

3.2 Crushing and Grinding (Comminution)

Isolation of an ore's Cu minerals into a concentrate requires that the ore be ground finely enough to liberate its Cu mineral grains from its non-Cu-mineral grains. The extent of grinding required to do this is fixed by the size of the mineral grains in the ore. It is ascertained by performing grinding/flotation tests.

Figure 3.2a shows the effect of grind size on recovery of Cu into concentrate. Figure 3.2b shows the corresponding Cu concentration in tailing. They indicate that there is an optimum grind size for maximum recovery of Cu-into-concentrate (minimum loss in tailing).

The reasons for this optimum are:

- (a) too large a grind size causes Cu minerals to remain combined with or hidden in non-Cu minerals – preventing their flotation
- (b) too fine a grind size causes 'slime' formation. This slime coats the Cu minerals and prevents some of them from being floated.

Liberation of mineral grains from each other generally requires grinding to ~100 μm diameter. Slime formation begins to adversely affect flotation when particles less than ~10 μm are formed.

Grinding requires considerable electrical energy, Table 3.1. This is another reason to avoid overly fine grinding.

3.2.1 Stages of comminution

Comminution is performed in three stages:

- (a) breaking the ore by explosions in the mine (blasting)
- (b) crushing of large ore pieces by compression in eccentric crushers, Fig. 3.3
- (c) wet grinding of the crushed ore in rotating 'tumbling mills' where abrasion, impact and compression all contribute to breaking the ore, Fig. 3.4.

The final fineness of grind is mainly determined by the number of times an ore particle passes through the grinding mills.

Separate crushing and grinding is necessary because it is not possible to break massive run-of-mine ore pieces while at the same time controlling fineness of grind for flotation.

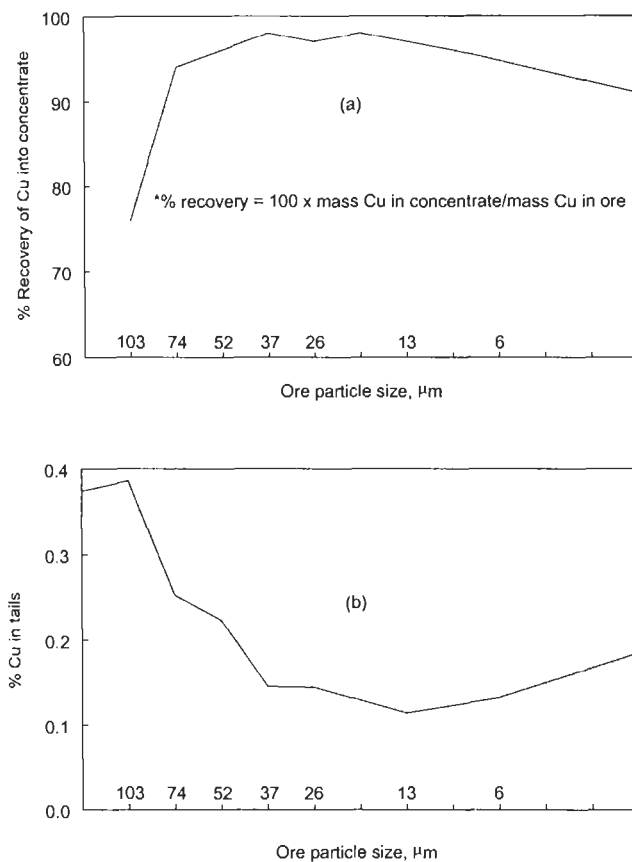


Fig. 3.2. Effect of grind particle size on (a) copper recovery and (b) % Cu in tailings. The presence of an optimum size is shown (Taggart, 1954). % recovery is calculated from ore input rate (tonnes/day), %Cu in ore, concentrate output rate (tonnes/day) and % Cu in concentrate.

3.2.2 Blasting

Blasting entails drilling holes in the mine, filling the holes with explosive and exploding fragments of rock from the mine wall. The explosions send cracks through the rock, releasing multiple fragments.

Fuerstenau *et al.* (1997) report that closer drill holes and larger explosive charges give smaller rock fragments. This may be useful for decreasing subsequent crushing requirements.

3.2.3 Crushing

Crushing is mostly done in the mine. This permits ore to be transported out of an open-pit mine by conveyor. It also permits easy hoisting of ore out of an underground mine.

The crushed ore is stored in a coarse-ore stockpile from which it is sent by conveyor to a semi-autogenous or autogenous grinding mill.

3.2.4 Grinding

Grinding takes the ore from crushing. It produces ore particles of sufficient fineness for Cu mineral recovery by flotation. The most common grinding mills are:

- (a) semi-autogenous and autogenous mills
- (b) ball mills.

Grinding is always done wet with mixtures of ~80 mass% solids and ~20 mass% water. A grinding circuit usually consists of one semi-autogenous or autogenous mill – and one or two ball mills.

Grinding and subsequent flotation are continuous, connected operations.

Autogenous mills tumble crushed ore without iron or steel grinding media. They are used when the crushed ore pieces are hard enough to perform all the grinding. Semi-autogenous mills tumble mainly ore but they use ~0.15 m³ of 13 cm iron or steel balls per 0.85 m³ of ore (i.e. 15 volume% ‘steel’) to assist grinding. Semi-autogenous mills are more common.

The semi-autogenous or autogenous mill grinds crusher product and prepares it for final grinding in a ball mill. Its product is usually passed over a large vibrating screen to separate oversize ‘pebbles’ from correct-size particles. The correct-size material is sent forward to a ball mill for final grinding. The oversize pebbles are recycled through a small eccentric crusher, then back to the semi-autogenous or autogenous mill. This procedure maximizes ore throughput and minimizes electrical energy consumption.

Ball mills tumble iron or steel balls. The balls are initially 5 to 10 cm diameter. They gradually wear away as grinding proceeds. Ball mills typically contain about 75% ore and 25% ‘steel’ (by volume). They give a controlled final grind.

The ball mill accepts the semi-autogenous or autogenous mill product. It produces uniform-size flotation feed. It is operated in closed circuit with a particle size measurement device and size control cyclones, Fig. 3.5. The

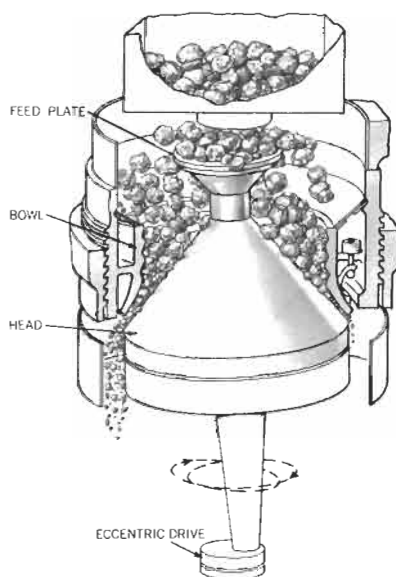


Fig. 3.3. Gyratory crusher for crushing run-of-mine ore to ~20 cm pieces. The crushing is done by compression of ore between the eccentrically rotating spindle and the fixed crusher walls. The crushing surface on the spindle can be up to 3 m in height.

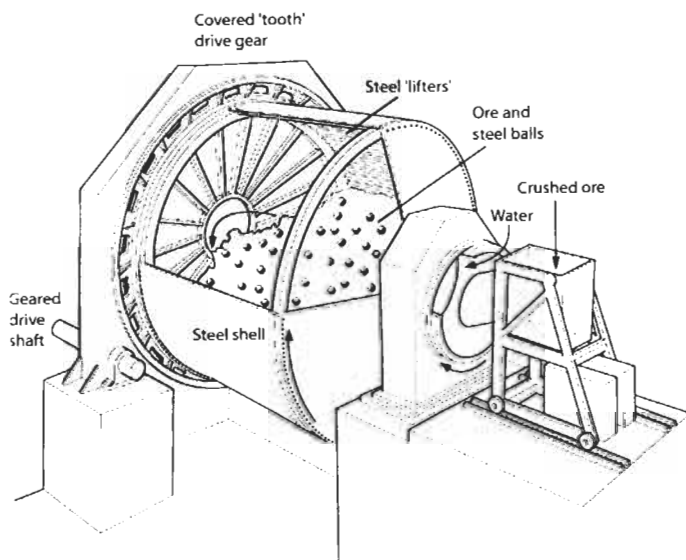


Fig. 3.4. Semi-autogenous grinding mill. It is a rotating barrel in which ore is broken by (i) itself and (ii) steel balls as they are lifted and fall off the moving circumference of the barrel. Drawing courtesy www.bradken.com.au

Table 3.1. Industrial crushing and grinding data for three copper concentrators, 2001. They all treat ore from large open-pit mines. Flotation details are given in Table 3.3.

Concentrator	Candalaria, Chile	Mexicana de Cobre, Mexico	Bagdad Copper, Arizona
Ore treated per year, tonnes	25 000 000	27 360 000	31 000 000
Ore grade, %Cu	0.9 – 1.0	0.522	0.4
Crushing			
primary gyratory crusher	one	2	one
diameter × height, m	1.52 × 2.26	1.52 × 2.26	1.5 × 2.25
power rating, kW	522	375 at ~600 RPM	450
product size, m	0.1-0.13	0.15	0.2
energy consumption, kWh per tonne of ore	0.3 (estimate)		
secondary crushers	no	6	no
First stage grinding			
mill type	semi-autogenous	ball mills	autogenous
number of mills	2	12	5
diameter × length, m	11 × 4.6	5 × 7.3	10 × 4
power rating each mill, kWh	12 000	4000	4500
rotation speed, RPM	9.4-9.8	~13.8	10
vol. % 'steel' in mill	12-15	32	0
ball size, initial	12.5 cm		
ball consumption	0.3 kg/tonne ore		
feed	70% ore, 30% H ₂ O		83% ore 17% H ₂ O
product size	80% <140 µm	80% <215 µm	4 cm
oversize treatment	22% ore recycle through two 525 kW crushers		screened and recycled through cone crushers
energy consumption, kWh per tonne of ore	7.82		8
Second stage grinding			
mill type	ball mills	ball mills	ball mills
number of mills	4	4	5
diameter × length, m	6 × 9	4.3 × 7.3	4.7 × 6.7
power rating each mill, kW	5600		2200
rotation speed, RPM			13
vol. % 'steel' in mill		~15	40
feed			85% ore, 15% H ₂ O
product size		80% <58 µm	80% <130 µm
energy consumption, kWh per tonne of ore	7 (estimate)		6
Hydrocyclones	14 Krebs (0.5 m diameter)	6	2 to 3 (0.85 m diameter)
Particle size monitor		yes	no

cyclones send correct-size material on to flotation and oversize back to the ball mill for further grinding.

3.3 Flotation Feed Particle Size

A critical step in grinding is ensuring that the final particles from grinding are fine enough for efficient flotation. Coarser particles must be isolated and returned for further grinding.

Size control is universally done by hydrocyclones, Fig. 3.5 (Krebs, 2002). The hydrocyclone makes use of the principle that, under the influence of a force field, large ore particles in a water-ore mixture (pulp) tend to move faster than small ore particles.

This principle is put into practice by pumping the grinding mill discharges into hydrocyclones at high speed, 5 to 10 m per second. The pulp enters tangentially, Fig. 3.5, so it is given a rotational motion inside the cyclone. This creates a centrifugal force which accelerates ore particles towards the cyclone wall.

The water content of the pulp, ~60 mass% H₂O, is adjusted so that:

- (a) the oversize particles are able to reach the wall, where they are dragged out by water flow along the wall and through the apex of the cyclone, Fig. 3.5
- (b) the correct (small) size particles do not have time to reach the wall before they are carried with the main flow of pulp through the vortex finder.

The principal control parameter for the hydrocyclone is the water content of the incoming pulp. **An increase in the water content of the pulp gives less hindered movement of particles. It thereby allows a greater fraction of the input particles to reach the wall and pass through the apex. This increases the fraction of particles being recycled for regrinding and ultimately to a more finely ground final product.**

A decrease in water content has the opposite effect.

3.3.1 Instrumentation and control

Grinding circuits are extensively instrumented and closely controlled, Fig. 3.6, Table 3.2. The objectives of the control are to:

- (a) produce particles of appropriate size for efficient flotation recovery of Cu minerals
- (b) produce these particles at a rapid rate
- (c) produce these particles with a minimum consumption of energy.

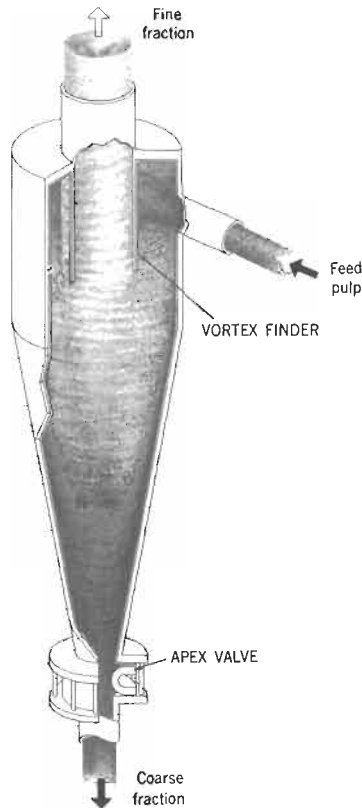


Fig. 3.5. Cutaway view of hydrocyclone showing tangential input of water-ore particle feed and separation into fine particle and coarse particle fractions. The cut between fine particles and coarse particles is controlled by adjusting the water content of the feed mixture, Section 3.3. Drawing from Boldt and Queneau, 1967 courtesy Inco Limited.

The most common control strategy is to:

- (a) insist that the sizes of particles in the final grinding product are within predetermined limits, as sensed by an on-stream particle size analyzer (Outokumpu, 2002a)
- (b) optimize production rate and energy consumption while maintaining this correct-size.

Fig. 3.6 and the following describe one such control system.

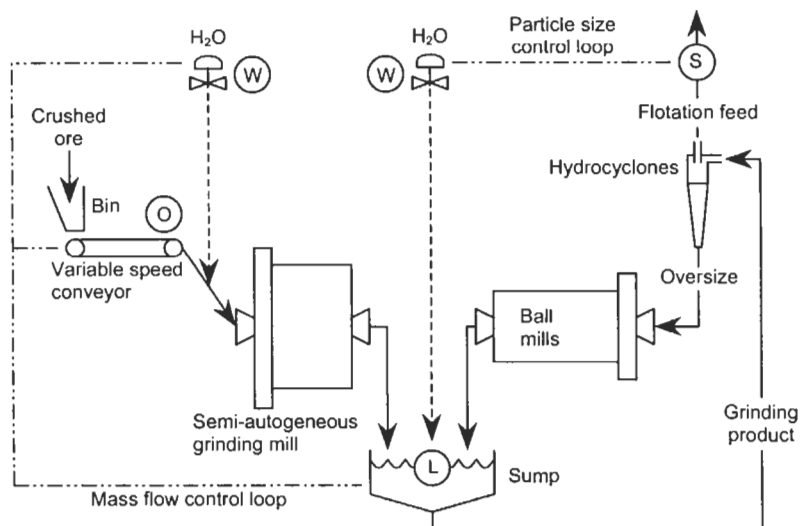


Fig. 3.6. Control system for grinding mill circuit (—— ore flow; - - - - water flow; - · - · - electronic control signals). The circled symbols refer to the sensing devices in Table 3.2. A circuit usually consists of a semi-autogenous grinding mill, a hydrocyclone feed sump, a hydrocyclone 'pack' (~6 cyclones) and one or two ball mills. (Screening and crushing of oversize semi-autogenous grinding mill pieces is not shown.)

3.3.2 Particle size control

The particle-size control loop in Fig. 3.6 controls the particle size of the grinding product by automatically adjusting the rate of water addition to the hydrocyclone feed sump. If, for example, the flotation feed contains too many large particles, an electronic signal from the particle size analyzer (S) automatically activates water valves to *increase* the water content of the hydrocyclone feed. This *increases* the fraction of the ore being recycled to the ball mills and gives a *finer* grind.

Conversely, too fine a flotation feed automatically cuts back on the rate of water addition to the hydrocyclone feed sump. This decreases ore recycle to the grinding meals, increasing flotation feed particle size. It also permits a more rapid initial feed to the ball mills and minimizes grinding energy consumption.

3.3.3 Ore throughput control

The second control loop in Fig. 3.6 gives maximum ore throughput rate without overloading the ball mill. Overloading might become a problem if, for example,

the ball mill receives tough, large particles which require extensive grinding to achieve the small particle size needed by flotation.

The simplest mass flow control scheme is to use hydrocyclone sump pulp level to adjust ore feed rate to the grinding plant. If, for example, pulp level sensor (L) detects that the pulp level is rising (due to tougher ore and more hydrocyclone recycle), it automatically slows the plant's input ore feed conveyor. This decreases flow rates throughout the plant and stabilizes ball mill loading and sump level.

Detection of a falling sump level, on the other hand, automatically increases ore feed rate to the grinding plant – to a prescribed rate or to the maximum capacity of another part of the concentrator, e.g. flotation.

Table 3.2. Sensing and control devices for grinding circuit shown in Fig. 3.6.

Sensing instruments	Symbol Fig. 3.6	Purpose	Type of device	Use in automatic control system
Ore tonnage weight-ometer	O	Senses feed rate of ore into grinding circuit	Load cells, conveyor speed	Controls ore feed rate
Water flow gages	W	Sense water addition rates	Rotameters	Control water/ore ratio in grinding mill feed
On-stream particle size analyzer	S	Senses a critical particle size parameter (e.g. percent minus 150 μm) on the basis of calibration curves for the specific ore	Measure ultrasound energy loss in de-aerated pulp (Outokumpu, 2002a)	Controls water addition rate to hydrocyclone feed (which controls the particle size of the final grinding circuit product)
Hydro-cyclone feed sump level indicator	L	Senses changes of pulp level in sump; triggers alarms for impending over-flow	Bubble pressure tubes; electric contact probes; ultrasonic echoes; nuclear beam	Controls rate of ore input into grinding circuit (prevents over-loading of ball mills or hydro-cyclones)
Ball mill load		Senses mass of ore in ball mill	Load cells; sound, bearing pressures; power draw	Controls rate of ore input into grinding circuit

There is, of course, a time delay (5 to 10 minutes) before the change in ore feed rate is felt in the hydrocyclone feed sump. The size of the sump must be large enough to accommodate further build-up (or draw-down) of pulp during this delay.

3.4 Froth Flotation

The indispensable tool for Cu ore beneficiation is froth flotation (Parekh and Miller, 1999). The principles of froth flotation are:

- (a) sulfide minerals are normally wetted by water but they can be conditioned with reagents (collectors) which cause them to become water repellent
- (b) this 'repellency' can be given selectively to Cu minerals, leaving other minerals 'wetted'
- (c) collisions between small rising air bubbles and the now-water repellent Cu minerals result in attachment of the Cu mineral particles to the bubbles
- (d) the other 'wetted' mineral particles do not attach to the rising bubbles.

Copper ore froth flotation entails, therefore:

- (a) conditioning a water-ore mixture (pulp) to make its Cu minerals water repellent while leaving its non-Cu minerals 'wetted'
- (b) passing a dispersed stream of small bubbles (~0.5 mm diameter) up through the pulp.

These procedures cause the Cu mineral particles to attach to the rising bubbles which carry them to the top of the flotation cell, Fig. 3.7. The other minerals are left behind. They depart the cell through an underflow system. They are mostly non-sulfide 'rock' with a small amount of Fe-sulfide.

The last part of flotation is creation of strong but short-lived froth when the bubbles reach the surface of the pulp. This froth prevents bursting of the bubbles and release of the Cu mineral particles back into the pulp. The froth overflows the flotation cell (often with the assistance of paddles, Fig. 3.7) and into a trough. There, it collapses and flows into a collection tank.

Copper flotation consists of a sequence of flotation cells designed to optimize Cu recovery and %Cu in concentrate, Fig. 3.10. The froth from the last set of flotation cells is, after water removal, Cu concentrate.

3.4.1 Collectors

The reagents (collectors) which create the water repellent surfaces on sulfide minerals are heteropolar molecules. They have a polar (charged) end and a non-

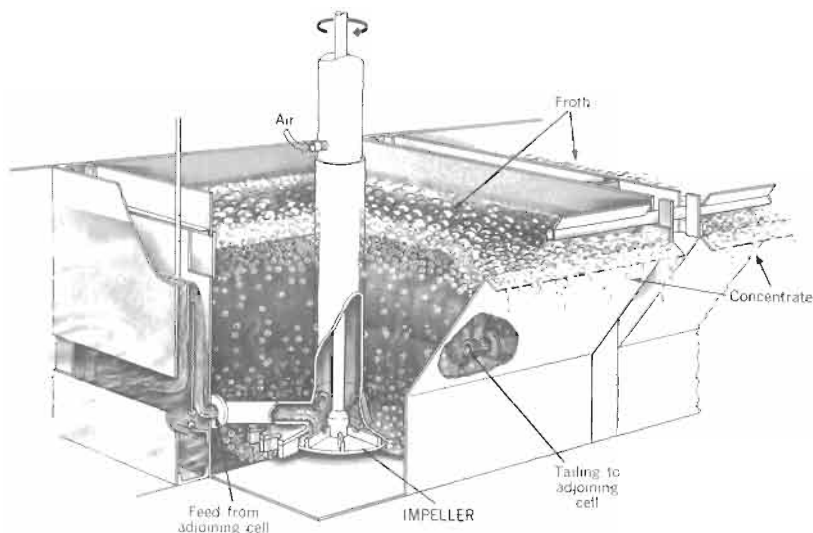


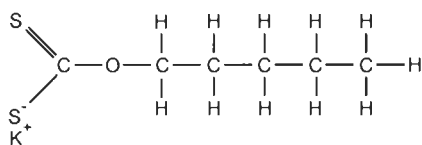
Fig. 3.7. Cutaway view of mechanical flotation cell. The method of producing bubbles and gathering froth are shown (Boldt and Queneau, 1967 courtesy Inco Limited). Flotation cells in recent-design copper concentrators are 100 to 150 m³ box or cylindrical tanks (Jonaitis 1999).

polar (hydrocarbon) end. They attach their polar (charged) end to the mineral surface (which is itself polar) leaving the non-polar hydrocarbon end extended outwards, Fig. 3.8. It is this orientation that imparts the water repellent character to the conditioned mineral surfaces.

3.4.2 Selectivity in flotation

The simplest froth flotation separation is sulfide minerals from waste oxide 'rock', e.g. andesite, granadiorite, granite, quartz. It uses collectors which, when dissolved in a water-ore pulp, preferentially attach themselves to sulfides. These collectors usually have a sulfur group at the polar end – which attaches to sulfide minerals but ignores oxides.

The most common sulfide collectors are xanthates, e.g.:



(Potassium amyl xanthate)

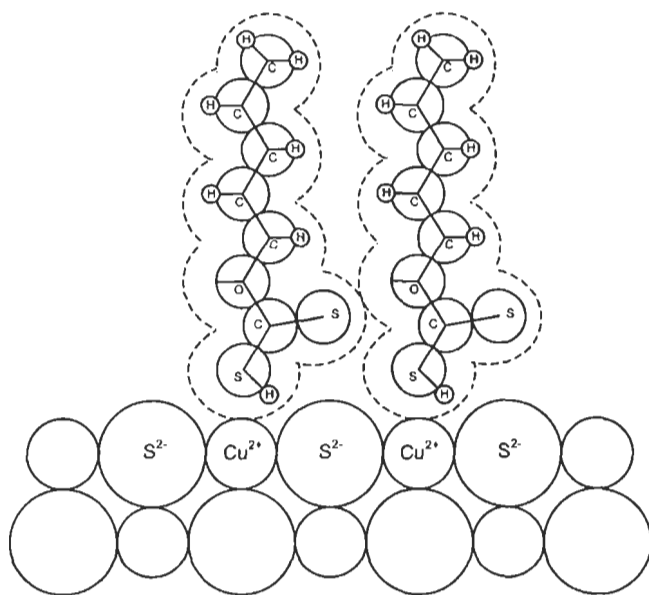


Fig. 3.8. Sketch of attachment of amyl xanthate ions to covellite. There is a hydrogen atom hidden behind each carbon of the hydrocarbon chain (after Hagihara, 1952).

Other sulfur molecules are also used, particularly dithiophosphates and thionocarbamates (Klimpel, 1999). Commercial collectors are often blends of several reagents. Far and away, however, the xanthates (e.g. potassium amyl xanthate, sodium ethyl xanthate and sodium isopropyl xanthate) are the most common Cu mineral collectors. Of the order of 0.01 kg is required per tonne of ore entering the flotation cells.

3.4.3 Differential flotation – modifiers

Separating sulfide minerals, e.g. chalcopyrite from pyrite, is somewhat more complex. It relies on modifying the surfaces of non-Cu sulfides so that the collector does not attach to them while still attaching to Cu sulfides.

The most common modifier is the OH^- (hydroxyl) ion. Its concentration is varied by adjusting the basicity of the pulp with burnt lime (CaO), occasionally sodium carbonate. The effect is demonstrated in Fig. 3.9 – which shows how chalcopyrite, galena and pyrite can be floated from each other. Each line on the graph marks the boundary between float and non-float conditions for the specific mineral – the mineral ‘floats’ to the left of its curve, to the right it doesn’t.

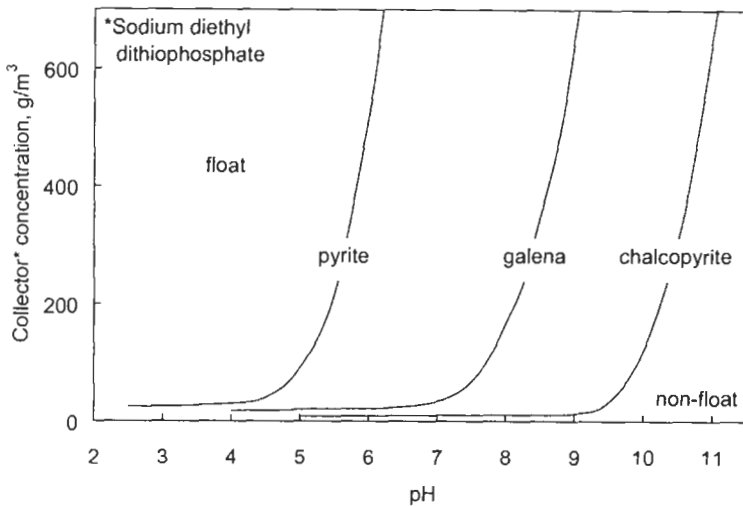


Fig. 3.9. Effects of collector concentration and pH on the floatability of pyrite, galena and chalcopyrite. Each line marks the boundary between 'float' and non-float conditions for the specific mineral (Wark and Cox, 1934). Precise float/non-float boundary positions depend on collector, mineral and water compositions.

The graph shows that:

- up to pH 5 (acid pulp): CuFeS_2 , PbS and FeS_2 all float
- between pH 5 and pH 7.5 (neutral pulp): CuFeS_2 and PbS float while FeS_2 is depressed
- between pH 7.5 and pH 10.5 (basic pulp): only CuFeS_2 floats.

Thus a bulk Pb-Cu sulfide concentrate could be produced by flotation at pH 6.5. Its Pb and Cu sulfides could then be separated at pH 9, i.e. after additional CaO addition.

The modifying effect of OH^- is due to its competition with collector anions (e.g. xanthates) for a place on the mineral surface. OH^- ions are, for example, selectively adsorbed on pyrite. This prevents appreciable xanthate adsorption on the pyrite, selectively 'depressing' it. However, too many OH^- ions will also depress chalcopyrite – so too much CaO must be avoided.

Another depressant for Fe-minerals is SO_3^{--} . It is produced by bubbling SO_2 into the pulp prior to flotation.

3.4.4 Frothers

Collectors and modifiers give selective flotation of Cu minerals from non-Cu minerals. *Frothers* create the strong but short-lived froth which holds the floated Cu minerals at the top of the cell. They give a froth which:

- (a) is strong enough in the flotation cell to support floated Cu minerals
- (b) breaks down quickly once it and its minerals overflow the cell.

Branch chain alcohols are the most common frothers (Mulukutla, 1993) – natural (e.g. pine oil or terpinol) or synthetic (methyl isobutyl carbinol, polyglycols and proprietary alcohol blends [Chevron Phillips, 2002]).

Frothers stabilize the froth by absorbing their OH^- polar end in water – while their branch chains form a cross-linked network in air. The froth should not be long-lived, so the branch chain hydrocarbon tails should not be too long.

3.5 Specific Flotation Procedures for Cu Ores

Selective flotation of Cu sulfide minerals (chalcopyrite, chalcocite, bornite) from Fe-minerals (pyrite, pyrrhotite) is usually done with xanthate, dithiophosphate or thionocarbamate collectors; burnt lime (CaO) for pH (OH^- ion) control; and branch chain alcohol frothers. A common flowsheet, industrial data and example reagents are shown in Fig. 3.10 and Table 3.3.

The flowsheet shows four sets of flotation cells:

- (a) 'rougher-scavengers' in which the incoming ground-ore pulp is floated under conditions which give efficient Cu recovery with a reasonable concentrate grade (15-20% Cu)
- (b) 'cleaners' in which non-Cu minerals in the rougher-scavenger concentrate are depressed with CaO to give a high grade Cu concentrate
- (c) 're-cleaners' which maximize concentrate grade (%Cu) by giving Fe-minerals and 'rock' a final depression
- (d) 'cleaner-scavengers' which, with the addition of more collector scavenge the last bit of Cu from the cleaner tails before they are discarded.

The froths from the rougher-scavengers and cleaner-scavengers are ground before being sent to the cleaners, Fig. 3.10. This releases previously 'locked-in' Cu mineral grains.

The *rougher-scavenger* and *cleaner-scavenger* cells are designed to maximize Cu recovery to concentrate. The *cleaner* and *re-cleaner* cells maximize concentrate grade.

Circuits like Fig. 3.10 give ~90% recovery of Cu sulfide minerals and ~30% Cu concentrate grade (with chalcopyrite mineralization).

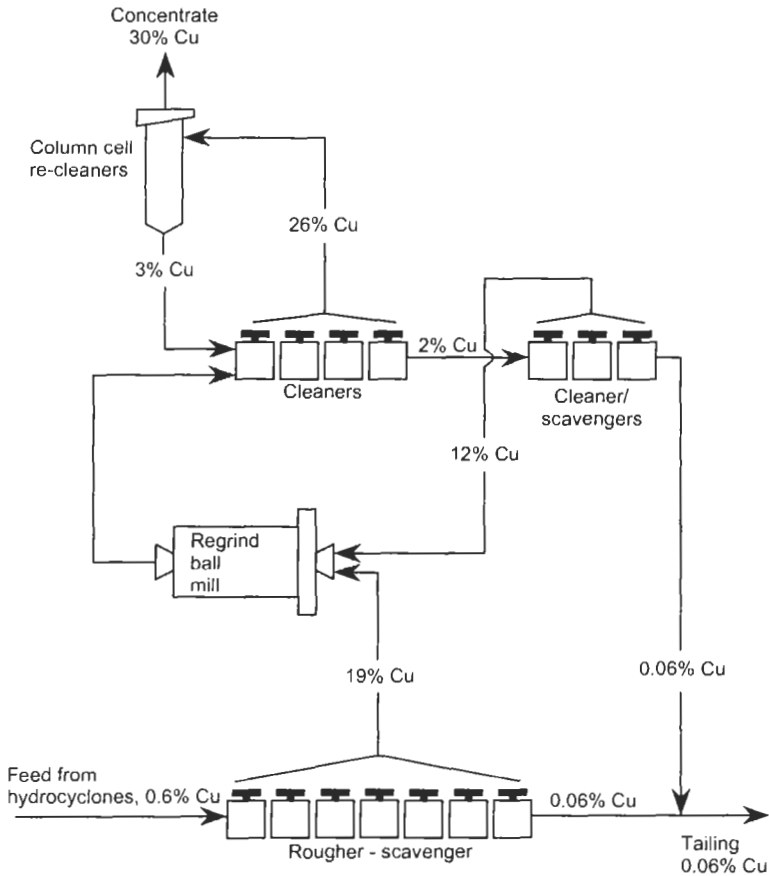


Fig. 3.10. Flowsheet for floating Cu sulfide concentrate from 'rock' and Fe sulfides. Residence times in each sector (e.g. rougher-scavenger cells) are 10-20 minutes. Representative mass flows in tonnes/day are:

Feed from hydrocyclones	40 000
Concentrate (re-cleaner froth)	720
Tailings	39 280
Rougher-scavenger froth	1 140
Cleaner-scavenger feed	500
Re-cleaner feed	850

Table 3.3. Industrial data from 3 copper concentrators, 2001. All three treat ore from large open pit mines. The equivalent crushing/grinding data are given in Table 3.1.

Concentrator	Candalaria, Chile	Mexicana de Cobre	Bagdad Copper, AZ
Ore treated per year, tonnes	25 000 000	27 360 000	31 000 000
Concentrate, tonnes/year		416 496	385 000
Ore grade, %Cu	0.9-1.0	0.522	
sulfide			0.4
'oxide'		0.058	0.02
Concentrate grade, % Cu	29-30	28.08	30.5
Tailings grade, % Cu		0.096	0.039
Cu recovery to concentrate, %	95% Cu, 82% Au 87% Mo	81.85	90.8
Rougher-scavenger flotation			
feed	cyclone overflow	cyclone overflow	cyclone overflow
number of cells	24	140	78
volume of each cell, m ³	85 and 128	38 and 14	18
cell type	Eimco	OK 38 and Wemco	OK and Wemco
mass% solids in feed		29	36
pH	10.4	9.6-10.5	10.3
collector	SF 323	thionocarbamate	Na ethyl xanthate
kg/tonne of ore		~0.0065	0.012
oily collector, kg/t of ore		0.018	0.009
frother	MIBC		Cytec 547
kg/tonne of ore		0.03	0.01
CaO, kg/tonne of ore	0.7	0.024	0.86
residence time, minutes		~20	10.5
Cleaner flotation			
feed	rougher concentrate ground in 4.27 m × 6.7 m ball mill		reground rougher- scavenger and cleaner- scavenger froth (80% <50µm)
number of cells		32	30
volume of each cell, m ³		14	2.8
cell type		Denver	Wemco/agitair
mass% solids in feed		20	13
pH		12.0-12.3	11.5
reagents		0.002	CaO
residence time, minutes			2.5
Cleaner-scavenger flotation			
feed			cleaner tails
number of cells		64	16
volume of each cell, m ³		14	8.5
cell type		Denver	Wemco
mass% solids in feed		20	13
pH		12-12.3	11.4
reagents		none	Na ethyl xanthate
Re-cleaner flotation			
feed			cleaner froth
number of cells		16	30
cell volume, m ³		14	2.8
cell type	column	Denver	mechanical
mass% solids in feed		35	16
pH		12.0-12.3	11
reagents		none	none
residence time, minutes			14.7

3.6 Flotation Cells

Fig. 3.7 shows a 'mechanical' flotation cell. Air bubbles are introduced into the pulp through a rotating agitator at the bottom of the cell. The agitator shears the air into the fine-size bubbles needed for ore attachment (~ 0.5 mm diameter as they enter the cell). It also disperses the bubbles across the cell.

3.6.1 Non-mechanical flotation cells

Most new Cu flotation plants use either (i) column or (ii) Jameson flotation cells for re-cleaning their concentrate (EMJ, 1998; Dufresne, 2000). These cells provide separate zones (Finch, 1998) for:

- (a) particle-bubble attachment
- (b) draining of non-attached low-Cu particles from the froth.

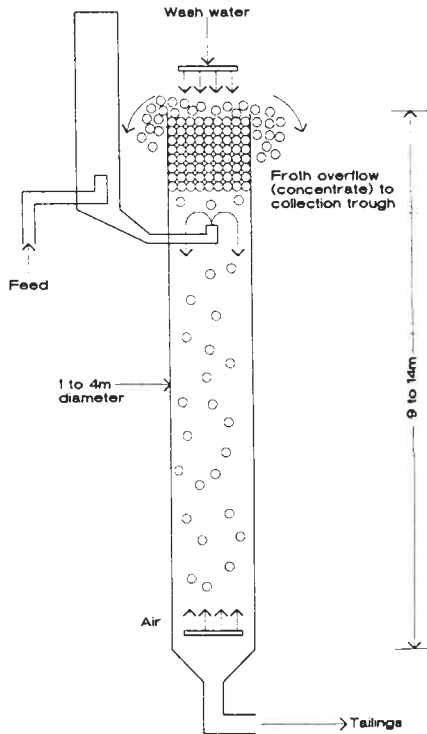


Fig. 3.11. Schematic view of column flotation cell. The lower section 'collects' the minerals. The upper section 'cleans' the froth. Column cells are often used for cleaning and re-cleaning duty – they are particularly effective at removing 'rock' from the final concentrate (Toro *et al.*, 1993).

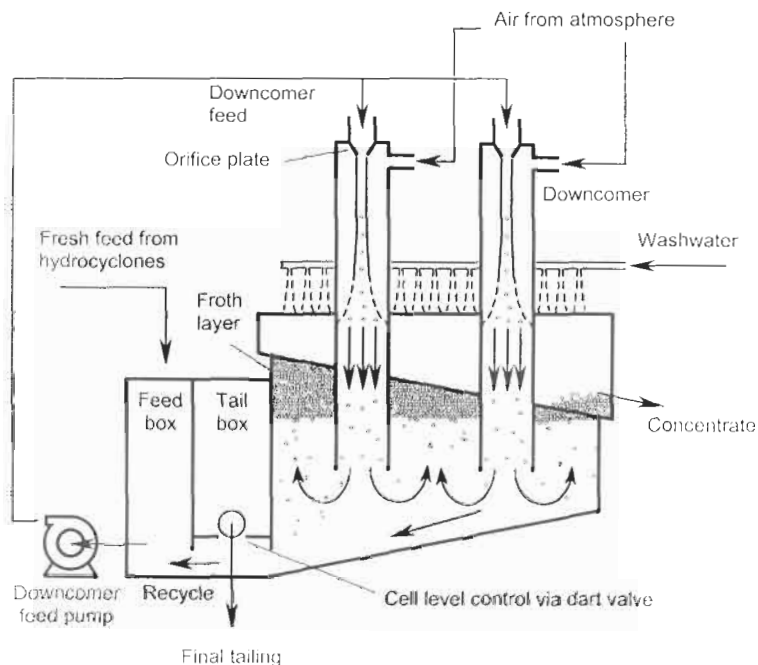


Fig. 3.12. Schematic view of Jameson cell (MIM, 2002), drawing courtesy of Stephen Smith. Excellent contact between air and mineral particles is provided by high-velocity air-pulp flow (~ 17 m/second) in the downcomers. Settling of non-Cu minerals is done in the body of the cell. Washing of the froth is done by water falling gently from above the cell.

Column cells provide a long vertical particle/bubble contact zone and a well-controlled froth-draining zone (Fig. 3.11). Jameson cells provide (i) intimate particle/bubble contact in highly turbulent down-comers (Fig. 3.12) and (ii) a well-controlled froth-draining zone (MIM, 2002).

Both are excellent tools for maximizing %Cu in a concentrator's final concentrate.

3.7 Sensors, Operation and Control

Modern flotation plants are equipped with sensors and automatic control systems (Jensen, 1999). The principal objectives of the control are maximization of Cu

recovery, concentrate grade (% Cu) and ore throughput rate. The principal variables sensed are:

- (a) ore particle size after grinding and regrinding (Outokumpu, 2002a)
- (b) % Cu, % solids, pH and mass flowrate of the process streams (especially the input and output streams)
- (c) froth height in the flotation cells.

Impeller speeds and air input rates in the flotation cells are also often sensed.

The adjustments made on the basis of the sensor readings are:

- (a) water flowrates into the hydrocyclone feed sumps to control grinding recycle, hence ore flotation feed (ore) particle size
- (b) flotation reagent (collector, frother, depressant) and water addition rates throughout the flotation plant
- (c) pulp level in the flotation cells, by adjusting the underflow valves in each cell.

Table 3.4 describes the sensors and the adjustments they make in the flotation cells.

Table 3.4. Sensors and their use in automatic flotation control and optimization.

Sensing instrument	Purpose	Type of Device	Use in automatic control
In-stream particle size monitor	Senses particle size after grind and regrind mills	Ultrasonic energy loss or laser beam	Controls water addition rates to hydrocyclone feed (which controls final grind size)
In-stream X-ray analysis for Cu	Determines % Cu in solids of various process streams (especially feed, tailing and concentrate)	X-ray energy dispersive analysis with probes in process streams	Controls collector, frother, modifier and water addition rates throughout the circuit. Adjusts valves in flotation cells to alter pulp levels
Flotation cell pulp level sensor	Determines pulp level in flotation cells	Float level, hydrostatic pressure, conductivity	Adjusts valves in flotation cells to maintain froth depths prescribed by supervisory computer
Pulp mass-flow gage and % solids-in-pulp gage	Determine mass and volumetric flow rates of process streams	Magnetic induction, Doppler effects, ultrasonic energy loss	Determine recycle flows in flotation circuit, permit optimization of recycle streams

3.7.1 Continuous process stream chemical analysis

Of particular importance in flotation control is continuous measurement of Cu concentration in the process streams solids. This is done by X-ray fluorescence analysis of:

- (a) samples which flow to a central X-ray analysis unit
- (b) small X-ray units in the process streams themselves.

The analyses are often done by fixed crystal wavelength dispersive spectrometry (Outokumpu, 2002b).

The analyses are used to monitor and optimize plant performance by automatically controlling (for example) reagent addition rates, grind size and flotation cell operation. In modern plants, the control is done by a supervisory computer.

3.8 The Flotation Product

The product from flotation contains ~75 mass% water, most of which must be removed before the concentrate can be transported and smelted. Most of this dewatering is performed by settling in large quiescent thickeners. The solids settle under the influence of gravity to the bottom of the thickener from where they are scraped to a central discharge by a slowly rotating rake. Faster settling is encouraged by adding small quantities of organic flocculants (e.g. polyacrylamides, Wills, 1993) to the input pulp. These cause flocculation of the fine particles and faster settling velocities.

The underflows from the thickeners still contain 30 to 40% water. This is lowered to 10 or 15% in rotary vacuum filters and dried to 8 mass% water in pressure filters (Larox, 2002) or ceramic disc vacuum filters (sometimes pressurized to 3 atmospheres gage, Outokumpu, 2002c).

The concentrate is shipped at ~8 mass% water. This water content is a compromise between the cost of shipping water and avoidance of concentrate dust loss during transport.

3.8.1 Tailings

Flotation tailings account for ~98% of the concentrator's ore feed. They are stored in large dams near the mine property. Water is reclaimed from the dams and recycled to the concentrator.

Most concentrators are zero water discharge plants. This minimizes water consumption and avoids mixing concentrator effluents with the surrounding

water table. Also, the pH of the tailings water is close to that required for rougher-scavenger flotation so its recycle minimizes CaO consumption.

3.9 Other Flotation Separations

For copper, flotation consists mainly of separating Cu sulfide minerals from non-sulfide 'rock' and Fe-sulfide minerals. Many Cu deposits also contain molybdenite. Others contain sphalerite (ZnS) and galena (PbS). These can all be separated from Cu minerals by selective flotation. Molybenite flotation is discussed here. Sphalerite, galena, Ni and Cu 'oxide' flotation is discussed in Biswas and Davenport (1994).

3.9.1 Molybdenite flotation from copper concentrates

Molybdenite (MoS_2) is found in many ores in western South and North America. It floats more easily than Cu minerals and is recovered with Cu in copper concentrates. It is floated from the copper concentrate with petroleum-based non-polar collectors (e.g. kerosene, fuel oil, proprietary oils) while depressing the Cu minerals with sodium hydrosulfide (~4 kg per tonne of MoS_2 concentrate) and other sulfide depressants (Castro *et al.*, 1999). Nitrogen is often used as the flotation bubble gas, to minimize oxidation of the hydrosulfide and other sulfide depressants. Recoveries of MoS_2 are ~70% overall (~90% in the MoS_2 flotation cells).

3.10 Summary

Copper sulfide ores must be concentrated before they can be economically transported and smelted. The universal technique for the concentration is froth flotation of finely ground ore.

Froth flotation entails attaching fine Cu sulfide mineral particles to bubbles and 'floating' them out of a water-ore mixture. The flotation is made selective by using reagents which make the Cu sulfide minerals water repellant while leaving the other minerals 'wetted'.

Typical Cu sulfide recoveries to concentrate are ~90%. Typical concentrate grades are 30% Cu (higher with chalcocite and bornite mineralization). Column and Jameson flotation cells are particularly effective at giving final high Cu concentrates.

Modern concentrators are automatically controlled to give maximum Cu recovery, maximum %Cu in concentrate and maximum ore throughput rate at minimum cost. Expert control systems help obtain these maxima.

On-stream particle size and X Ray fluorescence analyses are key components of this automatic control.

Suggested Reading

Hancock, B. A. and Pon, M. R. L. (1999) *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. II, Mineral Processing/Environment, Health and Safety*, TMS, Warrendale, PA.

Herbst, J. A. (2000) *Control 2000, Mineral and Metallurgical Processing*, SME, Littleton, CO.

Kawatra, S. K. (1997) *Comminution Practices*, SME, Littleton, CO.

Parekh, B. K. and Miller, J. D. (1999) *Advances in Flotation Technology*, SME, Littleton, CO.

References

Biswas, A.K. and Davenport, W.G. (1994) *Extractive Metallurgy of Copper, 3rd Edition*, Elsevier Science Press, New York, NY.

Boldt, J.R. and Queneau, P. (1967) *The Winning of Nickel*, Longmans Canada Ltd., Toronto, Section 3.

Castro, S.H., Henriquez, C. and Beas, E. (1999) Optimization of the phosphate Nokes process at the El Teniente by-product molybdenite plant. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. II Mineral Processing/Environment, Health and Safety*, ed. Hancock, B. A. and Pon, M. R. L., TMS, Warrendale, PA, 41 50.

Chevron Phillips (2002) ORFOM F2 Frother www.cpchem.com/miningchemicals (ORFOM F2 Frother).

Dufresne, M. W. (2000) The Collahuasi copper project, Chile. *CIM Bulletin*, **93**, 25 30.

EMJ (1998) Bajo de la Alumbrera, Argentina's first mining mega-project. *E&MJ*, **199**(5), pp. 46WW-54WW.

Finch, J.A. (1998) Mineral processing: and where are we going? comminution, flotation and gravity separations. *CIM Bulletin*, **91**, 68 72.

Fuerstenau, M.C., Chi, G., Bradt, R.C. and Ghosh, A. (1997) Increased ore grindability and plant throughput with controlled blasting. *Mining Engineering*, **49** (12), 70 75.

Gilchrist, J.D. (1993) *Extraction Metallurgy, 3rd Edition*, Elsevier Science Press, New York, NY.

Hagihara, H. (1952) Mono- and multiplayer adsorption of aqueous xanthate on galena surfaces. *J. Physical Chemistry*, **56**, 616 621.

Jensen, D. L. (1999) Flotation supervisory control at Cyprus Bagdad. In *Advances in Flotation Technology*, ed. Parekh, B. K. and Miller, J. D., SME, Littleton, CO, 433 440.

Jonaitis, A. J. (1999) Design, development, application and operating benefits of 100+ m³ Outokumpu TankCell flotation cells. In *Advances in Flotation Technology*, ed. Parekh, B. K. and Miller, J. D., SME, Littleton, CO, 371 380.

Klimpel, R. R. (1999) A review of sulfide mineral collector practice. In *Advances in Flotation Technology*, ed. Parekh, B. K. and Miller, J. D., SME, Littleton, CO, 115 127.

Krebs Engineers (2002) Krebs cyclones for mining and mineral processing www.krebs.com (Industrial uses, mining and mineral processing).

Larox (2002) Larox [filtration] News www.larox.com

MIM (2002) Jameson Cell, technology www.mimpt.com.au

Mulukutla, P.S. (1993) The need for specialty chemicals for flotation plant optimization in developing countries, in *Flotation Plants: Are They Optimized?*, ed. Malhotra, D., SME, Littleton, CO, 77 88.

Outokumpu PSI 200 Particle Size Instrument (2002a) www.outokumpu.com/mintec (Analysis and Process Control PSI 200).

Outokumpu On-Stream XRF Analysis (2002b) www.outokumpu.com/mintec (Analysis and Process Control On-stream XRF analysis. Also, XRF technology).

Outokumpu Filtration (2002c) www.outokumpu.com/mintec (Mineral Processing Technology, Filtration).

Parekh, B. K. and Miller, J. D. (1999) *Advances in Flotation Technology*, SME, Littleton, CO.

Taggart, A.F. (1954) *Handbook of Mineral Dressing*, John Wiley and Sons. Inc., New York, NY, 12:94.

Toro, H., Lee, K.Y. and Bebbardt, J.E. (1993) Column flotation: a technical analysis of sparger systems. In *Flotation Plants: Are They Optimized?*, ed. Malhotra, D., SME, Littleton, CO, 70 75.

Wark, I.W. and Cox, A.G. (1934) Principles of flotation, III, an experimental study of influence of cyanide, alkalis and copper sulfate on effect of sulfur-bearing collectors and mineral surfaces, *AIIME Transactions*, **112**, 288.

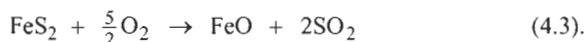
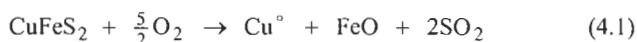
Wills, B.A. (1993) *Minerals Processing Technology*, 5th Edition, Elsevier Science Press, New York, NY.

CHAPTER 4

Matte Smelting Fundamentals

4.1 Why Smelting?

Beneficiation of copper ores produces concentrates consisting mostly of sulfide minerals, with small amounts of gangue oxides (Al_2O_3 , CaO , MgO , SiO_2). Theoretically, this material could be directly reacted to produce metallic Cu by oxidizing the sulfides to elemental copper and ferrous oxide:



These reactions are exothermic, meaning that they generate heat. As a result, the smelting of copper concentrate should generate (i) molten copper and (ii) molten slag containing flux oxides, gangue oxides and FeO. However, under oxidizing conditions, Cu tends to form Cu oxide as well as metal:



When this happens, the Cu_2O dissolves in the slag generated during coppermaking. The large amount of iron in most copper concentrates means that a large amount of slag would be generated. More slag means more lost Cu. As a result, eliminating some of the iron from the concentrate before final coppermaking is a good idea.

Fig. 4.1 illustrates what happens when a mixture of FeO, FeS and SiO_2 is heated to 1200°C . The left edge of the diagram represents a solution consisting only of FeS and FeO. In silica-free melts with FeS concentrations above ~31 mass%, a single oxysulfide liquid is formed. However, when silica is added, a liquid-state

miscibility gap appears. This gap becomes larger as more silica is added.

Lines *a*, *b*, *c* and *d* represent the equilibrium compositions of the two liquids. The sulfide-rich melt is known as *matte*. The oxide-rich melt is known as *slag*. Heating a sulfide concentrate to this temperature and oxidizing some of its Fe to generate a molten matte and slag, *i.e.*:

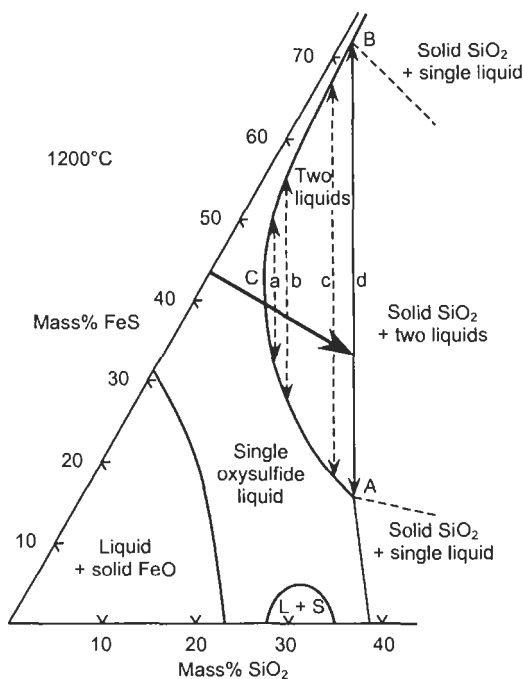
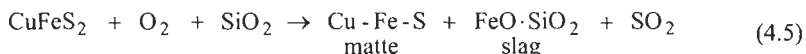


Fig. 4.1. Simplified partial phase diagram for the Fe-O-S-SiO₂ system showing liquid-liquid (slag-matte) immiscibility caused by SiO₂ (Yazawa and Kameda, 1953). The heavy arrow shows that adding SiO₂ to an oxy-sulfide liquid causes it to split into FeS-rich matte and FeS-lean slag. The compositions of points A and B (SiO₂ saturation) and the behavior of Cu are detailed in Table 4.1.

is known as *matte smelting*. It accomplishes the partial removal of Fe needed to make final coppermaking successful. Matte smelting is now performed on nearly all Cu-Fe-S and Cu-S concentrates. This chapter introduces the

fundamentals of matte smelting and the influence of process variables. Following chapters describe current smelting technology.

4.2 Matte and Slag

4.2.1. Slag

Slag is a solution of molten oxides. These oxides include FeO from Fe oxidation, SiO₂ from flux and oxide impurities from concentrate. Oxides commonly found in slags include ferrous oxide (FeO), ferric oxide (Fe₂O₃), silica (SiO₂), alumina (Al₂O₃), calcia (CaO) and magnesia (MgO). As Fig. 4.1 shows, small amounts of sulfides can also be dissolved in FeO–SiO₂ slags. Small amounts of calcia and alumina in slags decrease this sulfide solubility, Table 4.1.

The molecular structure of molten slag is described by dividing its oxides into three groups – acidic, basic and neutral. The best-known acidic oxides are silica and alumina. When these oxides melt, they polymerize, forming long polyions such as those shown in Fig. 4.2. These polyions give acidic slags high viscosities, making them difficult to work with. Acidic slags also have low solubilities for other acidic oxides. This can cause difficulty in coppermaking because impurities which form acidic oxides (e.g., As₂O₃, Bi₂O₃, Sb₂O₃) won't be removed in slag, i.e., they will remain in matte or copper.

Adding basic oxides such as calcia and magnesia to acidic slags breaks the polyions into smaller structural units. As a result, basic slags have low viscosities

Table 4.1. Compositions of immiscible liquids in the SiO₂–saturated Fe–O–S system, 1200°C (Yazawa and Kameda, 1953). Points A (slag) and B (matte) correspond to A and B in Fig. 4.1. Added Cu₂S (bottom data set) widens the miscibility gap. The Cu₂S reports almost entirely to the matte phase.

System	Phase	Composition (mass%)					
		FeO	FeS	SiO ₂	CaO	Al ₂ O ₃	Cu ₂ S
FeS–FeO–SiO ₂	"A" Slag	54.82	17.90	27.28			
	"B" Matte	27.42	72.42	0.16			
FeS–FeO–SiO ₂ + CaO	Slag	46.72	8.84	37.80	6.64		
	Matte	28.46	69.39	2.15			
FeS–FeO–SiO ₂ + Al ₂ O ₃	Slag	50.05	7.66	36.35		5.94	
	Matte	27.54	72.15	0.31			
Cu ₂ S–FeS–FeO–SiO ₂	Slag	57.73	7.59	33.83			0.85
	Matte	14.92	54.69	0.25			30.14

and high solubilities for acidic oxides. Up to a certain limit, adding basic oxides also lowers the melting point of a slag. Coppermaking slags generally contain small amounts of basic oxides.

Neutral oxides such as FeO and Cu₂O react less strongly with polyions in a molten slag. Nevertheless, they have much the same effect. FeO and Cu₂O have low melting points, so they tend to lower a slag's melting point and viscosity.

The slags produced in industrial matte smelting consist primarily of FeO, Fe₂O₃ and SiO₂, with small amounts of Al₂O₃, CaO and MgO, Table 4.2. Fig. 4.3 shows the composition limits for the *liquid* region in the FeO–Fe₂O₃–SiO₂ system at 1200°C and 1250°C. Along the top line, the slag is saturated with solid silica. Along the bottom boundary line, the slag is saturated with solid FeO. The boundary at right marks the compositions at which dissolved FeO and Fe₂O₃ react to form solid magnetite:

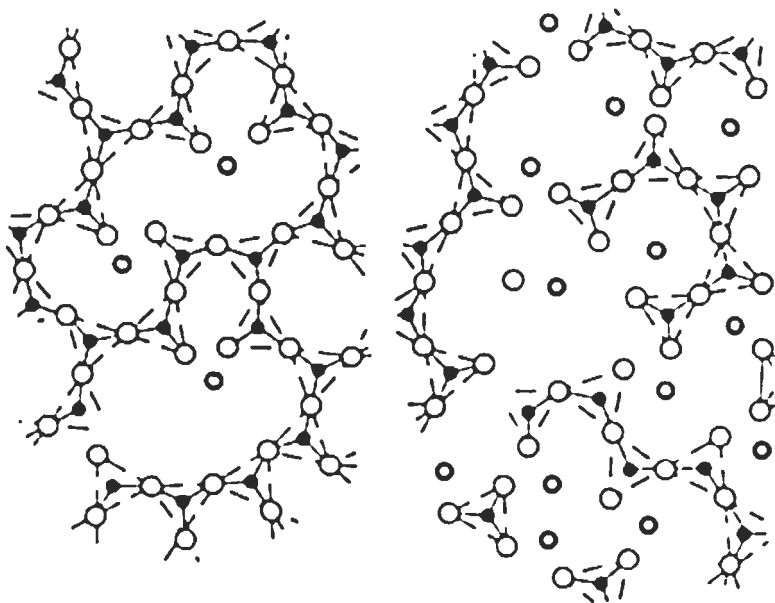
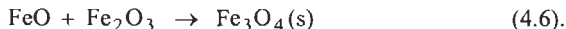


Fig. 4.2. Impact of basic oxides on the structure of silica polyions in molten slags. Adding basic oxides like CaO and MgO breaks up the polyions, reducing the melting point and viscosity of the slag ● = Si; ○ = O; ● = Ca²⁺ or Mg²⁺.

Table 4.2. Compositions of industrial concentrates, fluxes, mattes, slags and dusts for various matte-smelting processes, 2001.

Smelter & process	Concentrate					Flux			Matte				Slag							Dust					
	Cu	Fe	S	SiO ₂	other	SiO ₂	Al ₂ O ₃	other	Cu	Fe	S	O	Cu	SiO ₂	total Fe	Fe ₃ O ₄	S	Al ₂ O ₃	other	Cu	Fe	S	SiO ₂	other	
Caraiba Outokumpu flash	32	23	28	9	Al ₂ O ₃ 2 CaO 1 MgO 1	98		2	62	12	22		1.8	31	42	16	0.5		MgO 2	29			7	Al ₂ O ₃ 2 CaO 1	
Norddeutsche Outokumpu flash	33	24	31	5	Al ₂ O ₃ <2 CaO 1 Zn 1	85-95	5	CaO 2	65	12	22	1	1.5	32	39	5	0.6	4	CaO 3 MgO 1	26	15	12	3	Al ₂ O ₃ 2 CaO 1	
Toyo, Outokumpu flash	32	25	30	6		73	10	Fe ₂ O ₃ 4	63	10	22		1.3	33	37	13	0.6	5	CaO 1 MgO 2	20	15	9	7		
Chino Inco flash	29	25	32	7	Al ₂ O ₃ 1	90	4	Fe 2 Cu 2	59	16	23	Fe ₃ O ₄ 4	0.8	34	43	4	1	3		30	17	12	7	CaO 2	
Caletones Teniente	32	25	30	6	Al ₂ O ₃ 2 CaO 1 other 4	95	2	3	74	4	20	other 1	6 to 8	27	38	16	2.7	4	CaO 1 other 3	34	6	11	4	Al ₂ O ₃ 1	
Port Kembla Noranda	31	28	31	5	Al ₂ O ₃ 1 CaO 1 MgO 1	96			72	6	20		2	30	46	15	0.8	2	CaO 3	34	23	23	7	Al ₂ O ₃ 2	
Sterlite, India Isasmelt	30	28	31	9	CaO 2	85	1	4	63	13			0.7	29	44	3	0.7	4.9	CaO 3	33	32		10		
Olympic Dam OK flash direct- to-copper	41 to 56	16 to 23	25 to 30	3 to	Al ₂ O ₃ 1	95	1	Fe ₂ O ₃ 2	99		0.8	0.4	20 to 24	15 to 20	30 to 40			0.1	3	CaO 0.1	36	14		3	SO ₄ 30
Gresik Mitsubishi	32	25	31	9	Al ₂ O ₃ 2 CaO 0.5	90	3	1	68	8	22		0.7	33	39	2	0.5	5	CaO 6	63	9	19	1		
Onsan Mitsubishi	32	23	29	8	Al ₂ O ₃ 2 CaO 0.4	82	4	Fe 5	69	8	22		0.9	34	38	3	0.4	5	CaO 5	17	5	9	1	0.3	
Onahama Reverberatory	33	23	28	7	Al ₂ O ₃ 2 CaO 1 MgO 0.4	88	4	Fe 1.3 CaO 0.7	44	26	26		0.7	32	37	3	1	5	CaO 4	13	13	5	24	CaO 3	

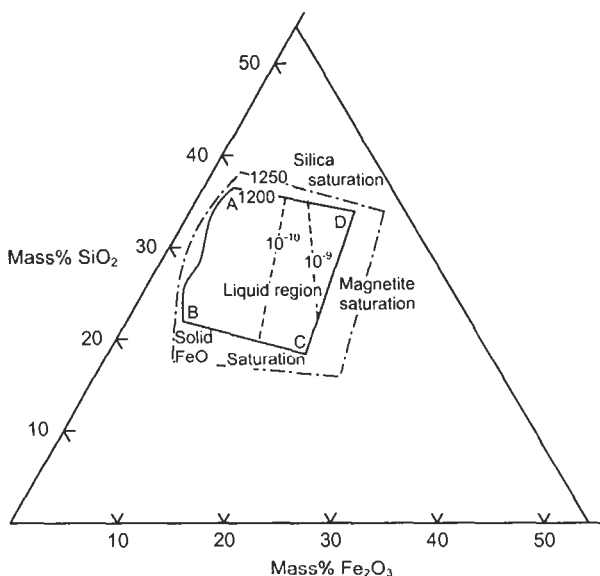


Fig. 4.3. Liquidus surface in the $\text{FeO}\text{--}\text{Fe}_2\text{O}_3\text{--}\text{SiO}_2$ system at 1200°C and 1250°C (Muan, 1955). Copper smelting processes typically operate near magnetite saturation (line CD).

Extensive oxidation and lower smelting temperatures encourage the formation of Fe_2O_3 in the slag. Avoiding these conditions minimizes magnetite precipitation.

Along the left-hand boundary, the slag is saturated either with metallic iron or solid fayalite (Fe_2SiO_4). Under the oxidizing conditions of industrial copper smelting, this never occurs. Table 4.2 lists the compositions of some smelter slags, including their Cu content. Controlling the amount of Cu dissolved in smelting slag is an important part of smelter strategy, Chapter 11.

Many measurements have been made of the viscosities of molten slags. These have been used to develop a model which calculates viscosities as a function of temperature and composition (Utigard and Warczok, 1995). The model relies on calculation of a viscosity ratio (VR). VR is the ratio of A , an equivalent mass% in the slag of acidic oxides, to B , an equivalent mass% of basic oxides:

$$VR = \frac{A}{B} \quad (4.7)$$

$$A = (\% \text{SiO}_2) + 1.5(\% \text{Cr}_2\text{O}_3) + 1.2(\% \text{ZrO}_2) + 1.8(\% \text{Al}_2\text{O}_3) \quad (4.8)$$

$$B = 1.2(\% \text{FeO}) + 0.5(\% \text{Fe}_2\text{O}_3 + \% \text{PbO}) + 0.8(\% \text{MgO}) + 0.7(\% \text{CaO}) + 2.3(\% \text{Na}_2\text{O} + \% \text{K}_2\text{O}) + 0.7(\% \text{Cu}_2\text{O}) + 1.6(\% \text{CaF}_2) \quad (4.9).$$

Utigard and Warczok related $\sqrt{VR}$ to viscosity by regression analysis against their existing database, obtaining:

$$\log \mu (\text{kg} / \text{m} \cdot \text{s}) = -0.49 - 5.1\sqrt{VR} + \frac{-3660 + 12080\sqrt{VR}}{T (\text{K})} \quad (4.10).$$

Fig. 4.4 shows the effect of temperature and composition on the viscosity of FeO, Fe₂O₃, SiO₂ slags.

The specific gravity of smelting slags ranges between 3.3 and 3.7. It decreases with increasing Fe₂O₃ and SiO₂ content (Utigard, 1994) and increases slightly with increasing temperature.

Slag electrical conductivity is strongly temperature-dependent, ranging at smelting and converting temperatures between 5 and 20 ohm⁻¹cm⁻¹ (Ziółek and Bogacz, 1987; Hejja *et al.*, 1994). It increases with Cu and iron oxide content and with basicity.

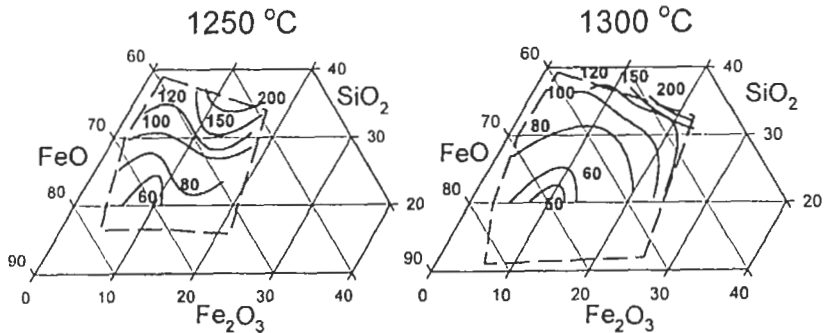


Fig. 4.4. Effect of temperature and composition on the viscosity of FeO, Fe₂O₃, SiO₂ slags, g/m·s (Vartiainen, 1998). Viscosity is seen to increase with increasing % SiO₂. For viscosity in kg/m·s, divide by 1000.

The surface tension of smelting slags is 0.35–0.45 N/m (Nakamura *et al.*, 1988). It decreases with increasing basicity, but is not strongly influenced by temperature.

4.2.2 Matte

As Fig. 4.1 shows, immiscibility of matte and slag increases with increasing silica content (Yazawa, 1956). A high sulfur/iron ratio also increases the completeness of separation as do calcia and alumina, Table 4.1.

There is some silica and oxygen solubility in matte, but Li and Rankin (1994) demonstrated that increasing Cu_2S in matte decreases these solubilities "dramatically". As a result, the typical industrial matte contains only about one percent oxygen, Table 4.2.

Mattes do not consist of polyions like those in slags. They appear instead to be best represented as molten salts (Shimpo *et al.*, 1986). Their specific gravity is higher than that of slags and so they form the bottom layer in smelting furnaces. As Fig. 4.5 shows, their melting points are lower than the 1200°C of most slags, Fig. 4.3.

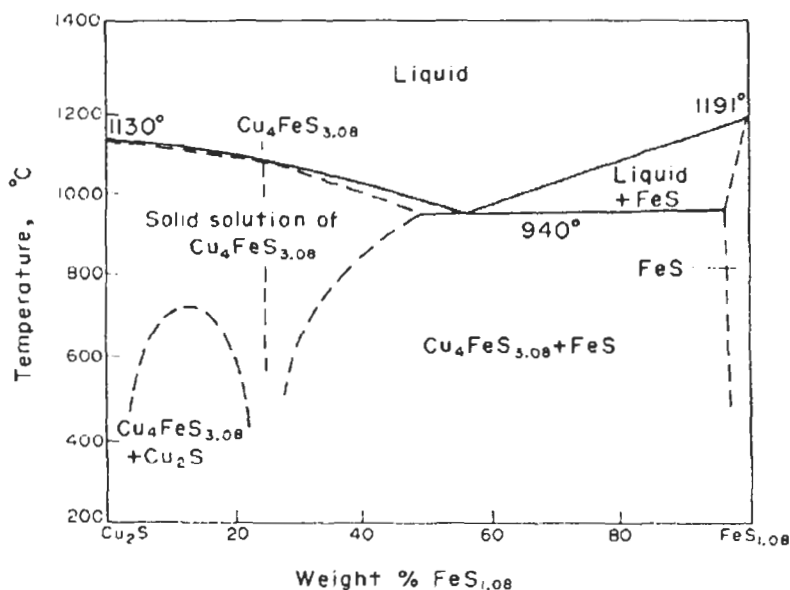


Fig. 4.5. Cu_2S - FeS phase diagram (Schlegel and Schuller, 1952). Actual matte melting temperatures are lower than the liquidus line temperature due to impurities in the matte.

Their viscosities are low as well – $\sim 0.003 \text{ kg/m}\cdot\text{s}$ vs. $0.2\text{--}1 \text{ kg/m}\cdot\text{s}$ for typical slags. Nevertheless, smelting furnaces are operated at about 1250°C , to ensure a

molten slag and superheated matte. This ensures that the matte and slag stay molten during tapping and transfer.

The surface tension of Cu_2S -FeS mattes ranges from 0.33–0.45 N/m, increasing with Cu_2S content. Temperature has little effect (Nakamura *et al.*, 1988; Kucharski *et al.*, 1994).

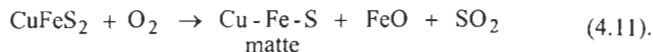
Specific gravity ranges linearly from 3.9 for pure FeS to 5.2 for pure Cu_2S . It decreases slightly with increasing temperature. Multiplying these specific gravities by the kinematic viscosities measured by Nikiforov *et al.* (1976), yields viscosities of about 0.003 kg/m·s for pure Cu_2S at 1250°C, falling to about 0.002 kg/m·s for mattes with 35 mass% FeS. The value then rises rapidly with increasing FeS. It decreases slowly with increasing temperature.

Measurements of interfacial tension between molten mattes and slags were reviewed by Nakamura and Toguri (1991). Interfacial tension increases from near zero in low-Cu mattes to about 0.20 N/m for high-Cu mattes (~70 mass% Cu_2S).

Matte specific electrical conductances are 200 to 1000 $\text{ohm}^{-1} \text{cm}^{-1}$ (Pound *et al.*, 1955; Liu *et al.*, 1980).

4.3 Reactions During Matte Smelting

The primary purpose of matte smelting is to turn the sulfide minerals in solid copper concentrate into three products: molten matte, molten slag and offgas. This is done by reacting them with O_2 . The oxygen is almost always fed as oxygen-enriched air. The initial reaction takes the form:



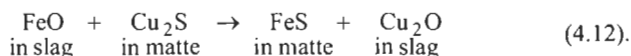
The stoichiometry varies, depending on the levels of chalcopyrite and other Cu-Fe sulfide minerals in the concentrate and on the degree of oxidation of the Fe.

As will be seen, smelting strategy involves a series of trade-offs. The most significant is that between matte grade (mass% Cu) and recovery. Inputting a large amount of O_2 will oxidize more of the Fe in the concentrate, so less Fe sulfide ends up in the matte. This generates a higher matte grade. On the other hand, using too much oxygen encourages oxidation of Cu, as shown previously:

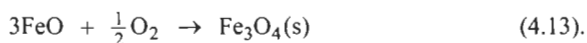


The Cu oxide generated by this reaction dissolves in the slag, which is undesirable. As a result, adding the correct amount of O_2 needed to produce an acceptable matte grade without generating a slag too high in Cu is a key part of smelter strategy.

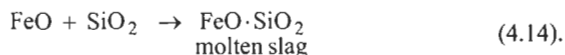
A second set of reactions important in smelter operation involves the FeO content of the slag. If the activity of FeO in the slag is too high, it will react with Cu_2S in the matte:



This reaction is not thermodynamically favored ($K_{eq} \sim 10^{-4}$ at 1200°C). However, a high activity of FeO in the slag and a low activity of FeS in the matte generate higher activities of Cu_2O in the slag. (This occurs if too much of the iron in the concentrate is oxidized.) This again gives too much Cu in the slag. In addition, FeO reacts with O_2 to form solid magnetite if its activity is too high:



As a result, lowering the activity of FeO in the slag is important. It is done by adding silica as a flux:



However, again there is a trade-off. Flux costs money and the energy required to heat and melt it also costs more as more silica is used. In addition, as Fig. 4.4 shows, the viscosities of smelting slags increase as the silica level rises. This makes slag handling more difficult, and also reduces the rate at which matte particles settle through the slag layer. If the matte particles can't settle quickly enough, they will remain entrained in the slag when it is tapped. This increases Cu losses. As a result, the correct levels of FeO and SiO_2 in the slag require another balancing act.

4.4 The Smelting Process: General Considerations

While industrial matte smelting equipment and procedures vary, all smelting processes have a common sequence of events. The sequence includes:

- (a) *Contacting particles of concentrate and flux with an O_2 -containing gas in a hot furnace.* This causes the sulfide minerals in the particles to rapidly

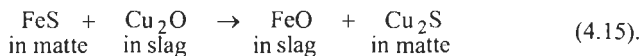
oxidize, Eqn. (4.11). The reactions are exothermic, and the energy they generate heats and melts the products.

The contact time between concentrate particles and the gas is short (a few seconds), so ensuring good reaction kinetics is essential. Nearly all smelters accomplish this by mixing the concentrate with the gas prior to injecting it into the smelting furnace. The use of oxygen-enriched air instead of air also improves reaction kinetics, and is increasingly popular.

Use of oxygen-enriched air or oxygen also makes the process more autothermal. Because less nitrogen is fed to the furnace, less heat is removed in the offgas. This means that more of the heat generated by the reactions goes into the matte and slag. As a result, less (or no) hydrocarbon fuel combustion is required to ensure the proper final slag and matte temperature, $\sim 1250^{\circ}\text{C}$.

A new method for contacting concentrate and O_2 is being used in submerged tuyere smelting furnaces. In these furnaces, concentrate is blown into a mixture of molten matte and slag, and the oxidation process takes place indirectly. This is discussed in Chapters 7 and 8.

- (b) *Letting the matte settle through the slag layer into the matte layer below the slag.* Most smelting furnaces provide a quiet settling region for this purpose. During settling, FeS in the matte reacts with dissolved Cu_2O in the slag by the reverse of Reaction (4.12):



This further reduces the amount of Cu in the slag. The importance of low slag viscosity in encouraging settling has already been mentioned. Keeping the slag layer still also helps. A trade-off is at work here, too. Higher matte and slag temperatures encourage Reaction (4.15) to go to completion and decrease viscosity, but they cost more in terms of energy and refractory wear.

- (c) *Periodically tapping the matte and slag through separate tap holes.* Feeding of smelting furnaces and withdrawing of offgas is continuous. Removal of matte and slag is, however, done intermittently, when the layers of the two liquids have grown deep enough. The location of tap holes is designed to minimize tapping matte with slag.

4.5 Smelting Products: Matte, Slag and Offgas

4.5.1 Matte

In addition to slag compositions, Table 4.2 shows the composition of mattes

tapped from various smelters. The most important characteristic of a matte is its grade (mass% Cu), which typically ranges between 45 and 75% Cu (56–94% Cu_2S equivalent). At higher levels, the activity of Cu_2S in the matte rises rapidly, and this pushes Reaction (4.12) to the right. Fig. 4.6 shows what happens as a result.

The rapidly increasing concentration of Cu in slag when the matte grade rises above 60% is a feature many smelter operators prefer to avoid. However, producing higher-grade mattes increases heat generation, reducing fuel costs. It also decreases the amount of sulfur to be removed during subsequent converting (decreasing converting requirements), and increases SO_2 concentration in the offgas (decreasing gas-treatment costs). In addition, almost all copper producers now recover Cu from smelting and converting slags, Chapter 11. As a result, production of higher-grade mattes has become more popular.

Most of the rest of the matte consists of iron sulfide (FeS). Table 4.3 shows the distribution of other elements in copper concentrates between matte, slag and offgas. Precious metals report almost entirely to the matte, as do most Ni, Se and Te.

4.5.2 Slag

As Table 4.2 shows, the slag tapped from the furnace consists mostly of FeO and SiO_2 , with a small amount of ferric oxide. Small amounts of Al_2O_3 , CaO and MgO are also present, as is a small percentage of dissolved sulfur (typically less than one percent). Cu contents range from less than 1 to as high as 7 percent. Higher Cu levels are acceptable if facilities are available for recovering Cu from smelter slag. SiO_2/Fe mass ratios are usually 0.7–0.8.

4.5.3 Offgas

The offgas from smelting contains SO_2 generated by the smelting reactions, N_2 from the air used for oxidizing the concentrate and small amounts of CO_2 , H_2O and volatilized impurity compounds. The strength of the offgas is usually 10 to 60 vol% SO_2 . The strength depends on the type of O_2 -containing gas used for smelting, the amount of air allowed to leak into the furnace and the grade of matte produced. Volume% SO_2 in smelter offgases has risen in recent years. This is due to increased use of oxygen in smelting, which reduces the amounts of nitrogen and hydrocarbon combustion gases passing through the furnace.

Smelter offgases may also contain substantial levels of dust (up to 0.3 kg/Nm^3). This dust comes from (i) small particles of unreacted concentrate or flux, (ii) droplets of matte/slag that did not settle into the slag layer in the furnace and (iii) volatilized elements in the concentrate such as arsenic, antimony, bismuth and lead, which have either solidified as the gas cools or reacted to form non-volatile compounds. The dust generally contains 20–40 mass% Cu, making it potentially

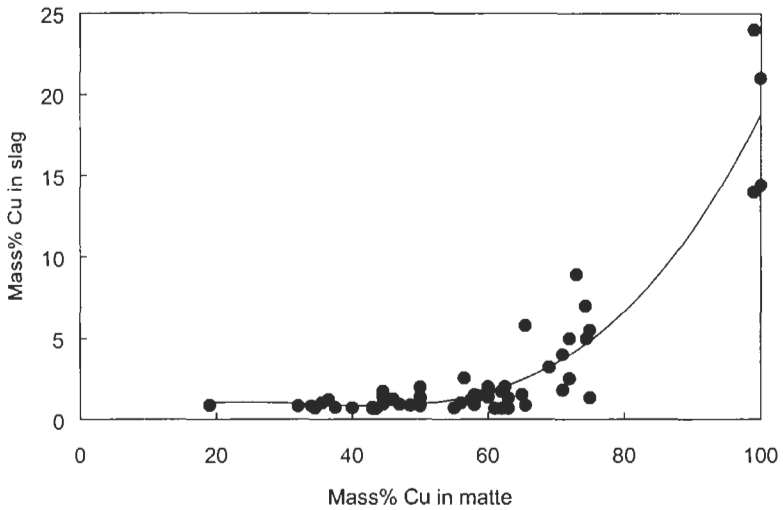


Fig. 4.6. %Cu in industrial smelting furnace slag (before slag cleaning) as a function of %Cu in matte, 1999-2001. The increase in %Cu-in-slag above 60% Cu-in-matte is notable.

Table 4.3. Estimated distribution of impurities during flash furnace production of 55% Cu matte (Steinhauser *et al.*, 1984). Volatilized material is usually condensed and returned to the furnace, so all impurities eventually leave the furnace in either matte or slag. Other industrial impurity distributions are shown in subsequent chapters.

	Matte	Slag	Volatilized*
Copper	99	1	0
Alkali/alkaline-earth elements, Aluminum, titanium	0	100	0
Ag, Au, Pt-group elements	99	1	0
Antimony	30	30	40
Arsenic	10	10	80
Bismuth	15	5	80
Cobalt	40	55	5
Lead	20	10	70
Nickel	50	45	5
Selenium	75	5	20
Zinc	15	45	40

* Not including solid dust from the furnace.

valuable. It is nearly always recycled to the smelting furnace, but it may be treated hydrometallurgically to recover Cu and remove deleterious impurities from the smelting circuit.

4.6 Summary

Matte smelting is the most common way of smelting Cu–Fe–S concentrates. It entails heating, oxidizing (almost always with oxygen–enriched air) and fluxing the concentrate at high temperatures, 1250°C. The products are:

- (a) molten Cu–Fe–S matte, 45–75% Cu, which is sent to oxidation converting to molten metallic copper, Chapters 9 and 10
- (b) molten Fe silicate slag, which is treated to recover Cu and then sold or stockpiled, Chapter 11
- (c) SO₂-bearing offgas, which is cooled, cleaned and sent to sulfuric acidmaking.

Matte smelting oxidizes most, but not all, of the Fe and S in its input concentrates. Total oxidation of Fe and S would produce molten Cu, but would also result in large Cu₂O losses in slag, Chapter 12. The expense of reducing this Cu₂O and settling the resulting copper almost always overwhelms the advantage of direct-to-copper smelting.

The next four chapters describe year 2002 industrial techniques for matte smelting.

Suggested Reading

Mackey, P.J. (1982) The physical chemistry of copper smelting slags – a review. *Can. Metall. Q.*, **21**, 221–260.

Nakamura, T. and Toguri, J.M. (1991) Interfacial phenomena in copper smelting processes. In *Copper 91-Cobre 91 Proceedings of the Second International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Díaz, C., Landolt, C., Luraschi, A.A. and Newman, C.J., Pergamon Press, New York, 537–551.

Utigard, T.A. and Warczok, A. (1995) Density and viscosity of copper/nickel sulphide smelting and converting slags. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Chen, W.J., Díaz, C., Luraschi, A. and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 423–437.

References

Hejja, A.A., Eric, R.H. and Howat, D.D. (1994) Electrical conductivity, viscosity and liquidus temperature of slags in electric smelting of copper–nickel concentrates. In *EPD Congress 1994*, ed. Warren, G.W., TMS, Warrendale, PA, 621–640.

- Kucharski, M., Ip, S.W. and Toguri, J.M. (1994) The surface tension and density of Cu_2S , FeS , Ni_3S_2 and their mixtures. *Can. Metall. Quart.*, **33**, 197 203.
- Li, H. and Rankin, J.W. (1994) Thermodynamics and phase relations of the Fe-O-S-SiO_2 (sat) system at 1200°C and the effect of copper. *Met. Mater. Trans. B*, **25B**, 79 89.
- Liu, C., Chang, M. and He, A. (1980) Specific conductance of Cu_2S , Ni_3S_2 and commercial matte. *Chinese Nonferrous Metals*, **32**(1), 76 78.
- Muan, A. (1955) Phase equilibria in the system $\text{FeO-Fe}_2\text{O}_3\text{-SiO}_2$. *Trans. A.I.M.E.*, **205**, 965 976.
- Nakamura, T., Noguchi, F., Ueda, Y. and Nakajyo, S. (1988) Densities and surface tensions of Cu-mattes and Cu-slugs. *J. Min. Metall. Inst. Japan*, **104**, 463 468.
- Nakamura, T. and Toguri, J.M. (1991) Interfacial phenomena in copper smelting processes. In *Copper 91-Cobre 91 Proceedings of the Second International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C., Luraschi, A.A. and Newman, C.J., Pergamon Press, New York, NY, 537 551.
- Nikiforov, L.V., Nagiev, V.A. and Grabchak, V.P. (1976) Viscosity of sulfide melts. *Inorg. Mater.*, **12**, 985 988.
- Pound, G.M., Derge, G. and Osuch, G. (1955) Electrical conductance in molten Cu-Fe-sulphide mattes. *Trans. AIME*, **203**, 481 484.
- Schlegel, H. and Schuller, A. (1952) Das Zustandsbild Kupfer-Eisen-Schwefel. *Zeitschrift für Metallkunde*, **43**, 421 428.
- Shimpo, R., Goto, S., Ogawa, O. and Asakura, I. (1986) A study on the equilibrium between copper matte and slag. *Can. Metall. Quart.*, **25**, 113 121.
- Steinhauser, J., Vartiainen, A. and Wuth, W. (1984) Volatilization and distribution of impurities in modern pyrometallurgical copper processing from complex concentrates. *JOM*, **36**(1), 54 61.
- Utigard, T.A. (1994) Density of copper/nickel sulphide smelting and converting slags. *Scand. J. Metall.*, **23**, 37 41.
- Utigard, T.A. and Warczok, A. (1995) Density and viscosity of copper/nickel sulphide smelting and converting slags. In *Copper 95-Cobre 95 Proceedings of the International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Chen, W.J., Diaz, C., Luraschi, A. and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 423 437.
- Vartiainen, A. (1998) Viscosity of iron-silicate slags at copper smelting conditions. In *Sulfide Smelting '98*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 363 371.
- Yazawa, A. (1956) Copper smelting. V. Mutual solution between matte and slag produced in the $\text{Cu}_2\text{S-FeS-FeO-SiO}_2$ system. *J. Mining Inst. Japan*, **72**, 305 311.

Yazawa, A. and Kameda, A. (1953) Copper smelting. I. Partial liquidus diagram for FeS-FeO-SiO₂ system. *Technol. Rep. Tohoku Univ.*, **16**, 40-58.

Ziółek, B. and Bogacz, A. (1987) Electrical conductivity of liquid slags from the flash-smelting of copper concentrates. *Arch. Metall.*, **32**, 631-643.

CHAPTER 5

Flash Smelting –Outokumpu Process

(Written with David Jones, Kennecott Utah Copper, Magna, UT)

Flash smelting accounts for over 50% of Cu matte smelting. It entails blowing oxygen, air, dried Cu-Fe-S concentrate, silica flux and recycle materials into a 1250°C hearth furnace. Once in the hot furnace, the sulfide mineral particles of the concentrate (e.g. CuFeS_2) react rapidly with the O_2 of the blast. This results in (i) controlled oxidation of the concentrate's Fe and S, (ii) a large evolution of heat and (iii) melting of the solids.

The process is continuous. When extensive oxygen-enrichment of the blast is practiced, it is nearly autothermal. It is perfectly matched to smelting the fine particulate concentrates ($\sim 100 \mu\text{m}$) produced by froth flotation.

The products of flash smelting are:

- (a) molten Cu-Fe-S matte, $\sim 65\%$ Cu, considerably richer in Cu than the input concentrate, Table 4.2*
- (b) molten iron-silicate slag containing 1 or 2% Cu
- (c) hot dust-laden offgas containing 30 to 70 volume% SO_2 .

The goals of flash smelting are to produce:

- (a) constant composition, constant temperature molten matte for feeding to converters, Fig. 1.1

* Two flash furnaces produce molten copper directly from concentrate, Chapter 12. In 2002 this is economic only for concentrates which give small quantities of slag. Another Outokumpu flash furnace produces molten copper from solidified/ground matte. This is flash converting, Chapter 10.

- (b) slag which, when treated for Cu recovery, contains only a tiny fraction of the Cu input to the flash furnace
- (c) offgas strong enough in SO_2 for its efficient capture as sulfuric acid.

There are two types of flash smelting – the Outokumpu process (~30 furnaces in operation) and the Inco process (~5 furnaces in operation). The Outokumpu process is described here, the Inco process in Chapter 6.

5.1 Outokumpu Flash Furnace

Fig. 5.1 shows a 2000-design Outokumpu flash furnace. It is 18 m long, 6 m wide and 2 m high (all dimensions inside the refractories). It has a 4.5 m diameter, 6 m high reaction shaft and a 5 m diameter, 8 m high offgas uptake. It has one concentrate burner and smelts about 1000 tonnes of concentrate per day. It has 5 matte tapholes and 4 slag tapholes.

Outokumpu flash furnaces vary considerably in size and shape, Table 5.1. They all, however, have the following five main features:

- (a) concentrate burners (usually 1, but up to 4) which combine dry particulate feed with O_2 -bearing blast and blow them downward into the furnace
- (b) a reaction shaft where most of the reaction between O_2 and Cu-Fe-S feed particles takes place
- (c) a settler where molten matte and slag droplets collect and form separate layers
- (d) water-cooled copper block tapholes for removing molten matte and slag
- (e) an uptake for removing hot SO_2 -bearing offgas.

5.1.1 Construction details (Kojo et al., 2000)

The interior of an Outokumpu flash furnace consists of high-purity direct-bonded magnesia-chrome bricks. The bricks are backed by water-cooled copper cooling jackets on the walls and by sheet steel elsewhere. Reaction shaft and uptake refractory is backed by water-cooled copper cooling jackets or by sheet steel, cooled with water on the outside.

The furnace rests on a 2-cm thick steel plate on steel-reinforced concrete pillars. The bottom of the furnace is air cooled by natural convection. Much of the furnace structure is in operating condition after 8 years of use. Slag line bricks may have eroded but the furnace can usually continue to operate without them. This is because magnetite-rich slag deposits on cool regions of the furnace walls.

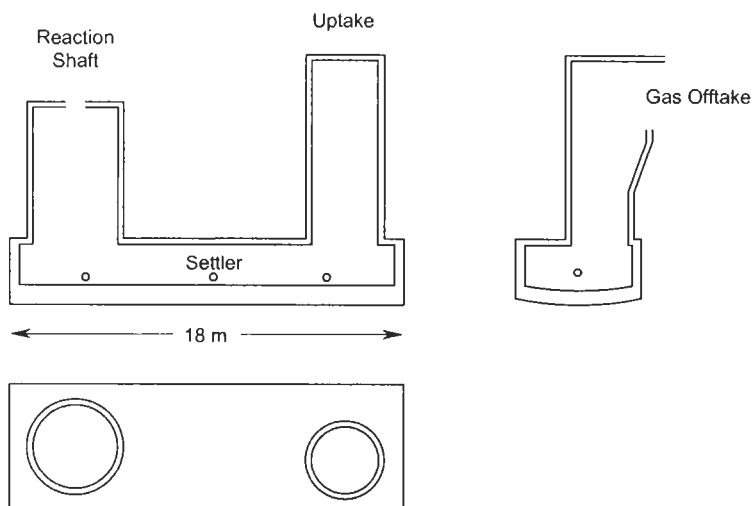


Fig. 5.1. Side and end views of a year 2000 Outokumpu flash furnace. This furnace was designed to smelt 1000 tonnes of concentrate per day. Note the offset offgas uptake. A concentrate burner is shown in Fig. 5.2. It sits atop the reaction shaft.

5.1.2 Cooling jackets

Recent design cooling jackets are solid copper with Cu-Ni (monel) alloy tube imbedded inside (Jones *et al.*, 1999, Kojo *et al.*, 2000). The tube is bent into many turns to maximize heat transfer from the solid copper to water flowing in the monel tube. The hot face of the cooling jacket is cast in a waffle shape. This provides a jagged face for refractory retention and magnetite-slag deposition (Voermann *et al.*, 1999; Kojo, *et al.*, 2000; Merry *et al.*, 2000). Jackets are typically 0.75 m × 0.75 m × 0.1 m thick with 0.03 m diameter, 0.004 m wall monel tube.

5.1.3 Concentrate burner (Fig. 5.2)

Dry concentrate and O₂-rich blast are combined in the furnace reaction shaft by blowing them through a concentrate burner. Dry flux, recycle dust and crushed reverts are also added through the burner.

A year 2000-concentrate burner consists of:

- (a) an annulus through which O₂-rich blast is blown into the reaction shaft

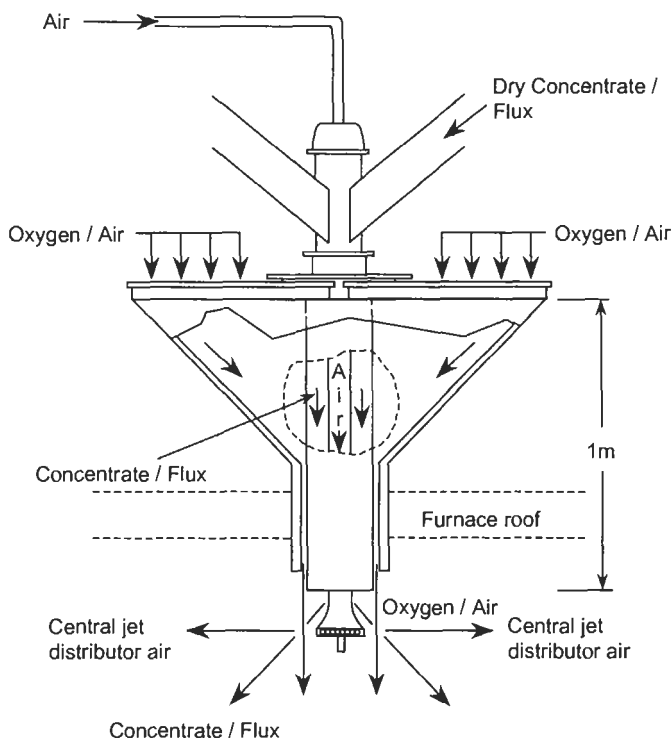


Fig. 5.2. Central jet distributor Outokumpu concentrate burner. The main goal of the burner is to create a uniform concentrate-blast suspension 360° around the burner. This type of burner can smelt up to 200 tonnes of feed per hour. Its feed consists mainly of dry (i) Cu-Fe-S concentrate, ~100 µm; (ii) silica flux, ~1 mm; (iii) recycle dust; and (iv) recycle crushed reverts*, ~1 mm.

- (b) a central pipe through which concentrate falls into the reaction shaft
- (c) a distributor cone at the burner tip, which blows air horizontally through the descending solid feed.

Special attention is paid to uniform distribution of blast and solid feed throughout the reaction shaft. It is achieved by introducing blast and solids vertically and uniformly into quadrants around the burner (Baus, 1999) and by blowing the solids outwards with central jet distributor air.

* Reverts are matte and slag inadvertently frozen during transport around the smelter. Examples are matte and slag (i) frozen in ladles and (ii) spilled during tapping and pouring.

5.1.4 Supplementary hydrocarbon fuel burners

All Outokumpu flash furnaces are equipped with hydrocarbon fuel burners atop the reaction shaft and through the settler walls and roof. Shaft-top burners keep the process in thermal balance. Settler burners eliminate cool zones in the furnace. They are also used to adjust slag temperature.

5.1.5 Matte and slag tapholes

Matte and slag are tapped through single-hole water-cooled copper ‘chill blocks’ imbedded in the furnace walls. The holes are typically 60-80 mm diameter. They are plugged with moist fireclay which is solidified by the heat of the furnace when the clay is pushed into the hole. They are opened by chipping out the clay and by melting it out with steel oxygen lances.

Matte is tapped via copper or refractory-lined steel launders into cast steel ladles for transport to converting.

Slag is tapped down water-cooled copper launders into:

- (a) an electric settling furnace for Cu settling and recovery
- (b) ladles for truck haulage to Cu recovery by slow cooling/grinding/flotation.

Both withdrawals are only partial. Reservoirs of matte and slag, ~0.5 m deep each are maintained in the furnace.

Tapping of matte is continuously rotated around its tapholes. This washes out solid buildups on the furnace floor by providing matte flow over the entire hearth.

5.2 Peripheral Equipment

The Outokumpu flash furnace is surrounded by:

- (a) concentrate blending equipment
- (b) solids feed dryer
- (c) flash furnace feed bins and feed system
- (d) oxygen plant
- (e) blast preheater (optional)
- (f) waste heat boiler
- (g) dust recovery and recycle system
- (h) gas cleaning system
- (i) sulfuric acid plant
- (j) Cu-from-slag recovery system.

Table. 5.1. Dimensions and production details

Smelter	Caraiba Metais S/A Dias d'Avila, Brazil	Norddeutsche Affinerie, Hamburg, Germany
Startup date	1982	1972
Size, inside brick, m		
hearth: w × l × h	6.8 × 24.3 × 2.9	6 × 20 × 3
reaction shaft		
diameter	5.5	6
height above settler roof	6.1	7.5
gas uptake		
diameter	5.1	4 × 8
height above roof	10	10
slag layer thickness	0.4	0.7
matte layer thickness	0.4	0.2-0.5
active slag tapholes	2	2
active matte tapholes	5	4
concentrate burners	1	1
Feed details tonnes/day		
new concentrate (dry)	2001 (32% Cu)	2850 (33% Cu)
silica flux	71 to 150	300-350
oxygen		
recycle flash furnace dust	120	230
converter dust	6	15
slag concentrate	0	no
reverts	60	150 (ladle sculls, slimes, various dusts)
other		375 molten converter slag
Blast details		
temperature, °C	200	ambient
volume% O ₂	60	50-60
flowrate, thousand Nm ³ /hr	40	40
Production details		
matte, tonnes/day	1000 (62% Cu)	1450 (65% Cu)
slag, tonnes/day	950 (1.7% Cu)	1600 (1.5% Cu)
mass% SiO ₂ /mass% Cu	0.74	0.85
Cu recovery, flash slag	electric furnace	electric furnace
Cu recovery, converter slag	electric furnace	recycle to flash furnace
offgas, thousand Nm ³ /hour	45	50-60
vol. % SO ₂ , leaving furnace	24	30-35
dust production, tonnes/day	101-120	230
matte/slag/offgas temperature	1230/1310/1350°C	1210/1220/1350°C
Fuel inputs, kg/hour		
hydrocarbon fuel burnt	oil 400 + natural	no
in reaction shaft	gas, 400 Nm ³ /hour	
hydrocarbon fuel		
in settler burners	oil, 600	oil, 1000; no coke

of six Outokumpu flash furnaces, 2001.

Nikko Mining Saganoseki, Japan	Sumitomo Metal Mining, Toyo Japan	LG Nikko Onsan, Korea	Kennecott Utah Copper, U.S.A.
1973	1971	1979	1995
6.8 × 20.1 × 2.2	6.7 × 19.9 × 2.5	4.87 × 20 × 2.15	7.7 × 23.9 × 1.9
6.2	6	4	7
5.9	6.4	6.2	8.1
3.1	3	3.6	5.0
6.3	7	8.4	11.9
0.3	0.1	0.4	0.4
0.8	0.9	0.5	0.5
2	2	2	5
6	3	4	4
1	1	1	1
3123 (34.8% Cu)	2190 (31.7% Cu)	1445 (31% Cu)	2815 (27.1% Cu)
191	320	122	207
	407	286 (99% O ₂)	
205	114	104	206
	15	14	40
157	70	0	70
68 (converter dust, leach plant residue, gypsum)	40 solid matte	22	47 sludges & residues
77 purchased scrap	83 copper residue		288 FC slag
ambient	450	160	ambient
69-75	48	80	75-85
27-33	34	11.2	30.6
1770 (65.5% Cu)	1240 (63% Cu)	693 (62.5% Cu)	1344 (71% Cu)
1386	1212 (1.3% Cu)	609 (2% Cu)	2025 (1.8)
0.85	0.89	0.7	0.64
electric furnace	electric fce with coal	electric furnace	slag flotation
solidify/flotation	solidify/flotation	same electric furnace	recycle to smelting
29-35	36.6	24	41
52-58 (calculated)	32.5	35	45
205	boiler 64, esp 64	104	boiler 125, esp 63
1258/1266/1266°C	1233/1241/1370°C	1220/1300/1300°C	1290/1330/1350°C
1900-2100 kg/hour fine coal with feed	348 oil, 100 pulverized coal	occasionally bunker C oil, 84 kg/h yearly avg	none
none	none	670 bunker C oil	occasionally

(a) to (e) are described here. (f) to (i) are described in Chapter 14. (j) is described in Chapter 11.

5.2.1 Concentrate blending system

Most flash furnaces smelt several concentrates plus small amounts of miscellaneous materials, e.g. precipitate Cu. They also smelt recycle dusts, sludges, slag flotation concentrate and reverts.

These materials are blended to give constant composition feed to the flash furnace. Constant composition feed is the surest way to ensure (i) smooth flash furnace operation and (ii) continuous attainment of target compositions and temperatures.

Two techniques are used:

- (a) bin-onto-belt blending by which individual feed materials are dropped from holding bins at controlled rates onto a moving conveyor belt
- (b) bedding, where layers of individual feed materials are placed on long (occasionally circular [MVT, 2002]) $\wedge$ shaped piles, then reclaimed as vertical slices of blend.

The blended feed is sent to a dryer. Flux may be included in the blending or added just before the dryer.

5.2.2 Solids feed dryer

Flash smelting's concentrate and flux are always dried to ensure even flow through the concentrate burner. Steam and rotary dryers are used (Sagedahl and Broenlund, 1999; Partinen *et al.*, 1999). The water contents of moist and dry feed are typically 8 and 0.2 mass% H₂O.

Rotary dryers evaporate water by passing hot gas from natural gas or oil combustion through the moist feed. The temperature of the drying gas is kept below ~500°C (by adding nitrogen, recycle combustion gas or air) to avoid spontaneous oxidation of the concentrate.

Steam dryers rotate hot, steam-heated stainless steel coils through the moist feed (Sagedahl and Broenlund, 1999). Steam drying has the advantages of:

- (a) efficient use of flash furnace waste heat boiler steam
- (b) little SO₂, dust and offgas evolution because hydrocarbon combustion isn't used
- (c) low risk of concentrate ignition because steam drying is done at a lower temperature ~200°C than combustion-gas drying ~500°C.

Steam drying is being adopted widely in new and existing Outokumpu flash smelters (Sagedahl and Broenlund, 1999; Isaksson and Lehner, 2000).

5.2.3 Bin and feed system

Dried feed is blown up from the dryer by a pneumatic lift system. It is caught in acrylic bags and dropped into bins above the flash furnace reaction shaft. It is fed from these bins onto drag or screw conveyors for delivery to the concentrate burner.

Bin design is critical for controlled feeding of the flash furnace. Fine dry flash furnace feed tends to 'hang up' on the bin walls or 'flood' into the concentrate burner. This is avoided by 'mass flow' bins (Marinelli and Carson, 1992) that are steep enough and smooth enough to give even flow throughout the bin.

The rate at which feed enters the concentrate burner is measured by supporting the feed bins on load cells. The rate of feeding is adjusted by varying the speed of the conveyers below the bins (Kopke, 1999, Suzuki *et al.*, 1998).

Other recent innovations include:

- (a) a revolving table feeder atop the concentrate burner (Suzuki *et al.*, 1998)
- (b) disc feeders and air slide conveyers (Goodwill *et al.*, 1999, Jones *et al.*, 1999).

Both systems are designed to give constant rate feeding and low wear.

5.2.4 Oxygen plant

The principal oxygen plant in an Outokumpu flash smelter is usually a liquefaction/ distillation unit, 200-1000 tonnes oxygen per day. It delivers 90-98 mass% O₂ industrial oxygen gas (2 atmospheres gage) to the flash furnace.

Some smelters also have a molecular sieve oxygen plant (vacuum or pressure swing absorption) to supplement their liquefaction/distillation oxygen. Molecular sieve plants come in small (~100 tonnes oxygen/day) units. They are suitable for incremental additions to a smelter's main oxygen plant.

Oxygen-enriched blast is prepared by mixing industrial oxygen and air as they flow to the concentrate burner. The oxygen is added through a diffuser (holed pipe) protruding into the air duct. The diffuser is located ~6 duct diameters ahead of the concentrate burner to ensure good mixing.

The rates at which oxygen and air flow into the concentrate burner are important

flash furnace control parameters. They are measured by orifice or mass flow flowmeters and are adjusted by butterfly valves.

5.2.5 Blast heater (optional)

Most Outokumpu flash furnaces use heated blast. The blast is heated typically to 100 to 450°C using hydrocarbon-fired shell-and-tube heat exchangers. Hot blast ensures rapid Cu-Fe-S concentrate ignition in the flash furnace. It also provides energy for smelting.

Modern, highly oxygen-enriched flash furnaces use ambient (~30°C) blast. Concentrate ignition is rapid with this blast at all temperatures.

5.2.6 Waste heat boiler (Peippo *et al.*, 1999; Westerlund *et al.*, 1999)

Offgas leaves an Outokumpu flash furnace at about 1300°C. Its sensible heat is recovered as steam in a horizontal waste heat boiler, Chapter 14.

5.2.7 Dust recovery

Outokumpu flash furnace offgases contain 0.1 to 0.2 kg of dust per Nm³ of offgas. About 70% of this dust drops out in the waste heat boiler. The remainder is caught in electrostatic precipitators (Parker, 1997, Ryan *et al.*, 1999) where the particles are (i) charged in a high voltage electrical field; (ii) caught on a charged wire or plate; and (iii) periodically collected as dust 'clumps' by rapping the wires and plates. Electrostatic precipitator exit gas contains ~0.1 gram of dust per Nm³ of gas (Conde *et al.*, 1999).

The collected dust contains ~25% Cu. It is almost always recycled to the flash furnace for Cu recovery. It is (i) removed from the boilers and precipitators by drag and screw conveyors; (ii) transported pneumatically to a dust bin above the flash furnace; and (iii) combined with the dried feed just before it enters the concentrate burner.

5.3 Furnace Operation

Table 5.1 indicates that Outokumpu flash furnaces:

- (a) smelt up to 3000 tonnes per day of new concentrate
- (b) produce ~65% Cu matte
- (c) use 50-80% O₂ blast, often slightly heated
- (d) burn hydrocarbon fuel to some extent.

This section describes how the furnaces operate.

5.3.1 Startup and shutdown

Operation of an Outokumpu flash furnace is begun by heating the furnace to its operating temperature with hydrocarbon burners or hot air blowers (Severin, 1998). The heating is carried out gently and evenly over a week or two to prevent uneven expansion and spalling of the refractories. Adjustable springs attached to fixed position I-beams keep the walls and hearth under constant pressure during the heating. Also, paper is inserted between newly laid hearth bricks to burn out and compensate for brick expansion during initial heat up. Concentrate feeding is begun as soon as the furnace is at its target temperature. Full production is attained in a day or so.

Shutdown consists of:

- (a) overheating the furnace for 7 to 10 days to melt solid buildups
- (b) starting hydrocarbon burners
- (c) stopping the concentrate burner
- (d) draining the furnace with hydrocarbon burners on
- (e) turning off the hydrocarbon burners
- (f) turning off the cooling water
- (g) allowing the furnace to cool at its natural rate.

5.3.2 Steady-state operation

Steady-state operation of a flash furnace entails:

- (a) feeding solids and blast at a constant rate
- (b) drawing SO_2 -rich gas from the gas uptake at a constant rate
- (c) tapping matte from the furnace on a scheduled basis or as-needed by the converters
- (d) tapping slag from the furnace on a scheduled basis or when it reaches a prescribed level in the furnace.

The next section describes how steady-state operation is attained.

5.4 Control (Fig. 5.3)

The Outokumpu flash furnace operator must smelt concentrate at a steady, specified rate while:

- (a) producing matte of specified Cu grade
- (b) producing slag of specified SiO_2 content
- (c) producing slag at specified temperature
- (d) maintaining a protective coating of magnetite-rich slag on the furnace interior.

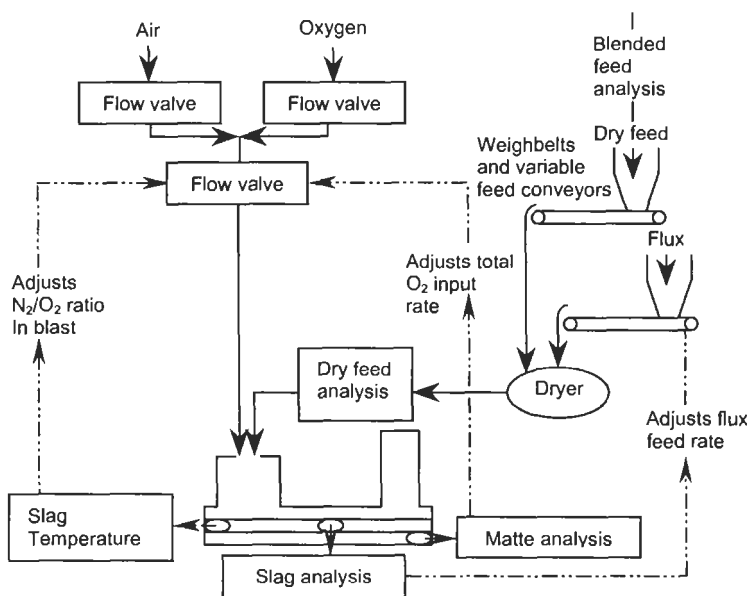


Fig. 5.3. Example control system for Outokumpu flash furnace. The three loops, left to right, control slag temperature, slag composition and matte composition. Slag temperature may also be controlled by adjusting reaction shaft hydrocarbon burner combustion rate. It is fine-tuned by adjusting settler burner combustion rates. Matte grades $\pm 1.5\%$ Cu and temperatures $\pm 20^\circ\text{C}$ are obtained.

5.4.1 Concentrate throughput rate and matte grade controls

Basic Outokumpu flash furnace strategy is to charge dried concentrate 'mix' to the furnace at a prescribed rate and to base all other controls on this rate.

Having chosen concentrate feed rate, the flash furnace operator must next select the grade (% Cu) of his product matte, i.e. the extent of Fe and S oxidation.

It is selected as a compromise between:

- (a) maximizing SO_2 evolution in the flash furnace (where it is captured efficiently)

and:

- (b) keeping enough Fe and S in the matte so that subsequent converting can operate autothermally while melting its required amount of Cu scrap and smelter recycle materials.

Physically, matte grade is set by adjusting the:

$$\frac{\text{O}_2 - \text{in} - \text{blast input rate}}{\text{concentrate feed rate}}$$

ratio until the target matte composition is obtained. A large ratio gives extensive Fe and S oxidation and high-grade (i.e. high % Cu) matte. A small ratio gives the opposite. Physically, the ratio is controlled by adjusting the rates at which air and oxygen enter the furnace, constant concentrate feed rate.

5.4.2 Slag composition control

The iron oxide formed by concentrate oxidation is fluxed with SiO_2 to form liquid slag. The amount of SiO_2 is based upon the slag having (i) a low solubility for Cu and (ii) sufficient fluidity for easy tapping and a clean matte/slag separation. An SiO_2/Fe mass ratio of 0.7 to 1.0 is used. It is controlled by adjusting the rate at which flux is fed to the solids feed dryer.

5.4.3 Temperature control

Matte and slag temperatures are measured as matte and slag flow from the furnace. Disposable thermocouple probes and optical pyrometers are used. Matte and slag temperatures are controlled by adjusting:

- (a) the rate at which N_2 'coolant' enters the furnace (mainly in air)
- (b) hydrocarbon burner combustion rates.

Slag temperature is adjusted somewhat independently of matte temperature by adjusting settler hydrocarbon burner combustion rates.

Matte and slag temperatures are typically 1250°C . They are chosen for rapid matte/slag separation and easy tapping. They are also high enough to keep matte and slag molten during transport to their destinations. Excessive temperatures are avoided to minimize refractory and cooling jacket wear.

5.4.4 Reaction shaft and hearth control (Davenport et al., 2001)

Long flash furnace campaign lives require that magnetite-rich slag be deposited in a controlled manner on the furnace's walls and hearth. Magnetite slag deposition is encouraged by:

- (a) highly oxidizing conditions in the furnace
- (b) low operating temperature
- (c) low SiO_2 concentration in slag.

It is discouraged by reversing these conditions and by adding coke or coal to the furnace.

5.5 Impurity Behavior

Flash furnace concentrates inevitably contain impurities from their original ore. They must be separated from Cu during smelting and refining. Table 5.2 shows that this is partially accomplished during flash smelting, i.e. portions of the impurities report to slag and offgas while almost all the Cu reports to matte. Important exceptions to this are gold, silver and platinum group metals. They accompany Cu through to electrefining (Fig. 1.1) where they are recovered as byproducts. Most Ni also follows Cu.

Table 5.2. Distribution of elements during Outokumpu flash smelting (Davenport *et al.*, 2001).

Element	% to matte	% to slag	% to offgas*
Cu	97	2	1
Ag	90-95	2-5	3-8
Au	95	2	3
As	15-40	5-25	35-80
Bi	30-75	5-30	15-65
Cd	20-40	5-35	25-60
Co	45-55	45-55	0-5
Ni	70-80	20-25	0-5
Pb	45-80	15-20	5-40
Sb	60-70	5-35	5-25
Se	85	5-15	0-5
Te	60-80	10-30	0-10
Zn	30-50	50-60	5-15

*collected as precipitated solids during gas cleaning

Industrial impurity distribution is complicated by recycle of:

- flash furnace and converter dusts
- flash furnace slag concentrate
- converter slag concentrate and (occasionally) molten converter slag
- solid reverts from around the smelter
- acid plant sludges.

Nevertheless, Table 5.2 provides guidance as to how impurities distribute themselves during flash smelting.

5.5.1 Non-recycle of impurities in dust

Impurities are also found in flash furnace dust, Table 4.2. This dust is usually

recycled to the flash furnace for Cu recovery, so it is not usually an escape route for impurities.

However, three flash smelters (Chuquicamata, Kennecott (Gabb *et al.*, 1995) and Kosaka (Maeda *et al.*, 1998) recover Cu from some of their dust hydrometallurgically rather than by recycle to the flash furnace. This allows the dust's impurities to escape the smelter in leach plant residues. It is particularly effective for removing As, Bi and Cd from the smelter. Pb is also removed, but to a lesser extent.

5.5.2 Other Industrial Methods of Controlling Impurities

Flash smelters that treat several concentrates blend their high and low impurity concentrates so that impurity levels in the smelter's product anodes (Fig. 1.1) are low enough for efficient electrorefining.

Flash smelters that are dedicated to treating high impurity concentrates control impurity-in-anode levels by:

- (a) minimizing dust recycle
- (b) modifying converting and fire refining to increase impurity removal (Newman *et al.*, 1991; Tenmaya *et al.*, 1993; Zhao and Themelis, 1996).

5.6 Future Trends

The major future development foreseen by Outokumpu is use of its flash furnace for (i) direct-to-copper smelting, Chapter 12 and (ii) continuous flash converting, Chapter 10 (Hanniala *et al.*, 1999). Both have the advantages of improved SO₂ capture and an SO₂-free workplace because they eliminate batch Peirce-Smith converting.

5.7 Summary

Outokumpu flash smelting accounts for more than half of Cu matte smelting. It is also used in two locations for direct-to-copper smelting and in one location for continuous converting.

It blows oxygen, air, dried concentrate, flux and particulate recycle materials as a well-dispersed mixture into a hot reaction shaft. Smelting reactions are extremely fast under these conditions. Outokumpu flash furnaces smelt up to 3000 tonnes of new concentrate per day.

Modern Outokumpu flash furnaces operate with high oxygen blast and very little hydrocarbon fuel. Most of the energy for heating and melting comes from Fe

and S oxidation. This operation also gives strong SO₂ offgas from which SO₂ can be captured efficiently as sulfuric acid.

Outokumpu flash furnaces are operated under automatic control to give constant temperature, constant composition products at a rapid rate and with minimum energy consumption. Matte and slag compositions are controlled by adjusting:

$$\frac{\text{O}_2 \text{ input rate}}{\text{concentrate feed rate}}$$

and:

$$\frac{\text{flux input rate}}{\text{concentrate feed rate}}$$

ratios. Product temperatures are controlled by adjusting (i) the N₂/O₂ ratio of the input blast and (ii) hydrocarbon fuel combustion rate.

Wide adoption of Outokumpu flash smelting is due to its efficient capture of SO₂, its rapid production rate and its small energy requirement. Its only limitation is its inability to smelt scrap.

Suggested Reading

Davenport, W.G., Jones, D.M., King, M.J. and Partelpoeg, E.H. (2001) *Flash Smelting, Analysis, Control and Optimization*, TMS, Warrendale, PA. www.tms.org

Sarkikoski, T. (1999) *A Flash of Knowledge*, Outokumpu Oyj, Espoo, Finland www.outokumpu.com

References

Baus, A. (1999) BHP San Manuel smelter rebuild. Paper presented at AIME Arizona Conference Meeting, Tucson, AZ, December 6, 1999.

Conde, C.C., Taylor B. and Sarma, S. (1999) Philippines Associated Smelting electrostatic precipitator upgrade. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 685 693.

Davenport, W.G., Jones, D.M., King, M.J. and Partelpoeg, E.H. (2001) *Flash Smelting, Analysis, Control and Optimization*, TMS, Warrendale, PA.

Gabb, P.J., Howe, D.L., Purdie, D.J. and Woerner, H.J. (1995) The Kennecott smelter hydrometallurgical impurities process. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrefining and Hydrometallurgy of Copper*, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G., The Metallurgical Society of CIM, Montreal, Canada, 591 606.

Goodwill, D.J., Jones, D.M. and Royal, T.A. (1999) Redesigning the flash furnace feed system at BHP Copper. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 517 531.

Hanniala, P., Helle, L. and Kojo, I.V. (1999) Competitiveness of the Outokumpu flash smelting technology in the third millennium. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 221 238.

Isaksson, O. and Lehner, T. (2000) The Ronnskar smelter project: production, expansion, start-up. *JOM*, 52 (8), 26 29.

Jones, D.M., Cardoza, R. and Baus, A. (1999) 1999 rebuild of the BHP San Manuel Outokumpu flash furnace. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 319 334.

Kojo, I.V., Jokilaakso, A. and Hanniala, P. (2000) Flash smelting and converting furnaces: a 50 year retrospect. *JOM*, 52 (2), 57 61.

Kopke, M. (1999) Expansion project of the smelter plant of Norddeutsche Affinerie AG, Germany. In *Proceedings of the 9th International Flash Smelting Congress*, Australia, June 6-12, 1999.

Maeda, Y., Inoue, H., Hoshikawa, Y., and Shirasawa, T. (1998) Current operation in Kosaka smelter. In *Sulfide Smelting '98: Current and Future Practices*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 305 314.

Marinelli, J. and Carson, J.W. (1992) Solve solids flow problems in bins, hoppers, and feeders. *Chemical Engineering Progress*, 88(5), 22 28.

Merry, J., Sarvinis, J. and Voermann, N. (2000) Designing modern furnace cooling systems. *JOM*, 52(2), 62 64.

MVT Materials Handling GmbH (2002) Circular bedding plant at Rudersdorfer Zement, Germany. www.mvt.de (Mixed plants)

Newman, C.J., MacFarlane, G., Molnar, K. and Storey, A.G. (1991) The Kidd Creek copper smelter - an update on plant performance. *Copper 91/Cobre 91, Volume 4, Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C., Luraschi, A. and Newman, C.J., Pergamon Press, New York, NY, 65 80.

Parker, K.R. (1997) *Applied Electrostatic Precipitation*, Chapman & Hall, London, U.K.

Partinen, J. Chen, S.L. and Tiitu, O. (1999) Development of more environment-friendly and cost-effective drying facility for copper concentrates. *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations And Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 533 544.

Peippo, R., Holopainen, H. and Nokelainen, J. (1999) Copper smelter waste heat boiler technology for the next millennium," in *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 71 82.

Ryan, P., Smith, N., Corsi, C. and Whiteus, T. (1999) Agglomeration of ESP dusts for recycling to plant smelting furnaces," In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 561 571.

Sagedahl, C.M. and Broenlund, H.J. (1999) Indirect drying of concentrates at copper and nickel smelters by means of innovative, cost effective environmental technologies. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 545 559.

Severin, N.W. (1998) Refractory dryout, how can we improve it? *Canadian Ceramics*, February 1998, 21 23

Suzuki, Y., Suenaga, C., Ogasawara, M. and Yasuda, Y. (1998) productivity increase in flash smelting furnace operation at Saganoseki smelter & refinery. In *Sulfide Smelting '98: Current and Future Practices*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 587 595.

Tenmaya, Y., Inoue, H., Matsumoto, M. and Watanabe, K. (1993) Current operation of converter and anode furnace in Kosaka Smelter. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 363 370.

Voermann, N., Ham, F., Merry, J., Veenstra, R. and Hutchinson, K. (1999) Furnace cooling design for modern, high-intensity pyrometallurgical processes. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 573 582.

Westerlund, K.A.M., Piehl, O. and Abeck, W. (1999) Tons and profit from understanding gas cooling and heat recovery. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 83 94.

Zhao, B. and Themelis, N.J. (1996) Kinetics of As and Sb removal from molten copper by Na_2CO_3 fluxing. In *EPD Congress 1996*, ed. Warren, G.W., TMS, Warrendale, PA, 515 526.

CHAPTER 6

Inco Flash Smelting

Inco flash smelting blows industrial oxygen, dried Cu-Fe-S concentrate, SiO_2 flux and recycle materials horizontally into a hot ($\sim 1250^\circ\text{C}$) furnace. Once in the furnace, the oxygen reacts with the concentrate by Reactions 1.1 and 1.2 to give:

- (a) molten matte, 55 to 60 mass% Cu
- (b) molten slag, 1 to 2 mass% Cu
- (c) offgas, 60 to 75 volume% SO_2 .

The matte is tapped into ladles and sent to converting, Fig. 1.6. The slag is tapped into ladles and sent to stockpile, with or without Cu-from-slag removal, Chapter 11. The offgas is water-quenched, cleaned of dust and sent to a sulfuric acid plant.

The Inco flash furnace is also used to recover Cu from molten recycle converter slag. The slag is poured into the furnace via a steel chute and water-cooled door, Fig. 6.1a.

At the start of 2002 there are five Inco flash furnaces in operation: at Almalyk, Uzbekistan (Ushakov, *et al.* 1975); Hayden, Arizona (Marczeski and Aldrich 1986); Hurley, New Mexico (Belew and Partelpoeg, 1993); and Sudbury, Ontario (two furnaces, Carr *et al.*, 1997, Humphris *et al.*, 1997; Molino *et al.*, 1997).

The Almalyk, Hayden and Hurley furnaces smelt Cu-Fe-S concentrates. The Sudbury furnaces smelt Ni-Cu-Co-Fe-S concentrates to produce $\sim 45\%$ Ni+Cu+Co matte and $\sim 1\%$ Ni+Cu+Co slag.

6.1 Furnace Details

The Inco flash furnace is made of high-quality MgO and $\text{MgO-Cr}_2\text{O}_3$ brick, Fig.

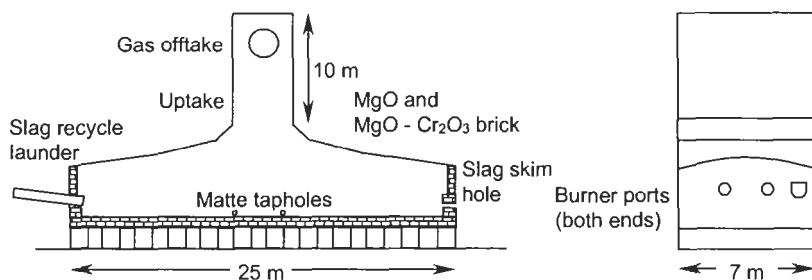


Fig. 6.1a. Side and end views of Inco flash furnace at Hurley, New Mexico.

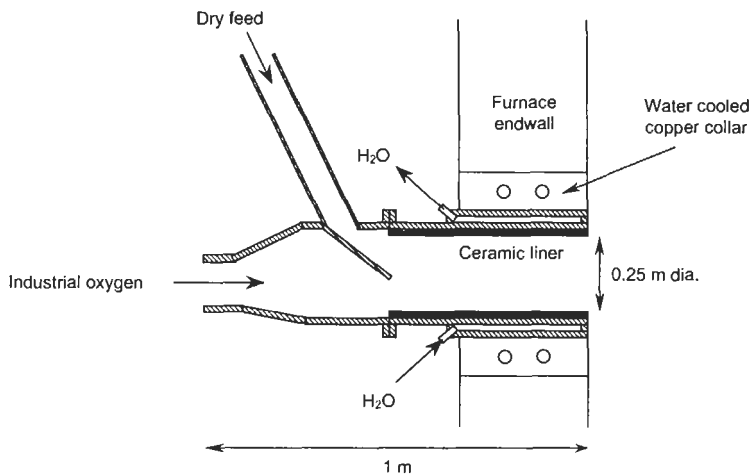


Fig. 6.1b. Details of Inco flash furnace concentrate burner.

6.1a. Its main components are:

- (a) concentrate burners, two at each end of the furnace
- (b) end- and sidewall water-cooled copper cooling jackets
- (c) a central offgas uptake
- (d) sidewall tapholes for removing matte
- (e) an endwall taphole for removing slag
- (f) an endwall chute for charging molten converter slag.

6.1.1 Concentrate burner

Inco concentrate burners are ~0.25 m diameter, 1 m long, 1 cm thick stainless steel pipes – water-cooled with an internal ceramic sleeve. They are fed with industrial oxygen, blown in horizontally, and dry feed, dropped in from above through an angled tube, Fig. 6.1b.

The diameter of the burner barrel gives an oxygen/feed entry velocity of ~40 meters per second. This velocity creates a concentrate/oxygen flame that reaches the central uptake. The burners are angled about 7 degrees down and 7 degrees in so that the flame plays on the slag surface rather than on the roof and walls.

6.1.2 Water cooling

Inco furnace side- and endwalls are fitted with water-cooled copper fingers, plates and shelves to maintain the integrity of the furnace structure. As in the Outokumpu furnace, water cooling causes magnetite-rich slag to deposit on the furnace walls. This protects the bricks and water-cooled copper, extending furnace life.

An Inco furnace can be operated for five or six years without reconstruction. Repairs are done yearly and while the smelter is stopped for non-furnace reasons, e.g. acid plant maintenance. The end of a furnace campaign is usually caused by excessive refractory erosion, especially at the slag line.

6.1.3 Matte and slag tapholes

The Inco furnace is equipped with four sidewall matte tapholes and an endwall slag taphole. Each consists of a single-hole refractory block fitted in a water-cooled copper plate. Tapping and plugging are similar to Outokumpu flash furnace tapping and plugging (Section 5.1.5). Reservoirs of slag, ~0.5 m deep and matte, 0.2-1.0 m deep are always kept in the furnace. The matte level is kept well below the slag taphole. This avoids accidental tapping of matte with slag.

Matte tapping is rotated continuously between the furnace's four tapholes to keep matte flowing across the entire floor. This minimizes localized magnetite buildups on the furnace floor.

6.1.4 Gas uptake

The central offgas uptake is brick or castable refractory backed by copper cooling jackets or stainless steel. A small amount of oxygen is injected into the uptake. It burns the elemental sulfur that is present in Inco furnace offgas. This prevents the sulfur from precipitating in downstream cooling and dust collection equipment.

Table 6.1. Inco flash furnace dimensions and production details, 2001.

Smelter	Phelps Dodge - Chino Mines Hurley, U.S.A.	Asarco Hayden, U.S.A.	Inco Ltd. Sudbury, Canada
Furnace commissioning	1984	1983	1993
Size, inside brick, m			
hearth: w × l × h	5.5 × 22 × 5	5.5 × 22 × 5	6.4 × 29 × 5
gas uptake			
width	3.5	3	4 × 4
height above settler roof	10	10	15
slag layer thickness	0.6	0.5	0.5
matte layer thickness	0.15	0.6	1.0
active matte tapholes	4	4	4
active slag tapholes	1	1	1
concentrate burners	4	4	4
Feed details, tonnes/day			
industrial oxygen	485	450	450
new concentrate	1725	1900	1700
concentrate grade	29% Cu	27% Cu	20% (Cu+Ni+Co)
silica flux	130	155	350
sludges (slimes)	135		100
converter dust	35		10
reverts*	225, crushed reverts	~70	130
liquid converter slag	285	30 ladles/day	550

Blast details

blast temperature, °C	ambient	ambient	ambient
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Production details

matte, tonnes/day	850	1020	850
matte grade, %Cu	58	58	24%Cu + 21%Ni
matte temperature, °C	1190	1220	1230
slag, tonnes/day	1100	1160	1600
slag % Cu	0.9	1.5 max	0.6 Cu, 0.5 Ni
SiO ₂ /Fe ratio	0.74	0.83	0.87
slag temperature, °C	1250	1230	1280
Cu recovery, flash slag	discard	flotation, Chapter 11	discard
Cu recovery, converter slag	recycle molten to flash furnace	recycle molten to flash furnace	recycle molten to flash furnace
offgas, thousand Nm ³ /hour	21		18-20
volume% SO ₂ in offgas	75		50-60
offgas temperature, °C	1270		1300
dust production, tonnes/day	135 in sludges		100 dry tonnes

Fuel inputs

natural gas	occasionally (through burners above concentrate burners)	for downtimes longer than 0.5 hour	minimal, only as fine tuning
coke	petroleum coke (~1 mm) occasionally added with crushed reverts	for downtimes longer than 0.5 hour, added through slag return launder or revert feeder	1-2 tonnes/hr

* Reverts are matte and slag inadvertently frozen during transport around the smelter. Examples are matte and slag frozen in ladles and matte and slag spilled during tapping and pouring.

6.2 Auxiliary Equipment

The auxiliary equipment required for Inco flash smelting is:

- (a) oxygen plant, Section 5.2.4
- (b) concentrate blending system, Section 5.2.1
- (c) solids feed dryer
- (d) four concentrate burner feed systems
- (e) offgas cooling system
- (f) dust recovery and recycle system
- (g) sulfuric acid plant, Chapter 14.

6.2.1 Solids feed dryer (Carr, *et al.*, 1997)

Inco furnace solid feed (concentrate, flux, reverts, recycle sludges) is dried to give an even flow of solids through the concentrate burners. This is essential to create a uniform oxygen-concentrate suspension in the furnace. Natural gas-fired fluid bed dryers are used. The dryer feed is typically 10 mass% H₂O, the dried product, ~0.2 mass% H₂O. The fluidization gas is combustion gas plus air ~330°C. A fixed bed of 1 to 10 mm gravel distributes the fluidization gas across the bed.

The fluidized dried feed particles and their surrounding gas are drawn at ~90°C through acrylic or aramid fabric tubes stretched on wire frameworks. About 99.99% of the concentrate is caught on the outside of the fabric. It is removed by reverse nitrogen or air pulsation and dropped into a large storage bin. From there it is sent by conveyors or air slides (Jones *et al.*, 1999) to four dry charge bins above the furnace, one for each concentrate burner.

6.2.2 Concentrate burner feed system

The solid charge to the Inco flash furnace consists mainly of dried feed blend from the fluid bed dryer. It drops from its dry charge bins onto drag or screw conveyors which then drop it into the concentrate burners.

The feed system may also include separate 'touch-up' flux, 'touch-up' revert and converter dust bins. Material is drawn from these bins as needed to control flash furnace products temperature and slag composition, Section 6.4.

The rate of withdrawal from each bin is controlled by adjusting the speed of the drag or screw conveyor beneath the bin.

6.2.3 Offgas cooling and dust recovery systems (Humphris *et al.*, 1997; King and Phipps, 1998)

Inco offgas is cooled and cleaned of dust in:

- (a) a water-spray evaporation cooler where the offgas is cooled from $\sim 1230^{\circ}\text{C}$ to 80°C and where 90% of the entrained dust is removed as sludge
- (b) cyclones, scrubbers, and wet electrostatic precipitators
- (c) a fabric filter.

The equipment is stainless steel to minimize corrosion. The offgas (60 to 75 volume% SO_2) is pulled through the equipment by fans, which push the gas onwards to a sulfuric acid plant for SO_2 capture.

Solids from the cooler and dust removal equipment contain $\sim 35\%$ Cu. The Cu is recovered by neutralizing and de-watering the sludge then recycling it through the concentrate dryer and flash furnace.

6.3 Operation

Inco flash smelting begins by heating the furnace to its operating temperature over several days. Natural gas combustion or externally heated hot air are used. Concentrate smelting is then begun, achieving full smelting rate in about 8 hours.

Smelting is ended by overheating the furnace; tapping out all the slag (by raising matte level to the slag taphole); turning off the concentrate burners; draining the matte as quickly as possible and allowing the furnace to cool at its natural rate.

6.3.1 Steady operation and control

Smelting consists of steadily blowing industrial oxygen and dry feed into the furnace while continuously removing offgas and intermittently tapping matte and slag. The goals of the smelting are to:

- (a) smelt dry concentrate at a specified rate ~ 1800 tonnes/day
- (b) produce matte of specified composition $\sim 60\%$ Cu
- (c) produce slag of specified composition and temperature $\sim 34\% \text{SiO}_2$, 1250°C .

The furnace operator uses four main adjustable parameters to achieve these goals:

- (a) dry feed rate
- (b) dry feed composition
- (c) industrial oxygen input rate
- (d) natural gas combustion rate.

Coke may also be added to the furnace, to supplement or replace natural gas.

6.4 Control Strategy (Fig. 6.2)

Basic Inco flash furnace control strategy entails:

- (a) setting dried feed rate at its set-point value
- (b) setting industrial oxygen input rate to obtain the required matte grade
- (c) setting % flux in concentrate burner feed to obtain the required slag composition
- (d) setting (i) % reverts in burner feed and (ii) natural gas combustion rate to obtain the required slag temperature.

6.4.1 Dried feed rate control

An Inco flash furnace is operated at a constant dried feed blend input rate. All other input rates (e.g. industrial oxygen input rate) are based on this dried feed input rate. Physically, dried feed rate is set by adjusting the rate at which conveyors draw the feed from overhead bins into the flash furnace's concentrate burners, Fig. 6.2. Dried feed rate is chosen so that the furnace smelts concentrate at a management-designated rate.

6.4.2 Matte grade control

The grade of matte being produced by Inco flash furnaces is ~60% Cu. This grade allows most of the SO₂ in the feed to be captured efficiently by the flash furnace offgas system while leaving enough Fe and S in the matte for autothermal converting with melting of recycle materials and purchased scrap. It can also allow the flash furnace slag (~1% Cu) to be discarded without Cu-removal treatment.

Target matte grade is obtained by setting the ratio:

$$\frac{\text{industrial oxygen input rate}}{\text{dried feed blend input rate}}$$

so that Fe and S oxidation gives 60% Cu matte. The ratio is adjusted by varying oxygen input rate.

6.4.3 Slag composition control

Slag composition is chosen to give a fluid slag and efficient matte slag separation. 34% SiO₂ is typical. It is obtained by adjusting the amount of flux in the dryer feed blend. It is obtained more exactly by controlling the:

$$\frac{\text{'touch - up' flux feed rate}}{\text{dried feed blend input rate}}$$

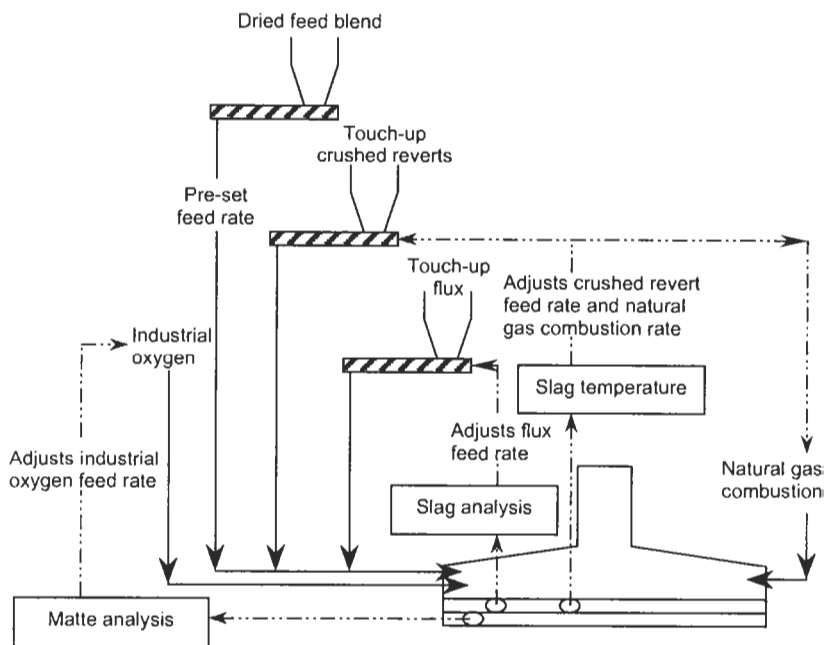


Fig. 6.2. Example control system for Inco flash furnace. Dried feed blend input rate is held constant. Matte grade is controlled by adjusting industrial oxygen input rate. Slag composition is controlled by adjusting % flux in dryer feed and 'touch-up' flux feed rate. Slag temperature is controlled by adjusting % reverts in dryer feed, 'touch-up' revert input rate and natural gas combustion rate.

ratio. The ratio is controlled by adjusting the speed of the conveyors beneath the 'touch-up' flux bins.

6.4.4 Temperature control

The operating temperature of an Inco flash furnace is chosen to give good slag fluidity and efficient matte-slag separation. A slag temperature of $\sim 1250^{\circ}\text{C}$ is usual. It is obtained by adjusting (i) revert input rate (ii) natural gas combustion rate and (iii) coke addition rate.

Reverts are low- or no-fuel value coolants, i.e. they contain considerably less unoxidized Fe and S 'fuel' than concentrate. So increasing the:

$$\frac{\text{revert feed rate}}{\text{dried feed blend input rate}}$$

ratio cools the furnace products and vice versa.

Natural gas combustion heats the furnace products. So increasing the

$$\frac{\text{natural gas combustion rate}}{\text{dried feed blend input rate}}$$

ratio warms the furnace products and vice versa. Coke (added with 'touch-up' reverts) combustion has the same effect.

Balancing the above ratios allows the furnace operator to obtain his prescribed slag temperature while maintaining his prescribed matte grade. Natural gas combustion rate adjustment gives especially fine temperature control.

Matte temperature is not controlled separately from slag temperature. Matte is slightly cooler than slag due to heat flow through the bottom of the furnace.

6.4.5 Control results

Experience has shown that the above control scheme gives matte grades $\pm 3\%$ Cu while keeping slag temperature at its set point $\pm 20^\circ\text{C}$. The fluctuations are due to (i) variations in feed compositions and feed rates and (ii) intermittent converter slag return. They could be decreased by:

- (a) improving the constancy of feed composition, i.e. by improved blending (Medel, 2000)
- (b) installing constant mass feed rate equipment (Jones *et al.*, 1999).

6.4.6 Protective magnetite-slag coating

The walls and floor of the Inco furnace are protected by a coating of magnetite-rich slag. Thickening of this coating is favored by:

- (a) highly oxidizing conditions in the furnace (i.e. production of high grade matte)
- (b) low slag and matte temperatures
- (c) a low slag SiO_2 content
- (d) intensive water cooling.

Thinning of the coating (to prevent excessive buildup on the furnace floor) is favored by the opposites of (a) to (d).

6.5 Cu-in-Slag and Molten Converter Slag Recycle

An advantage of Inco flash smelting is that its slag can be sufficiently dilute in

Cu (<1%) for it to be discarded without Cu-recovery treatment (exception, Hayden, Table 6.1. This avoids the Cu-recovery costs of most modern Cu-smelting processes. It is aided by ensuring that the matte level is kept well below the slag taphole.

In addition, most of the Cu in converter slag (~5% Cu) can be removed by recycling the converter slag through the flash furnace. This is done by all four North American furnaces.

6.6 Inco vs. Outokumpu Flash Smelting

There are many more Outokumpu flash furnaces than Inco flash furnaces. This is probably because of Outokumpu's:

- (a) single concentrate burner in place of Inco's four-burners
- (b) water-cooled reaction shaft, which handles flash smelting's huge heat release better than Inco's horizontal combustion layout
- (c) recovery of offgas heat in a waste heat boiler
- (d) engineering and operational support.

6.7 Summary

The Inco flash furnace uses industrial oxygen (no air) blast to smelt Cu-Fe-S and Ni-Cu-Co-Fe-S concentrates. It produces high Cu and high Ni-Cu-Co mattes. It introduces dry feed and industrial oxygen through four horizontal burners and removes SO₂ offgas through a central gas uptake. The offgas is water-quenched and sent to a sulfuric acid plant to capture its SO₂.

Very little nitrogen enters the Inco furnace so its blast and offgas handling systems are small. Also, the offgas is strong in SO₂, 60-75 volume%, ideal for SO₂ capture.

The process's slag can contain less than 1% Cu so it can be discarded without Cu-recovery treatment. This gives it a cost advantage over most other modern smelting techniques. Also, converter slag can be recycled through the furnace for Cu recovery. This procedure upsets, however, an otherwise steady process.

Suggested Reading

Davenport, W.G., Jones, D.M., King, M.J. and Partelpocg, E.H. (2001) *Flash Smelting, Analysis, Control and Optimization*, TMS, Warrendale, PA.

References

- Belew, B.G. and Partelpoeg, E.H. (1993) Operating improvements at the Phelps Dodge Chino smelter. Paper presented at the TMS annual meeting, Denver, Colorado, February 21 to 25, 1993.
- Carr, H., Humphris M.J. and Longo, A. (1997) The smelting of bulk Cu-Ni concentrates at the Inco Copper Cliff smelter. In *Proceedings of the Nickel-Cobalt 97 International Symposium, Vol. III Pyrometallurgical Operations, Environment, Vessel Integrity in High-Intensity Smelting and Converting Processes*, ed. Diaz, C., Holubec, I. and Tan, C.G., Metallurgical Society of CIM, Montreal, 5 16.
- Humphris, M.J., Liu, J. and Javor, F. (1997) Gas cleaning and acid plant operations at the Inco Copper Cliff smelter. In *Proceedings of the Nickel-Cobalt 97 International Symposium, Vol. III Pyrometallurgical Operations, Environment, Vessel Integrity in High-Intensity Smelting and Converting Processes*, ed. Diaz, C., Holubec, I. and Tan C.G., Metallurgical Society of CIM, Montreal, 321 335.
- Jones, D.M., Cardoza, R. and Baus, A. (1999) Rebuild of the BHP San Manuel Outokumpu flash furnace. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 319 334.
- King, M.J. and Phipps, R.D. (1998) Process improvements at the Phelps Dodge Chino smelter. In *Sulfide Smelting '98, Current and Future Practices*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 535 548.
- Marczeski, W.D. and Aldrich, T.L. (1986) Retrofitting Hayden plant to flash smelting, TMS, Warrendale, PA, Paper A86-65.
- Medel, F. (2000) Sampling and materials handling, receive and homogenization of concentrate, paper presented at Arizona Conference of SME Spring 2000 Smelting Division Meeting, La Caridad Smelter, Mexico, June 3, 2000.
- Molino, L., Diaz, C.M., Doyle, C., Hrepic, J., Slayer, R., Carr, H. and Baird, M.H.I. (1997) Recent design improvements to the Inco Flash Furnace uptake. In *Proceedings of the Nickel-Cobalt 97 International Symposium, Vol. III Pyrometallurgical Operations, Environment, Vessel Integrity in High-Intensity Smelting and Converting Processes*, ed. Diaz, C., Holubec, I. and Tan, C.G., Metallurgical Society of CIM, Montreal, 527 537.
- Ushakov, K.I., Bochkarev, L.M., Ivanov, A.V., Shurchov, V.P., Sedlov, M.V. and Zubarev, V.I. (1975) Assimilation of the oxygen flash smelting process at the Almalyk plant. *Tsvetnye Metally* (English translation), **16** (2), 5 9.

CHAPTER 7

Noranda and Teniente Smelting

Noranda and Teniente smelting use large, ~5 m diameter × 20 m long cylindrical furnaces, Figs. 1.5, 7.1 and 7.2. The furnaces always contain layers of molten matte (72-75% Cu) and slag. O₂ for concentrate oxidation is provided by blowing oxygen-enriched air through tuyeres into the furnace's molten matte layer.

Cu-Fe-S concentrate is:

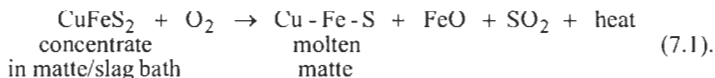
- (a) dried and blown into the furnace through 3 to 10 dedicated tuyeres
- (b) thrown moist (~8% H₂O) with flux, recycle materials and scrap onto the surface of the liquids through an end wall.

The products of the processes are:

super high-grade molten matte, 72 to 75% Cu (~1220°C)
slag, ~6% Cu
offgas, 15-25 volume% SO₂.

The matte is sent to Peirce-Smith converting for coppermaking. The slag is sent to a Cu recovery process. The offgas is sent to cooling, dust recovery and a sulfuric acid plant.

All or most of the heat for heating and melting the charge comes from Fe and S oxidation, i.e. from reactions like:



Natural gas, coal or coke may be burnt to supplement this heat.

In 2002, there are 4 Noranda furnaces and 10 Teniente furnaces operating around the world (Mackey and Campos, 2001). Operating data for three Noranda furnaces and three Teniente furnaces are given in Tables 7.1 and 7.3.

7.1 Noranda Process (Mackey and Campos, 2001; Harris, 1999)

The Noranda furnace is a horizontal steel barrel lined inside with about 0.5 m of magnesia-chrome refractory (Norsmelt, 2002). Industrial furnaces are 4.5 to 5.5 m diameter and 18 to 26 m long. They have 35 to 65 tuyeres (5 or 6 cm diameter) along the length of the furnace, Fig. 7.1.

Noranda smelting entails:

- (a) continuously feeding moist concentrate, flux, reverts, scrap and coal/coke through a furnace endwall onto the bath
- (b) continuously blowing oxygen-enriched air 'blast' (30 to 50 volume% O₂, 1.4 atmospheres, gage) through tuyeres into the furnace's molten matte layer
- (c) continuously drawing offgas through a large mouth and hood at the top of the furnace
- (d) intermittently tapping matte and slag
- (e) intermittently charging recycle molten converter slag through the furnace mouth.

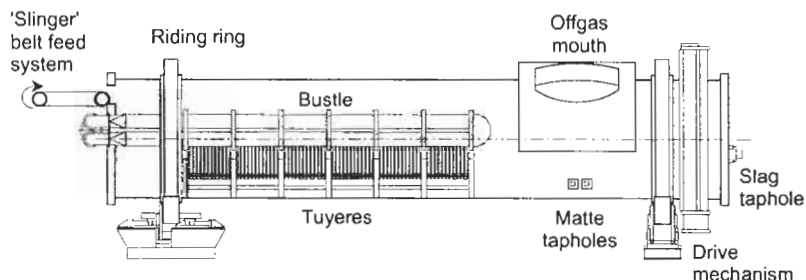


Fig. 7.1. Noranda smelting furnace. It is cylindrical, ~5 m diameter × 20 m long. It smelts up to 3000 tonnes of concentrate per day. Concentrate is charged to the top of the bath or dried and injected through specialized tuyeres. The concentrate is oxidized by blowing oxygen-enriched air through tuyeres into the molten matte layer, Fig. 9.1b.

Table 7.1. Operating details of 3 Noranda smelting furnaces. The new Altonorte furnace will inject most of its concentrates (dried) through 10 concentrate injection tuyeres.

Smelter	Port Kembla, Aust.	Noranda, Québec	Altonorte, Chile
Startup date	1991	1973	2002 (design data)
Furnace details			
length × diameter, m	19 × 4.5	21.3 × 5.1	26.4 × 5.3
slag layer thickness	0.2-0.5	0.3-0.6	0.4
matte layer thickness	0.95-1.15	0.9-1.15	1.1-1.3
active slag tapholes	1	1	1
active matte tapholes	1	1	2
auxiliary burners	2	0	2
Tuyere details			
tuyeres (total)	35	54	66
diameter, cm	5	5.4	6.35
active air blast tuyeres	20-22	54	47
concentrate injection tuyeres	0	0	10
Type of charge	100% to top of bath	100% to top of bath	95% thru tuyeres, 5% to top of bath
Feed, t/day (dry basis)			
new concentrate	1400-1500(30% Cu)	2200-3000	2400 (35% Cu)
silica flux	190-210	200-250	170-200
slag concentrate	0	300-350	210-230
recycle dust	20 Noranda 20 converter 20 baghouse	50-75 Noranda + converter	40-50 Noranda
reverts	0	100-250	120-140
other	5 granulated converter slag	liquid converter slag	liquid converter slag
Tuyere blast details			
volume% O ₂	48	35-45	36-40
flowrate per tuyere, Nm ³ /minute	17	19-23	20-22
Products, tonnes/day			
matte, tonnes/day	600-700 (72% Cu)	800-1000 (70-72% Cu; 3-5% Fe)	1100-1150(75% Cu)
slag, tonnes/day	800-900 (2-3% Cu)	1600-2200 (3-5% Cu)	1400-1500 (5-6% Cu)
mass% SiO ₂ /mass% Fe	0.69	0.6-0.7	0.59
Cu recovery, Noranda slag	electric furnace	solidification/flotation	solidification/flotation
Cu recovery, converter slag	molten to Noranda furnace	molten to Noranda furnace	molten to Noranda furnace
offgas, thousand Nm ³ /hour	52	135-150	57-63
vol% SO ₂ , leaving furnace (wet)	16	15-20	25
dust production, t/day	20	50-75	40-50 (all recycled)
matte/slag/offgas T, °C	1190/1190/1200	1200/xx/xx	1215/1215/1243
Consumptions, kg/tonne of concentrate			
hydrocarbon fuel	26 kg coal 9 Nm ³ natural gas	0-10 coal in solid charge	5-10 metallurgical coke in solid charge
oxygen	130-150		170

The tuyeres are periodically cleared by breaking blockages with a steel bar. This ensures an even flow of 'blast'. A Gaspé puncher is used, Fig. 1.6a.

The furnace is equipped with a rotation mechanism. It is used to correctly position the tuyere tips in the molten matte layer and to roll the tuyeres above the liquids during maintenance and repair. It also automatically rolls the tuyeres above the liquids in the event of a power failure or other emergency.

7.2 Reaction Mechanisms

The reaction mechanisms in the Noranda furnace are:

- (a) sulfide concentrates and SiO_2 flux are thrown into the furnace from a 'slinger' belt – they are quickly absorbed and melted when they fall into the tuyere-blast stirred matte/slag bath
- (b) the dense sulfide drops fall toward the matte layer and are oxidized by tuyere O_2 and by Cu and Fe oxides
- (c) Fe oxides react with SiO_2 flux to form slag – which rises to the top of the bath
- (d) SO_2 from the oxidation reactions rises through the bath and leaves the furnace along with N_2 from the tuyere blast and $\text{CO}_2/\text{H}_2\text{O}_{(\text{g})}$ from hydrocarbon combustion.

Other parts of the charge, e.g. scrap, sludges and recycle materials melt and undergo oxidation and slagging. Oxides rise to the slag layer while copper and precious metals (from scrap) descend to the matte layer.

7.2.1 Tuyere injection of concentrates

The new Noranda furnace in the Altonorte smelter (startup, 2002) will dry 95% of its concentrate and blow it into the furnace through 10 dedicated 6.35 cm tuyeres. The remainder of the concentrates along with flux, reverts and scrap will be charged moist on the bath surface. The advantages of tuyere-injection are:

- (a) uniform distribution of concentrate along the furnace, hence uniform lengthwise heat generation
- (b) a small energy requirement due to the absence of H_2O in the dried concentrate
- (c) little H_2O in the offgas (giving efficient cooling in the furnace's water evaporation offgas-cooling system)
- (d) little dust carryout, ~1% of solid feed.

These advantages are expected to outweigh the capital and operating costs of the injection equipment.

In the furnace, the tuyere-injected concentrates are quickly melted and oxidized in front of the tuyeres, Eqn. 7.1. The resulting matte falls while Fe oxide rises and meets with top-charged silica flux to form molten slag.

7.2.2 Separation of matte and slag

Matte and slag are intimately mixed in the tuyere region. They are allowed to separate in a quiet tuyere-free zone at the slag-tap end of the furnace, Fig. 7.1. Matte falls, SO_2/N_2 gas rises and slag forms a layer dilute enough in Cu for tapping from the furnace. It contains ~5% Cu, 30% dissolved and 70% in entrained matte. It is tapped from the furnace and sent for Cu recovery to solidification/ comminution/flotation or electric furnace settling, Chapter 11.

7.2.3 Impurity behavior

Table 7.2 describes impurity behavior during Noranda smelting. It shows that harmful impurities report mainly to slag and offgas. It also shows that most As, Bi, Pb and Sb can be removed from the Cu circuit by not recycling offgas 'solids' to smelting or converting.

Table 7.2. Impurity distribution during Noranda smelting (Harris, 1999). Most impurities report to slag and offgas. Ni mostly reports to matte -- and continues with Cu into the electrorefinery where it is recovered as nickel sulfate byproduct. Au, Ag and Pt metals also follow Cu.

Element	% to matte	% to slag	% to offgas
As	8	12	80
Bi	9	12	79
Ni	77	22	1
Pb	13	13	74
Sb	15	31	54
Zn	6	84	10

7.2.4 Scrap and residue smelting

The feed to the Noranda furnace at Noranda, Quebec includes up to 20% scrap. The scrap includes precious metal and Cu:

- slags
- ashes
- residues (up to 14% moisture)
- wire cables
- precious metal ingots
- jewelry
- telephone scrap
- automobile parts
- precious metal computer and electronic scrap.

Tuyere-blast stirring in the Noranda furnace rapidly melts these materials and causes their precious metals and Cu to be rapidly absorbed in matte. Also, the high temperature and intensity of smelting cause potentially harmful organic compounds to be oxidized completely to CO_2 and $\text{H}_2\text{O}_{(\text{g})}$ *.

7.3 Operation and Control

Noranda smelting is started by heating the furnace with hydrocarbon burners. Molten matte is then poured in through the furnace mouth (tuyeres elevated). Once a meter or so of molten matte is in place, the tuyere 'blast' is started and the tuyeres are rolled into the molten matte to begin oxidation and heat generation.

Concentrate and flux feeding is then started and normal smelting is begun. About a week is taken to heat the furnace, provide the molten matte and attain full production.

The initial molten matte is prepared by melting matte pieces or high-Cu concentrate in a converter or unused furnace in the smelter.

Smelting is terminated by inserting hydrocarbon burners into the furnace, stopping smelting and pouring slag then matte out the furnace mouth.

7.3.1 Control

Once steady operation has been reached, the furnace is controlled to:

- (a) smelt concentrates, scrap and other metal-bearing solids at the company's prescribed rates
- (b) produce matte and slag of prescribed composition and temperature
- (c) maintain constant depths of matte and slag in the furnace.

Matte composition is controlled by adjusting the ratio:

$$\frac{\text{total O}_2 \text{ input rate}}{\text{solid feed input rate}}.$$

The ratio is **increased to increase** matte grade (i.e. to increase Fe and S oxidation) and vice versa. It is often altered by adjusting solid feed input rate at a constant O_2 -in-blast injection rate. This gives constant rate SO_2 delivery to the sulfuric acid plant.

Matte/slag temperature ($\sim 1200^\circ\text{C}$) is controlled by altering the ratio:

*Smelters take great care with beryllium alloy scrap in their feed. Beryllium can be carcinogenic so contact with it must be avoided.

$$\frac{\text{hydrocarbon combustion rate}}{\text{solid feed mixture input rate}}$$

The ratio is increased to raise temperature and vice versa. It is altered by adjusting coal/coke feed rate and natural gas combustion rate.

Matte/slag temperature may also be controlled by adjusting the N₂/O₂ ratio of the tuyere 'blast'.

Slag composition is controlled by adjusting the ratio:

$$\frac{\text{flux input rate}}{\text{solid feed mixture input rate}}$$

The target SiO₂/Fe ratio is ~0.65.

In addition, the mix of metal-bearing solid feed to the furnace is controlled to keep impurity levels-in-matte at or below pre-set values. This is done to avoid excessive impurity levels in the smelter's product anodes.

Feed rates and O₂ input rate are monitored continuously. Matte samples are taken every hour (analyses being returned 15 minutes later) – slag samples every two hours. Bath temperature is monitored continuously with optical pyrometers in two tuyeres (Prevost *et al.*, 1999).

Matte and slag depths are monitored hourly with a vertical steel bar. This is done to:

- (a) ensure that there is enough matte above the tuyeres for efficient O₂ utilization
- (b) give an even blast flow by maintaining a constant liquidostatic pressure at the tuyere tips (Wraith *et al.*, 1999).

The depths are adjusted by altering matte and slag tapping frequency.

7.4 Production Rate Enhancement

The smelting rate of the furnace at Noranda, Quebec has more than doubled since 1978. Most of the increase has been due to increased O₂-enrichment of the tuyere blast. Oxygen enrichment increases the rate at which O₂ is blown through the tuyeres for a given blower capacity. This increases concentrate oxidation rate, hence heat evolution and melting rates.

7.4.1 *Choice of matte grade*

The Noranda process was initially conceived as a direct-to-copper smelting process. The furnace at Noranda produced molten copper from 1973 to 1975. It was switched to high-grade matte production to (i) lower impurity levels in the smelter's anode copper and (ii) increase smelting rate. All Noranda furnaces now produce 72-75% Cu matte. Matte grade is discussed further in Section 7.12.1.

7.5 **Noranda Future**

The new millennium has seen Noranda smelting expand into Chile and China – and reinstate itself in Australia. Tuyere injection of dry concentrates into the Altonorte smelter's new furnace will increase the thermal and production efficiency of the process. Noranda smelting will soon account for more than 5% of the world's copper smelting.

7.6 **Teniente Smelting**

Teniente smelting shares many features with Noranda smelting (Mackey and Campos, 2001; Harris, 1999). It:

- (a) uses a cylindrical furnace with submerged tuyeres, Fig. 7.2
- (b) blows oxygen enriched air through the tuyeres into molten matte
- (c) feeds dry concentrate through dedicated tuyeres
- (d) (often) charges moist concentrate onto its matte/slag surface
- (e) produces high-Cu matte, which it sends to Peirce-Smith converting.

Table 7.3 gives operating details of three Teniente smelting furnaces.

7.6.1 *'Seed' matte*

Teniente smelting evolved from smelting concentrates in Peirce-Smith converters, Chapter 9. Early Teniente smelting always included molten matte (from another smelting furnace) in its charge. Some Teniente furnaces still do, Table 7.3.

Teniente furnaces have proven, however, to be successful stand-alone smelting units. Molten matte is no longer needed. This has permitted shutdown of many reverberatory furnaces that formerly supplied Teniente furnaces with matte. This trend is continuing.

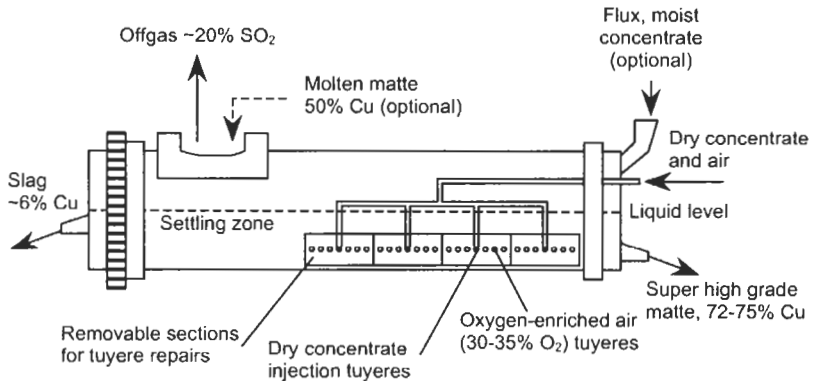


Fig. 7.2. Schematic of Teniente smelting furnace, ~20m long. The furnace is cylindrical. It is rotated to position its tuyeres properly. The concentrate injection system and tuyeres are completely separate from the oxygen-air 'blast' system. The injection system operates at ~7 atmospheres gage – the 'blast' system at ~1.25 atmospheres gage. A furnace typically has 4 concentrate-injection tuyeres and 45 'blast' tuyeres. Operating details of Teniente furnaces are given in Table 7.3. A tuyere is shown in Fig. 9.1b.

7.7 Process Description

Teniente furnaces are 4 to 5 m diameter and 14 to 22 m long inside refractory. The furnace barrels are steel, ~5 cm thick, lined with about 0.5 m of magnesia-chrome refractory. The furnaces have 35 to 50 tuyeres (5 or 6 cm diameter) along 65% of their length. The remaining 35% of the furnace length is a quiet Cu-from-slag settling zone.

All Teniente furnaces blow dry concentrate into the furnace through 3 or 4 dedicated tuyeres, Table 7.3. Flux, recycle materials and (often) moist concentrate are charged onto the matte/slag surface. Reactions are similar to those in the Noranda furnace.

The principal products of the process are:

- (a) molten matte, 72 to 75% Cu matte
- (b) molten Fe-silicate slag, ~6% Cu
- (c) offgas, 12-25 volume% SO₂.

7.8 Operation (Alvarado *et al.*, 1995; Torres, 1998)

Teniente smelting is begun by:

Table 7.3. Operating details of three Teniente furnaces. All inject dried concentrate through tuyeres. All are autothermal.

Smelter	CODELCO Caletones, Chile	Mexicana de Cobre, Mexico	ZCCM, Nkana Zambia
Startup date	1989	1997	1994
Furnace details, inside brick			
length × diameter, m	21 × 4.2	20.8 × 4.5	18.2 × 4.5
slag layer thickness	0.9	0.4	0.3-0.5
matte layer thickness	1	1.1	1
active slag tapholes	1	1	1
active matte tapholes	2	1	1
auxiliary burners	1	0	1
Tuyere details			
tuyeres (total)	47	44	40
diameter, cm	6.35	6	5
active air blast tuyeres	42	44	36
concentrate injection tuyeres	4	3	starting 2001
Feed, tonnes/day (dry basis)			
dry concentrate through tuyeres	1850 (31.8% Cu)	1084 (28% Cu)	starting 2001
moist concentrate onto bath surface	0	216 (8% H ₂ O)	300 (32% Cu) 8% H ₂ O
molten matte	0-100		920-1035
silica flux	200 (95% SiO ₂)	121 (90% SiO ₂)	70-100 (90%)
other	120 molten slags 200 solid reverts		
Tuyere blast details			
volume% O ₂	35	29	32
flowrate per tuyere, Nm ³ /minute	20	18	
Products, tonnes/day			
matte, tonnes/day	775 (74.3% Cu)	439 (72% Cu)	625 (74-75%)
slag, tonnes/day	1500 (6-8% Cu)	740 (5% Cu)	460 (4-6% Cu)
mass% SiO ₂ /mass% Fe	0.67	0.6	0.6-0.8
Cu recovery, Teniente slag	Teniente slag cleaning furnace	electric furnace	recycle to rever- beratory
Cu recovery, converter slag	recycle to smelting furnace	electric furnace	recycle to rever- beratory
offgas, thousand Nm ³ /hour	60	135	25
volume% SO ₂ , leaving furnace	25	12	19-22
matte/slag/offgas temperatures, °C	1220/1240/1250	1220/1240/1220	1200/1250/1250
Consumptions, kg/tonne of concentrate			
hydrocarbon fuel	0 (autothermal)	0 (autothermal)	0 (autothermal)
oxygen	180	266	140

- (a) preheating the furnace with hydrocarbon burners
- (b) charging molten matte to the furnace (with tuyeres elevated)
- (c) blowing oxygen-enriched air through the tuyeres
- (d) rotating the tuyeres into the matte
- (e) starting normal feeding of concentrate, flux and recycles.

Feed rates are then gradually increased till full production is attained. Startup to full production takes about one week.

The initial charge of matte comes from another furnace in the smelter, i.e. a reverberatory, flash or electric slag cleaning furnace. In smelters without another furnace, the initial molten matte is prepared by melting matte pieces or high-grade concentrate in a converter or other unused furnace.

7.9 Control

Steady operation of a Teniente furnace consists of:

- (a) continuous injection of dried concentrate and air through 3 or 4 dedicated tuyeres
- (b) continuous blowing of oxygen-enriched air through 'blast' tuyeres
- (c) continuous surface charging of flux and solid recycle materials onto the bath surface
- (d) continuous withdrawal of offgas
- (e) intermittent tapping of matte and slag
- (f) occasional recycling of molten converter matte through the furnace mouth.

The operation is controlled to:

- (a) produce matte and slag of specified compositions and temperature
- (b) protect the furnace refractories, Section 7.9.2

while:

- (c) smelting solid feed at a specified or maximum rate.

7.9.1 Temperature control

Liquid temperature is measured by optical pyrometer (e.g. MIKRON M78 two-color infrared pyrometers [Mikron Instrument Company, 2002]). The pyrometers are sighted on the slag tapping stream or onto the molten bath itself.

Slag temperature ($\sim 1240^{\circ}\text{C}$) is controlled by adjusting revert feed rates and blast oxygen enrichment level (i.e. N_2 'coolant' input rate). It is typically controlled within about $\pm 10^{\circ}\text{C}$ (Torres, 1998).

7.9.2 Slag and matte composition control

Matte and slag compositions are measured by on-site X-ray analysis. Results are available 20 to 30 minutes after a sample is taken.

Slag composition is controlled by adjusting flux feed rate. It is controlled to an SiO_2/Fe ratio of 0.65. This, plus good temperature control gives a slag Fe_3O_4 content of $20 \pm 4\%$, which maintains a protective (but not excessive) layer of solid magnetite on the furnace refractory.

Matte %Cu is controlled by adjusting:

$$\frac{\text{total O}_2 \text{ input rate}}{\text{concentrate feed rate}}$$

This ratio controls the degree of Fe and S oxidation, hence matte composition.

7.9.3 Matte and slag depth control

Matte and slag depths are measured frequently by inserting a steel bar vertically from above. Matte depth is controlled to give $\sim 1/2$ m of matte above the tuyeres. This ensures efficient use of tuyere O_2 .

Heights of matte and slag above the tuyeres are also controlled to be as constant as possible. This gives a constant liquidostatic pressure above the tuyeres, hence a constant flow of blast. The heights are kept constant by adjusting matte and slag tapping frequencies.

7.9.4 Furnace shell thermography

Several smelters do a weekly temperature scan on their Teniente furnace shell (Torres, 1998; Alvarado *et al.*, 1995). Infrared (e.g. Thermacam [FLIR Systems, 2002]) imaging is used.

The infrared image gives a picture of refractory wear in the furnace. It is particularly useful in identifying thin refractory 'hot spots'.

Refractory wear in these 'hot spot' regions can be slowed by (i) spraying water externally on the 'hot spot' while (ii) creating conditions for rapid magnetite deposition (low SiO_2 -in-slag; low temperature) inside the furnace.

7.10 Impurity Distribution

Table 7.4 shows impurity behavior during Teniente smelting. As with Noranda smelting, As, Bi, Pb, Sb and Zn are largely removed in slag and offgas. Se is

removed less efficiently.

Teniente impurity removal appears to be slightly less effective than Noranda impurity removal, Table 7.2. This may, however, be due to differences in furnace feeds and measurement techniques.

Table 7.4. Impurity distribution during Teniente smelting (Harris, 1999; *Mendoza et al, 1995).

Element	% to matte	% to slag	% to offgas
As	6	7	87
Bi	23	40	37
Ni	80	19	1
Pb	22	25	53
Sb	19	30	51
Se*	58	39	1
Zn	11	85	4

7.11 Teniente Future

The last decade of the 20th Century saw Teniente smelting free itself from its dependence on 'seed matte' from another smelting process. It also saw installation of Teniente furnaces in Africa and North America. Teniente smelting will soon reach 15% of world copper smelting.

7.12 Discussion

7.12.1 Super-high matte grade and SO₂ capture efficiency

Noranda and Teniente smelting oxidize most of the Fe and S in their concentrate feed. This is shown by the super-high Cu grade (72 to 75% Cu) of their product matte. Extensive S oxidation is advantageous because continuous smelting furnaces capture SO₂ more efficiently than discontinuous batch converters.

Noranda and Teniente smelting gain this SO₂ advantage from the violent stirring created by submerged injection of blast. The stirring dissolves and suspends magnetite in slag, preventing excessive deposition on the furnace refractories even under the highly oxidizing conditions of super-high grade matte production.

7.12.2 Campaign life and hot tuyere repairing

The campaign lives of Noranda and Teniente furnaces are one to two years. Refractory wear in the tuyere region is often the limiting factor.

Most Teniente furnaces mount their tuyeres in 4 detachable panels (Mackey and

Campos, 2001). These panels can be detached and replaced without cooling the furnace. This significantly improves furnace availability (Beene *et al.*, 1999) but may eventually weaken the furnace structure.

7.12.3 Furnace cooling

Chapters 5 and 6 show that flash furnaces need to be cooled by many copper water-jackets and sprays. Noranda and Teniente furnaces use very little water cooling due to their simple barrel design and submerged oxidation reactions. This cooling simplicity is a significant advantage.

7.12.4 Offgas waste heat recovery

Almost all Noranda and Teniente furnaces cool their offgases by water evaporation rather than by waste heat boilers.

Improved smelting control and increased waste heat boiler reliability may make waste heat boilers economic for future Noranda and Teniente furnace installations. Waste heat boiler steam will be especially valuable for steam drying (Section 5.2.2) of tuyere-injection concentrates.

7.13 Summary

Noranda and Teniente smelting are submerged-tuyere smelting processes. They oxidize Fe and S by blowing oxygen-enriched air through tuyeres into a matte-slag bath. The principal product is super-high grade matte, 72-75% Cu.

Both use horizontal refractory-lined cylindrical furnaces with a horizontal line of submerged tuyeres. The furnaces are rotatable so that their tuyeres can be rolled out of the liquids when blowing must be interrupted.

Concentrate feed is dried and blown into the matte/slag bath through dedicated tuyeres or charged moist onto the bath surface. Tuyere injection is increasing due to its even concentrate and heat distributions; high thermal efficiency and tiny dust evolution.

Submerged blowing of blast causes violent stirring of the matte/slag bath. This results in rapid melting and oxidation of the furnace charge. It also prevents excessive deposition of solid magnetite in the furnace even under highly oxidizing conditions. The violent stirring also permits extensive smelting of scrap and reverts.

Noranda and Teniente smelting account for 15 to 20% of world copper smelting. They are the dominant smelting method in Chile and are used around the world.

Suggested Reading

Alvarado, R., Lértora, B., Hernández, F. and Moya, C. (1995) Recent development in the Teniente Converter. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Volume IV Pyrometallurgy of Copper*, ed. Chen, W.J., Díaz, C., Luraschi, A. and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 83 101.

Harris, C. (1999) Bath smelting in the Noranda Process Reactor and the El Teniente Process Converter compared. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Volume V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 305 318.

Mackey, P.J. and Campos, R. (2001) Modern continuous smelting and converting by bath smelting technology. *Canadian Metallurgical Quarterly*, **40**(3), 355 375.

Torres, W.E. (1998) Current Teniente Converter practice at the SPL Ilo smelter. In *Sulfide Smelting '98, Current and Future Practices*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 147 157.

References

Alvarado, R., Lértora, B., Hernández, F. and Moya, C. (1995) Recent development in the Teniente Converter. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Volume IV Pyrometallurgy of Copper*, ed. Chen, W.J., Díaz, C., Luraschi, A. and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 83 101.

Beene, G., Mponda, E. and Syamujulu, M. (1999) Breaking new ground – recent developments in the smelting practice at ZCCM Nkana Smelter, Kitwe, Zambia. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Volume V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 205 220.

FLIR Systems (2002) Thermography www.flir.com

Harris, C. (1999) Bath smelting in the Noranda Process Reactor and the El Teniente Process Converter compared. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Volume V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 305 318.

Mackey, P.J. and Campos, R. (2001) Modern continuous smelting and converting by bath smelting technology. *Canadian Metallurgical Quarterly*, **40**(3), 355 375.

Mendoza, H., Luraschi, A.A., Riveros, G.A. and Cerna, M.H. (1995) Use of a predictive model for impurity behavior at the Chuquicamata smelter. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Volume IV Pyrometallurgy of Copper*, ed. Chen, W.J., Díaz, C., Luraschi, A. and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 281 298.

Mikron Instrument Company (2002) M78 fiber optic 2-color infrared temperature transmitter www.mikroninst.com

Norsmelt (2002), The Noranda smelting process. www.norsmelt.com

Prevost, Y., Lapointe, R., Levac, C.A. and Beaudoin, D. (1999), First year of operation of the Noranda continuous converter. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Volume V Smelting Operations and Advances*, ed. George, D.B. Chen, W.J. Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 269-282.

Torres, W.E. (1998) Current Teniente Converter practice at the SPL Ilo smelter. In *Sulfide Smelting '98, Current and Future Practices*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 147 157.

Wraith, A.E., Mackey, P.J., Levac, C.A. and Element, P. (1999), Converter and bath smelting vessel design – blast delivery and tuyere performance: a reassessment of design characteristics. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Volume V Smelting Operations and Advances*, ed. George, D.B. Chen, W.J. Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 67 82.

CHAPTER 8

Ausmelt/Isasmelt Matte Smelting

Chapters 5 and 6 describe flash smelting, the predominant worldwide technology for producing copper mattes. The advantages of flash smelting are well-known and the technology is well established. However, flash smelting also has disadvantages. The biggest is its use of fine, dry concentrate particles as feed. Fine particles react faster, which is desirable. However, they also settle less quickly. As a result, flash furnaces generate considerable quantities of dust. To reduce this dust generation, a large settling area is built into flash furnaces. This increases the size of the vessel, and thus its cost.

In 1971, researchers at the [Australian] Commonwealth Scientific and Industrial Research Organization began investigating the use of top-lancing technology for injecting coal into tin slags to improve reduction kinetics (Pritchard and Hollis, 1994). This research led to the development of technology suitable for a variety of pyrometallurgical applications (Robilliard, 1994; Mounsey and Robilliard, 1994), including smelting and converting of sulfide concentrates. This technology is now marketed by two separate organizations under the names Ausmelt and Isasmelt. The technology has found commercial application worldwide. It has become a significant factor in copper smelting.

Both Ausmelt and Isasmelt smelting are based on the technology developed at CSIRO in the 1970's. Their furnaces (Fig. 8.1, Table 8.1) and operating procedures (Table 8.2) are similar. Because of this, they are described together throughout.

8.1 Basic Operations

Ausmelt/Isasmelt copper smelting entails dropping moist solid feed into a tall cylindrical furnace while blowing oxygen-enriched air through a vertical lance into the furnace's matte/slag bath (Pritchard and Hollis, 1994). The products of

the process are a matte/slag mixture and strong SO_2 offgas. The matte/slag mixture is tapped periodically into a fuel-fired or electric settling furnace for separation. The settled matte (~60% Cu) is sent to conventional converting. The slag (0.7% Cu) is discarded.

The offgas (25% SO_2) is drawn from the top of the smelting furnace through a vertical flue. It is passed through a waste heat boiler, gas cleaning and on to a sulfuric acid plant. A small amount of oxygen is blown through the side of the smelting furnace or lance (about halfway up) to ensure that sulfur leaves the furnace as SO_2 rather than S_2 . This prevents sulfur condensation in the gas cleaning system.

Most of the energy for smelting comes from oxidizing the concentrate charge. Additional energy is provided by combusting (i) oil, gas, or coal fines blown through the vertical lance and (ii) coal fines in the solid charge.

8.2 Feed Materials

Ausmelt/Isasmelt feed is moist concentrate, flux and recycle materials, sometimes pelletized, Table 8.2. Drying of the feed is not necessary because the smelting reactions take place in the matte/slag bath rather than above it. Moist feed also decreases dust evolution.

Oxygen enrichment of the air blown into an Ausmelt/Isasmelt furnace is standard practice. The 'blast' typically contains 50 to 60 volume% O_2 . O_2 levels higher than this tend to cause excessive lance wear.

Because of (i) this upper limit on O_2 enrichment and (ii) the presence of moisture in the solid feed, autothermal operation is usually not achieved. Instead, hydrocarbon fuel is added. Ausmelt/Isasmelt furnaces are designed to use natural gas, oil and coal. A cool lance tip is important for reducing lance wear. As a result, coal is often added to the feed as a partial substitute for flammable fuel oil and natural gas (Binegar, 1995).

8.3 The Isasmelt Furnace And Lance (Isasmelt Technology, 2002)

Figure 8.1 shows an Isasmelt furnace. It is a vertically aligned steel barrel, ~3.5 m in diameter and ~12 m high. Depending on size, it smelts up to 3000 tonnes of concentrate per day. It is lined inside with chrome-magnesite refractory, sometimes backed with copper watercooling blocks, Table 8.1. Its roof consists of water-cooled copper slabs or steel panels (Binegar, 1995).

Figure 8.2 shows an Isasmelt lance. It consists of a stainless steel outer pipe (up

to 0.5 m diameter) for oxygen-enriched air and a steel inner pipe for oil or natural gas. The outer pipe is normally immersed about 0.3 m into the furnace slag. The inner pipe ends about 1 m above the slag surface.

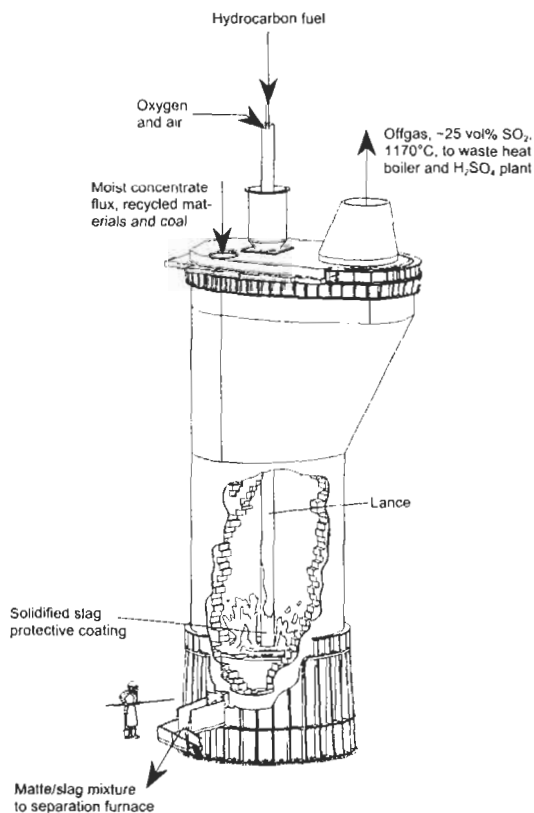


Fig. 8.1. Cutaway view of Isasmelt furnace, 2001. A furnace is typically ~3.5 m diameter and 12 m high. It smelts up to 3000 tonnes of new concentrate per day. The outside of the furnace is often watercooled with copper cooling blocks. The main product of the furnace is a mixture of molten matte and slag, which is sent to an electric or gas-fired matte/slag separation furnace.

Table 8.1. Construction details of three Isasmelt furnaces and one Ausmelt furnace. A description of a lance 'swirler' is given on the last line.

Smelter	Mt. Isa Mines Mt. Isa, Australia	Sterlite Copper Tuticorin, India	Phelps Dodge Miami, AZ, USA	Zhong Tiao Shan Houma, P.R. China
Furnace type	Isasmelt	Isasmelt	Isasmelt	Ausmelt
Startup date	1992	1996	1992	1999
Furnace details				
diameter, m	3.75	2.85	3.5	4.4
height, m		11	13	11.9
bath depth, m	1-2	0.6-2	1-2	1.2
number of tapholes	1	2 (1 in use)	2	1
description of taphole	hole in water- cooled Cu block	410 mm diame- ter hole in wa- ter-cooled Cu block	hole in water- cooled Cu block	hole in refractory- lined Cu block
auxiliary burners		4 m long pipe furnace oil/air burner	yes	yes
furnace cooling system		internal water- cooling jackets (tapping block and below) and shell water cur- tain	water- cooled Cu blocks	
Lance details				
inside fuel line pipe diameter		8 mm		
construction material	mild steel	mild steel	mild steel	
lance pipe diameter, mm	500 mm	250 & 300 mm	500 mm	
construction material	stainless steel	316L stainless steel	stainless steel	
tip penetration into bath	0.3 m	0.3m	0.45 m	0.35 m
overall lance length		15.5 m	17 m	15.6 m
swirler description		6 vanes, ~235 mm long, posi- tioned ~600 mm from lance tip		

Table 8.2. Operational details of three Isasmelt furnaces and one Ausmelt furnace.

Smelter	Mt. Isa Mines Australia	Sterlite Copper Tuticorin, India	Phelps Dodge Miami, USA	Zhong Tiao Shan P.R. China
Furnace Type	Isasmelt	Isasmelt	Isasmelt	Ausmelt
Feed details, tonnes per day				
type of charge	moist, pelletized	moist, non-pelletized	moist, non-pelletized	
% moisture in charge	10	6-8	10	
new concentrate (dry basis)	2850 (25-27% Cu)	1500-1600 (27-31% Cu)	2200 (28% Cu)	625 (17-22% Cu)
silica flux	75	260	340	
lime flux	0	40	30	
reverts	100	100-150	240	
other	50	20 tonnes esp dust plus sludges	50	
coal	10			
Lance inputs				
blast flowrate, Nm ³ /minute	750	300	481	333
volume% O ₂ in blast	60	63	50	40
hydrocarbon fuel /tonne concentrate	natural gas	furnace oil 23 kg	natural gas 34 Nm ³	coal
O ₂ , kg/tonne of concentrate	~290 (author estimate)	228	~180 (author estimate)	~285 (author estimate)
Products,				
matte/slag mix- ture destination	rotary holding furnace	rotary holding furnace	electric furnace	holding furnace
offgas destination	acid plant via waste heat boiler	acid plant via water evap- oration gas cooler	acid plant via waste heat boiler	acid plant
offgas flowrate		70 000 Nm ³ /hr	54 000 Nm ³ /hr	
volume% SO ₂	27	22-25	20-25	11-13
dust production, tonnes/day	25	20	15	6
liquids/offgas temperatures, °C	1220/1220	(1150- 1180)/1150	1170/1050	(1200-1300)/x
Liquid products after settling				
matte, tonnes/day	1300 62% Cu	700 61-63% Cu	1100 58% Cu	160 60% Cu
slag, tonnes/day	1270		1150	
%Cu		0.75-0.8	0.7	~0.6
%SiO ₂ /%Fe	0.78	0.75	0.7	0.8
destination	mill/ concentrator	granulation /discard	discard	granulation /discard

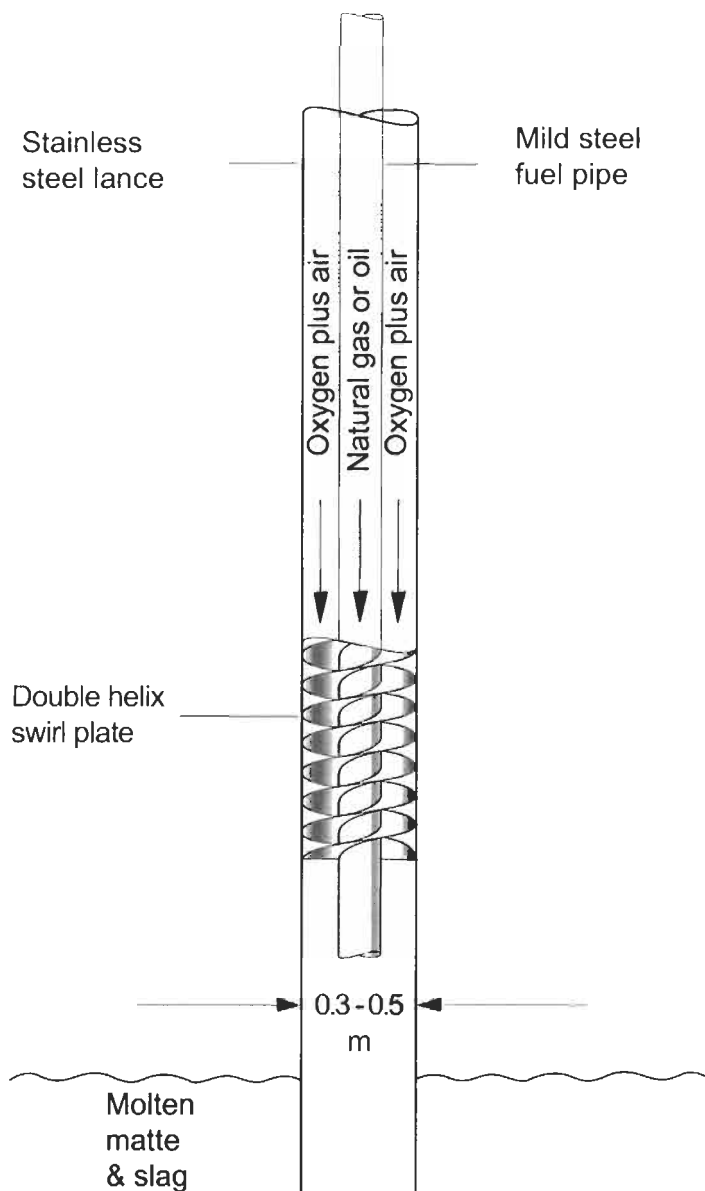


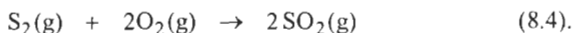
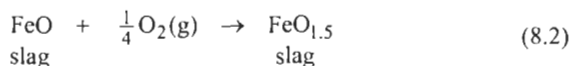
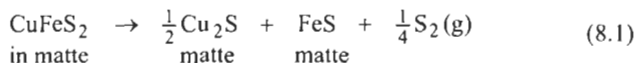
Fig. 8.2. Sketch of Isasmelt lance tip. Vanes for swirling blast down the lance tip are shown. The swirling gives rapid heat transfer from lance to blast, causing a protective layer of slag to freeze on the outside of the lance tip (Solnordal and Gray, 1996).

The lance tip is cooled by swirling the enriched air 'blast' in the annulus between the pipes. The swirled gas extracts heat from the outside pipe and causes a protective slag layer to freeze on the pipe surfaces. Helical swirl vanes in the annulus are used to create this effect, Fig. 8.2.

Despite this, the immersed lance tip slowly erodes away. The lance is lowered to compensate for this erosion. It is removed and replaced when ~1 m has eroded – about every week (Binegar, 1995). The used lances are refurbished for re-use by welding a new 1 m section of outside pipe to the bottom tip. Lance wear is minimized by avoiding excessive immersion and %O₂-in-blast.

8.4 Smelting Mechanisms

Ausmelt/Isasmelt smelting is different from flash smelting in that the smelting reactions take place primarily in the bath rather than above the melt. As a result, the reaction sequence is different. It is commonly believed that dissolved magnetite in the slag serves as a catalyst of sorts for the overall process (Binegar, 1995; Mounsey *et al.*, 1999). Mounsey *et al.*, list the reaction sequence as follows:



As a result, the presence of about 5% magnetite in the slag is important (Binegar, 1995). This requires a low bath temperature (1150–1200°C) and low silica/iron ratio (0.7–0.8 for Isasmelt, 0.6–0.7 for Ausmelt).

8.4.1 Impurity elimination

Player (1996) reports impurity elimination into slag and offgas during Isasmelt smelting as: 91% As, 85% Cd, 75% Bi, 68% Zn, 60% Sb, 60% Tl, 45% Pb, and 30% Te. Elimination of As, Bi, Pb, and Sb is encouraged by decreasing oxygen enrichment. Offgas solids are recycled to the smelting furnace for Cu recovery, so they are not usually an escape route for impurities.

8.5 Startup and Shutdown

Smelting is started by:

- (a) preheating the furnace
- (b) slowly charging about 2 m of solid slag pieces
- (c) melting the slag, using the lance as an oxy-fuel burner
- (d) immersing the smelting lance in the molten slag
- (e) beginning normal concentrate smelting.

At least one day is required. Smelting is terminated by stopping the solid feed, draining the furnace and turning off the lance. The furnace is then allowed to cool at its natural rate.

Steady operation consists of continuous feeding of solid charge through the roof feed port and continuous blowing of oxygen-enriched air into the molten bath. The furnace is computer controlled to give a specified concentrate smelting rate while producing matte and slag of desired composition and temperature. Matte/slag temperature is sensed by thermocouples embedded in the furnace walls. It is controlled by adjusting the rate at which fossil fuel is supplied through the lance.

Matte and slag compositions are determined by X-ray fluorescence analysis of samples from each matte/slag tap. The compositions are controlled by adjusting the furnace's O_2 /concentrate and flux/concentrate input ratios.

8.6 Current Installations

Ausmelt and Isasmelt have been active in commercializing their technology over the past ten years. This has resulted in several new installations. Ausmelt's installations include (Ausmelt Commercial Operations, 2002):

- (a) a smelter for Cu/Ni leach residue operated by Anglo American in Bindura, Zimbabwe (1996)
- (b) a lead smelter converted to copper matte production for Consolidated Goldfields in Tsumeb, Namibia (1996)
- (c) the Zhong Tiao Shan Cu smelting and converting facility in Houma, China (1999)
- (d) a smelter to be operated by Anhui Tongdu Copper in Tongling, China (startup, 2002).

Isasmelt's copper processing installations include (Isasmelt Installations, 2002):

- (a) Mt. Isa smelter, Mt. Isa, Queensland, Australia (1992)
- (b) Phelps Dodge smelter, Miami, Arizona, USA (1992)

- (c) Sterlite smelter, Tuticorin, India (1995)
- (d) Union Minière secondary copper smelter, Chapter 22, Hoboken, Belgium (1997)
- (e) Yunnan Copper smelter under construction at Kunming, China (startup 2001).

8.7 Other Coppermaking Uses of Ausmelt/Isasmelt Technology

Ausmelt/Isasmelt smelting is the outgrowth of technology originally designed for use in tin smelting (Robilliard, 1994). Ausmelt in particular have been active since then in developing uses for their furnace beyond sulfide matte smelting (Hughes, 2000).

One of these is matte converting, which has been demonstrated on a small scale. The Ausmelt furnace for converting is similar to that used for smelting (Mounsey *et al.*, 1999). In fact, in small smelters, smelting and converting can be performed in the same furnace (Mounsey *et al.*, 1998).

The matte/slag mixture produced by smelting is allowed to settle, the slag is tapped, and the lance is reinserted into the matte for converting. A two-step process is used. It begins by converting the matte to molten Cu_2S (white metal) followed by tapping slag. It is finished by oxidizing the Cu_2S to copper and SO_2 . As in the case of smelting, magnetite in the slag appears to act as a catalyst for the converting reactions.

The process is autothermal, although some coal is added to reduce the copper oxide content of the slag to about 15% Cu. The first Ausmelt furnace specifically dedicated to matte converting recently came on-line in the Houma copper smelter in China (Mounsey *et al.*, 1999).

Unfortunately, discontinuous two-step smelting/converting sends an intermittent stream of SO_2 to acidmaking. For this reason, it is unlikely to become prominent.

Ausmelt technology is also useful for recovering copper from non-sulfide materials, particularly slags and sludges (Hughes, 2000). Its ability to control air and fuel inputs means that conditions can be changed from oxidizing to reducing without transferring material to a second furnace. This is particularly effective for smelting Cu/Ni hydrometallurgical residues.

8.8 Summary

Ausmelt and Isasmelt smelting is done in vertically aligned cylindrical furnaces

~3.5 m diameter and 12 m high. The smelting entails:

- (a) dropping moist concentrate, flux and recycle materials into a molten matte/slag bath in a hot furnace
- (b) blowing oxygen-enriched air through a vertical lance into the matte/slag bath.

Most of the energy for smelting is obtained from oxidizing the concentrate's Fe and S.

The vertical lance consists of two pipes – the inner for supplying supplementary hydrocarbon fuel, the annulus for supplying oxygen-enriched air. The outer pipe penetrates ~0.3 m into the bath. The inner pipe ends ~1 m above the bath. The oxygen-enriched blast is swirled down the lower part of the lance by helical swirl vanes. This causes rapid heat extraction from the lance into the cool blast and solidification of a protective slag coating on the lance's outer surface. This is a unique feature of the process.

The principal product of the furnace is a matte/slag mixture. It is tapped into a hydrocarbon fired or electric settling furnace. The products after settling are 60% Cu matte and 0.7% Cu slag.

The main advantages of the process are:

- (a) its small 'footprint', which makes it easy to retrofit into existing smelters
- (b) its small evolution of dust.

The 1990's and early 2000's saw Ausmelt and Isasmelt smelting adopted around the world. It should soon account for 5% of world copper smelting.

The future may see dry concentrate injection through the lance. This will improve the thermal efficiency of the process.

Suggested Reading

Binegar, A.H. (1995) Cyprus Isasmelt start-up and operating experience. In *Copper95-Cobre 95 Proceedings of the Third International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Chen, W.J., Díaz, C., Luraschi, A., and Mackey, P.J., The Metallurgical Society of CIM, Montreal, 117-132.

Mounsey, E.N., Li, H., and Floyd, J.W. (1999) The design of the Ausmelt technology smelter at Zhong Tiao Shan's Houma smelter, People's Republic of China, in *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., and Weddick, A.J., TMS, Warrendale, PA, 357-370.

Player, R.L., Fountain, C.R., Nguyen, T.V., and Jorgensen, F.R. (1992) Top-entry submerged injection and the Isasmelt technology. In *Savard/Lee International Symposium on Bath Smelting*, ed. Brimacombe, J.K., Mackey, P.J., Kor, G.J.W., Bickert, C., and Ranade, M.G., TMS, Warrendale, PA, 215 229.

References

Ausmelt Commercial Operations (2002) <http://www.ausmelt.com.au/comops.html>

Bincgar, A.H. (1995) Cyprus Isasmelt start-up and operating experience. In *Copper95-Cobre 95 Proceedings of the Third International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Chen, W.J., Díaz, C., Luraschi, A., and Mackey, P.J., The Metallurgical Society of CIM, Montreal, 117 132.

Hughes, S. (2000) Applying Ausmelt technology to recover Cu, Ni, and Co from slags. *JOM*, **52** (8), 30 33.

Isasmelt Installations (2002) <http://www.mimpt.com.au/isasmelt-installations.html>

Isasmelt Technology (2002) <http://www.mimpt.com.au/isasmelt-technology.html>

Mounsey, E.N., Floyd, J.M., and Baldock, B.R. (1998) Copper converting at Bindura Nickel Corporation using Ausmelt technology. In *Sulfide Smelting '98*, ed. Asteljöki, J.A., and Stephens, R.L., TMS, Warrendale, PA, 287 301.

Mounsey, E.N., Li, H., and Floyd, J.W. (1999) The design of the Ausmelt technology smelter at Zhong Tiao Shan's Houma smelter, People's Republic of China. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., and Weddick, A.J., TMS, Warrendale, PA, 357 370.

Mounsey, E.N., and Robilliard, K.R. (1994) Sulfide smelting using Ausmelt technology. *JOM*, **46** (8), 58 60.

Player, R.L. (1996) Copper Isasmelt – Process investigations. In *Howard Worner International Symposium on Injection in Pyrometallurgy*, ed. Nilmani, M. and Lehner, T., TMS, Warrendale, PA, 439 446.

Pritchard, J.P. and Hollis R. (1994) The Isasmelt copper-smelting process. *Int. Miner. Met. Technol.*, **1**, 125 128.

Robilliard, K. (1994) The development of Siros melt, Ausmelt and Isasmelt. *Int. Miner. Met. Technol.*, **1**, 129 134.

Solnordal, C.B. and Gray, N.B. (1996) Heat transfer and pressure drop considerations in the design of Siros melt lances. *Met. and Mater. Trans. B*, **27B** (4), 221 230.

CHAPTER 9

Batch Converting of Cu Matte

Converting is oxidation of molten Cu-Fe-S matte to form molten 'blister' copper (99% Cu). It entails oxidizing Fe and S from the matte with oxygen-enriched air or air 'blast'. It is mostly done in the Peirce-Smith converter, which blows the blast into molten matte through submerged tuyeres, Figs. 1.6 and 9.1. Several other processes are also used or are under development, Section 9.6 and Chapter 10.

The main raw material for converting is molten Cu-Fe-S matte from smelting. Other raw materials include silica flux, air and industrial oxygen. Several Cu-bearing materials are recycled to the converter – mainly solidified Cu-bearing reverts and copper scrap.

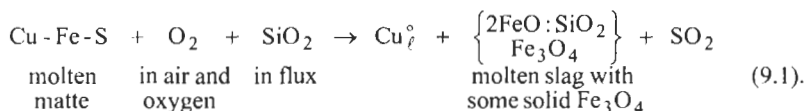
The products of converting are:

- (a) molten blister copper which is sent to fire- and electrorefining
- (b) molten iron-silicate slag which is sent to Cu recovery, then discard
- (c) SO₂-bearing offgas which is sent to cooling, dust removal and H₂SO₄ manufacture.

The heat for converting is supplied entirely by Fe and S oxidation, i.e. the process is autothermal.

9.1 Chemistry

The overall converting process may be described by the schematic reaction:



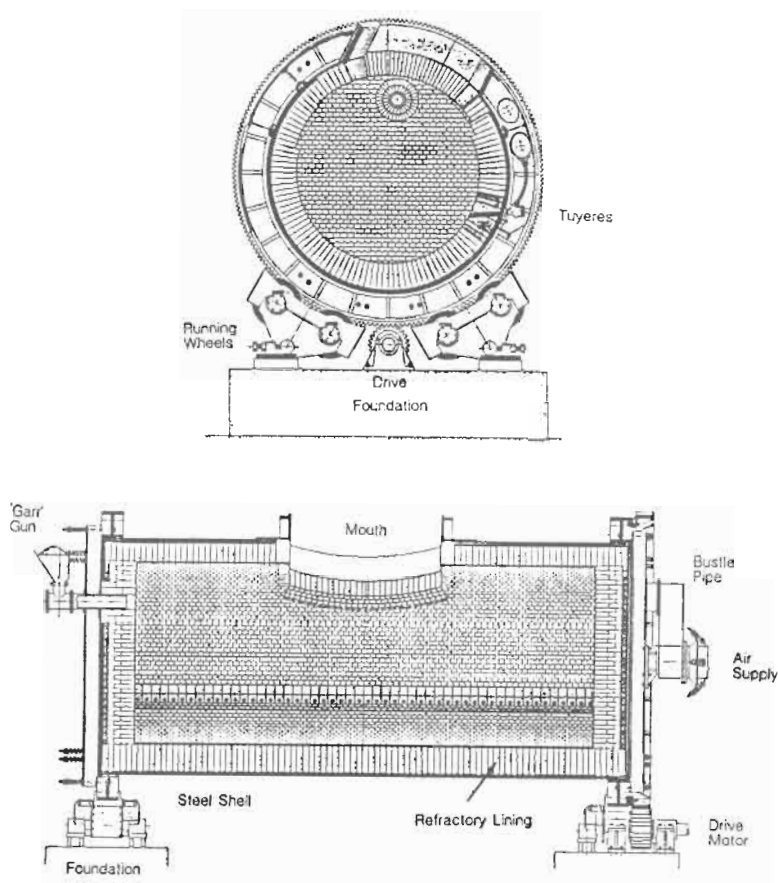


Fig. 9.1a. Peirce-Smith Converter. Note the blast supply, rotating seal and bustle pipe connected to the tuyeres. Flux and Cu-bearing reverts are added from bins above the offgas uptake or by air gun ('Garr Gun') through an end of the converter. The converter rotates around its long axis in order to (i) lift its tuyeres out of the liquids when it is not blowing and (ii) submerge them correctly in the matte during blowing, Fig. 1.6b. (Converter drawing courtesy Harbison-Walker Refractories, Pittsburgh, PA)

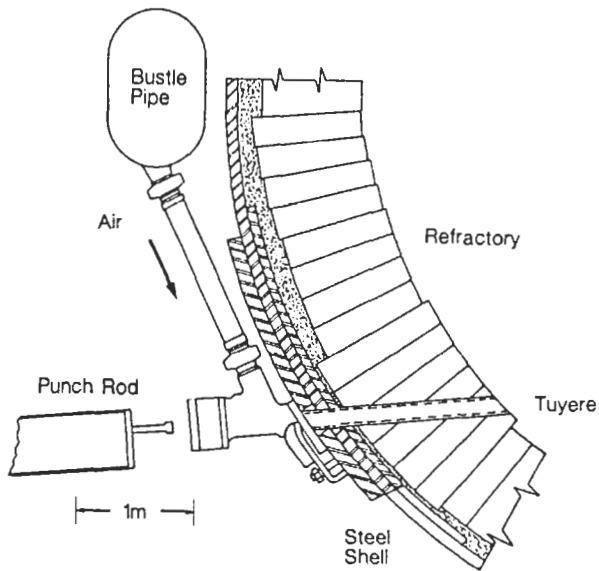
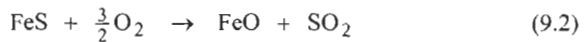


Fig. 9.1b. Details of Peirce-Smith converter tuyere (from Vogt *et al.*, 1979). The tuyeres are nearly horizontal during blowing. 'Blast' pressure is typically 1.2 atmospheres (gage) at the tuyere entrance. Reprinted by permission of TMS.

Converting takes place in two stages:

- (a) the slag-forming stage when Fe and S are oxidized to FeO, Fe₃O₄ and SO₂ by reactions like:



The melting points of FeO and Fe₃O₄ are 1385°C and 1597°C so silica flux is added to form a liquid slag with FeO and Fe₃O₄. The slag-forming

stage is finished when the Fe in the matte has been lowered to about 1%. The principal product of the slag-forming stage is impure molten Cu_2S , 'white metal', $\sim 1200^\circ\text{C}$.

- (b) the coppermaking stage when the sulfur in Cu_2S is oxidized to SO_2 . Copper is not appreciably oxidized until it is almost devoid of S. Thus, the blister copper product of converting is low in both S and O (0.001-0.03% S, 0.1-0.8% O). Nevertheless, if this copper were cast, the S and O would form SO_2 bubbles or blisters which give blister copper its name.

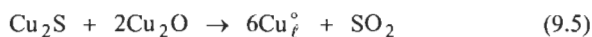
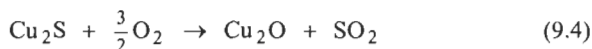
Industrially, matte is charged to the converter in several steps with each step followed by oxidation of FeS from the charge. Slag is poured from the converter after each oxidation step and a new matte addition is made. In this way, the amount of Cu in the converter gradually increases until there is sufficient (100-250 tonnes Cu as molten Cu_2S) for a final coppermaking 'blow'. At this point, the Fe in the matte is oxidized to about 1%, a final slag is removed, and the resulting Cu_2S 'white metal' is oxidized to molten blister copper. The converting process is terminated the instant copper oxide begins to appear in samples of the molten copper.

The copper is poured from the converter into ladles and craned molten to a fire-refining furnace for S and O removal and casting of anodes. A start-to-finish converting cycle is 6 to 12 hours, Table 9.2.

9.1.1 Coppermaking reactions

Blowing air and oxygen into molten 'white metal' creates a turbulent Cu_2S -copper mixture. The products of oxidation in this mixture are SO_2 , molten copper and copper oxide. The molten copper is dense and fluid. It quickly sinks below the tuyeres.

The most probable coppermaking reactions are:



though some copper may be made directly by:



In principle, there are three sequential steps in coppermaking as indicated on the Cu-S phase diagram, Fig. 9.2a.

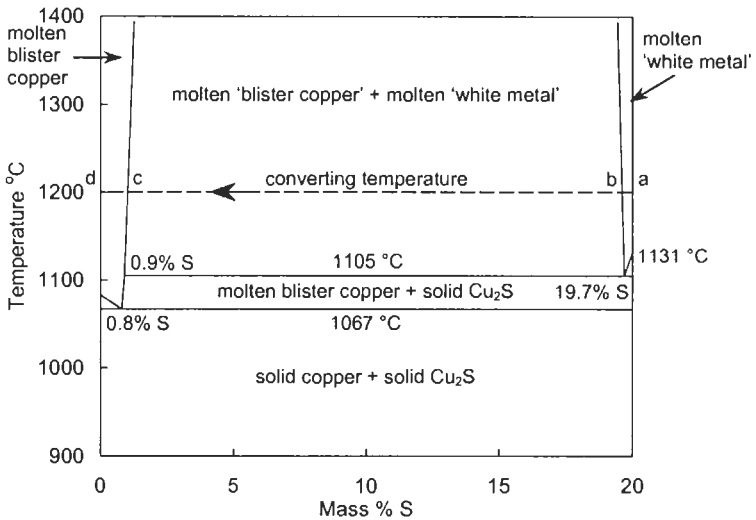


Fig. 9.2a. Cu-S equilibrium phase diagram showing coppermaking reaction path (a, b, c, d, 1200°C) (Sharma and Chang, 1980).

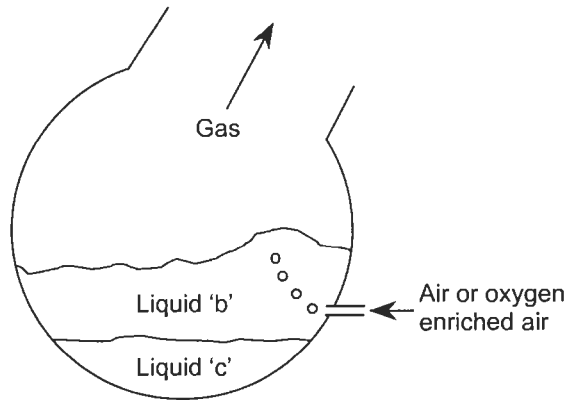
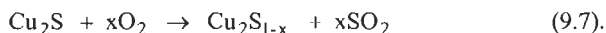


Fig. 9.2b. Sketch of Peirce-Smith converter and its two immiscible liquids during the coppermaking stage of converting (after Peretti, 1948). In practice, the liquid 'b' region is a Cu₂S-Cu-Cu₂O-gas foam/emulsion from which metallic copper 'c' descends and SO₂ and N₂ ascend. The immiscibility of copper and Cu₂S is due to their different structures – copper is metallic while Cu₂S is a semiconductor.

- (a) The first blowing of air and oxygen into the Cu_2S removes S as SO_2 to give S-deficient 'white metal', but no metallic copper. The reaction for this step is:



It takes place until the S is lowered to 19.6% (point b, 1200°C, Fig. 9.2a).

- (b) Subsequent blowing of air and oxygen causes a second liquid phase, metallic copper (1% S, point c), to appear. It appears because the average composition of the liquids is now in the liquid-liquid immiscibility region. The molten copper phase is dense and sinks to the bottom of the converter, Fig. 9.2b. Further blowing oxidizes additional S from the Cu_2S and the amount of molten copper increases at the expense of the 'white metal' according to overall Reaction (9.6). As long as the combined average composition of the system is in the immiscibility range, the converter contains both 'white metal' (19.6% S) and molten copper (1% S). Only the proportions change.
- (c) Eventually the 'white metal' becomes so S deficient that the sulfide phase disappears and only molten copper (1% S) remains. Further blowing removes most of the remaining S (point d). Great care is taken during this period to ensure that the copper is not overoxidized to Cu_2O . This care is necessary because Cu_2S is no longer available to reduce Cu_2O back to Cu by Reaction (9.5).

Step (a) is very brief, i.e. very little S oxidation is required. Step (c) is also brief. Its beginning is marked by a change in the converter flame color from clear to green when metallic copper begins to be oxidized in front of the tuyeres. This tells the converter operator that the copper blow is nearly finished.

9.1.2 Elimination of impurities during converting

The principal elements removed from matte during converting are Fe and S. However, many other impurities are partially removed as vapor or in slag. Table 9.1 shows some distributions. The outstanding feature of the data is that impurity retention in the product blister copper increases significantly with increasing matte grade (%Cu in matte). This is because high-Cu mattes have less 'blast' blown through them and they form less slag.

The table also shows that significant amounts of impurities report to the offgas. They are eventually collected during gas cleaning. They contain sufficient Cu to be recycled to the smelting furnace. However, such recycle returns all impurities to the circuit.

Table 9.1. Distribution of impurity elements during Peirce-Smith converting of low and high grade mattes (Vogt *et al.*, 1979, Mendoza and Luraschi, 1993). Ag, Au and the Pt metals report mainly to blister copper. Tenmaya *et al.*, 1993 report that extra blowing of air at the end of the coppermaking stage lowers As, Pb and Sb in the converter's product copper.

	54% Cu matte feed			70% Cu matte feed		
	distribution %			distribution %		
Element	to blister copper	to converter slag	to converter offgas	to blister copper	to converter slag	to converter offgas
As	28	13	58	50	32	18
Bi	13	17	67	55	23	22
Pb	4	48	46	5	49	46
Sb	29	7	64	59	26	15
Se	72	6	21	70	5	25
Zn	11	86	3	8	79	13

For this reason, some smelters treat the dusts for impurity removal before they are recycled (Shibasaki and Hayashi, 1991). Bismuth, in particular, is removed because (i) it causes brittleness in the final copper anodes and (ii) it can be a valuable byproduct.

9.2 Industrial Peirce-Smith Converting Operations (Tables 9.2, 9.3)

Industrial Peirce-Smith converters are typically 4 m diameter by 11 m long, Table 9.2. They consist of a 5 cm steel shell lined with ~0.5 m of magnesite-chrome refractory brick. Converters of these dimensions treat 300-700 tonnes of matte per day to produce 200-600 tonnes of copper per day. A smelter has two to five converters depending on its overall smelting capacity.

Oxygen-enriched air or air is blown into a converter at ~600 Nm³/minute and 1.2 atmospheres gage. It is blown through a single line of 5 cm diameter tuyeres, 40 to 60 per converter. It enters the matte 0.5 to 1 m below its surface, nearly horizontal (Lehner *et al.*, 1993).

The flowrate per tuyere is about 12 Nm³/minute at a velocity of 80 to 120 meters per second. Blowing rates above about 17 Nm³/minute/tuyere cause slopping of matte and slag from the converter (Johnson *et al.*, 1979). High blowing rates without slopping are favored by deep tuyere submergence in the matte (Richards, 1986).

About half of the world's Peirce-Smith converters enrich their air blast with industrial oxygen, up to ~29 volume% O₂-in-blast, Table 9.2.

Table 9.2. Production details of industrial

Smelter	Norddeutsche Affinerie Hamburg, Germany	Onahama Smelting and Refining Onahama, Japan
Converter type	Pearce-Smith	Pearce-Smith
Number of converters		
total	3	5
hot	2	4
blowing at one time	2	3
Converter details		
diameter × length, inside shell, m	4.6 × 12.2	four: 3.96 × 9.15 one: 3.96 × 11.0
number of tuyeres		
total	62	48
active	60	44
tuyere diameter, cm	6	5
usual blast rate per converter		
slag blow, Nm ³ /minute	700	520
copper blow, Nm ³ /minute	700-800	500
usual volume% O ₂ in blast		
slag blow	23	21, then 60 minutes at 29
copper blow	23	21
SO ₂ in offgas, volume%	8-13	9
Production details (per converter)		
Inputs (tonnes/cycle)		
molten matte	270 (64% Cu)	140 (43% Cu)
source	Outokumpu flash	Reverberatory
Other inputs (tonnes)	furnace + ESCF	
slag blow	15t ladle skulls + 10t secondaries	90t concentrate + 2.5t reverts
copper blow	75t Cu scrap	50t Cu scrap etc.
Outputs, (tonnes/cycle)		
blister copper		120
slag		150
average mass %Cu		5
mass%SiO ₂ /mass%Fe		0.63
Cycle time		
usual converter cycle time, hours	9	13
slag blow, hours	2	5
copper blow, hours	4.5	3
Campaign details		
time between tuyere line repairs, days	60	100
copper produced between tuyere line repairs, tonnes	50 000	21 600
time between complete converter re- lines, years	1	-
refractory consumption, kg/tonne of Cu	1.93	-

Peirce-Smith and Hoboken converters.

Mexicana de Cobre Nacazari, Mexico	Caraiba Metals Bahia, Brazil	CODELCO Caletones, Chile	Sumitomo Toyo, Japan
Peirce-Smith	Hoboken	Peirce-Smith	Peirce-Smith
3	3	4	3
2	2	3	2
1 or 2	-	-	1
4.57 × 10.67	4.16 × 11.4	three 4.5 × 10.6 one 4.0 × 10.6	4.2 × 11.9
56	42	48	58
56	36	46	
5	5.08	6.35	5
700	350-558	only copper blow	730
750	350-558	600	770
23.26	25	none	21, then 60 min. at 26% O ₂
23.26	25	21	21
7.5	12	15	11
211 (66.5% Cu)+73 WM Outokumpu flash furnace + Teniente furnace	180 (62% Cu) Outokumpu flash furnace	200 (74.3% Cu) Teniente & slag cleaning furnaces	230 (63% Cu) Outokumpu flash furnace
15t mostly reverts	5.8 tonnes of reverts	none	5t mostly reverts
30t Cu scrap etc.	60 tonnes anodes, cathodes, molds, reverts, etc.	35 tonnes reverts	40t Cu scrap etc.
210	180	145	195
66	56	30	63
8	3	25	6.5
-	0.51	-	0.48
6.61	8.6	7 to 7.5	9.6
2.66	1.75	none	1.5
3.0	3.91	5	3.3
120	125 tuyere & body	30 tuyere line (180 tuyere line & body)	95
40 000	54 000	11 200	45 400
1	2.5	2.0	2-3
2.5	2.25	4.5	1.5

Table 9.3. Representative analyses of converter raw materials and products, mass%. The data are from recent industrial surveys and Johnson *et al.*, 1979, Pannel, 1987 and Lehner, *et al.*, 1993.

	Cu	Fe	S	O	As	Bi	Pb	Sb	Zn	Au	Ag
Matte	45-75	3-30	20-23	1-3	0-0.5	0-0.1	0-1	0-0.5	0-1	0-0.003	0-0.3
White metal(Cu_2S)	79	~1	~20	<1							
Blister copper	~99	0.001-0.3	0.001-0.3	0.1-0.8	0-0.2	0-0.03	0-0.5	0-0.1	0	0-0.004	0-0.5

	Cu	Total Fe	SiO_2	Fe_3O_4 ($\ell+s$)	Al_2O_3	CaO	MgO	ZnO	H_2O
Flux			70-98		0-10	0-5	0-2	0	1-5
Converter slag	4-8	35-50	15-30	20-25	0-5	0-5	0-1	0-5	0

9.2.1 Tuyeres and offgas collection

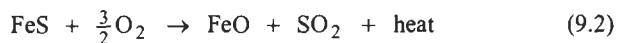
Peirce-Smith tuyeres are carbon steel or stainless steel pipes embedded in the converter refractory (Figs. 1.6 and 9.1b). They are joined to a distribution 'bustle' pipe which is affixed the length of the converter and connected through a rotatable seal to a blast supply flue. The blast air is pressurized by electric or steam driven blowers. Industrial oxygen is added to the supply flue just before it connects to the converter.

Steady flow of blast requires periodic clearing ('punching') of the tuyeres to remove matte accretions which build up at their tips – especially during the slag blow (Fig. 9.3, Bustos *et al.*, 1984, 1988). Punching is done by ramming a steel bar completely through the tuyere. It is usually done with a Gaspé mobile carriage puncher (Fig. 1.6) which runs on rails behind the converter. The puncher is sometimes automatically positioned and operated (Dutton and Simms, 1988; Fukushima *et al.*, 1988).

Peirce-Smith converter offgas is collected by a steel hood (usually water cooled) which fits as snugly as possible over the converter mouth (Fig. 1.6, Sharma *et al.*, 1979, Pasca, *et al.*, 1999). The gas then passes through a waste heat boiler or water-spray cooler, electrostatic precipitators and a sulfuric acid plant. Peirce-Smith converter offgases contain ~8 volume% SO₂ (slag blow) to ~10 volume% SO₂ (copper blow) after cooling and dust removal, Table 9.2.

9.2.2 Temperature control

All the heat for maintaining the converter liquids at their specified temperatures results from Fe and S oxidation, i.e. from reactions like:



Converter temperature is readily controlled with this heat by:

- (a) raising or lowering O₂ enrichment level, which raises or lowers the rate at which N₂ 'coolant' enters the converter
- (b) adjusting revert and scrap copper 'coolant' addition rates.

9.2.3 Choice of temperature

Representative liquid temperatures during converting are:

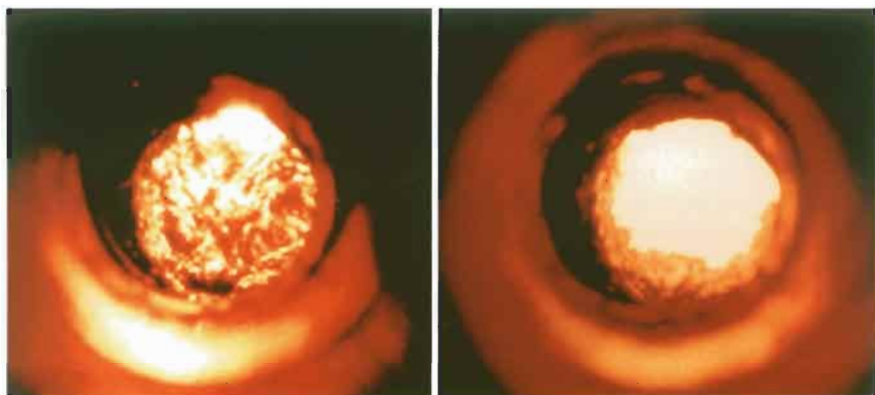


Fig. 9.3. Photograph showing buildup of accretion at the interior end of a Peirce-Smith converter tuyere (Bustos *et al.*, 1984). Left, tuyere is nearly blocked; right, the accretion has dislodged spontaneously. Bustos *et al.* (1988) report that accretion 'tubes' are formed in front of the tuyeres. They also indicate that tuyere blockage is discouraged by high matte temperature and oxygen-enrichment of the blast. This is particularly important near the end of the slag blow and the start of the copper blow. Clear tuyere conditions at the beginning of the copper blow often give 'free blowing' conditions (without punching) during most or all of the copper blow. (Photograph courtesy of Dr. Alejandro Bustos, Air Liquide).

input matte	1200°C
skimmed slag	1220°C
final blister copper	1200°C.

The high temperature during the middle of the cycle is designed to give (i) rapid slag formation and (ii) fluid slag with a minimum of entrained matte. It also discourages tuyere blockage (Bustos *et al.*, 1987). An upper limit of about 1250°C is imposed to prevent excessive refractory wear.

9.2.4 Temperature measurement

Converter liquid temperature is measured by means of (i) an optical pyrometer

sighted downwards through the converter mouth or (ii) a two-wavelength optical pyrometer periscope sighted through a tuyere (Pelletier *et al.*, 1987). The tuyere pyrometer appears to be more satisfactory because it sights directly on the matte rather than through a dust-laden atmosphere.

9.2.5 Slag and flux control

The chief objective of creating a slag in the converter is to liquify newly formed solid FeO and Fe₃O₄ so they can be poured from the converter. SiO₂-bearing flux (e.g. quartz, quartzite, sand) is added for this purpose.

A common indicator of slag composition is the ratio:

$$\frac{\text{mass\% SiO}_2 \text{ in slag}}{\text{mass\% Fe in slag}}$$

Enough SiO₂-in-flux is added to give SiO₂/Fe ratio of ~0.5. Acceptable Fe₃O₄ levels are typically 12-18% (Eltringham, 1993). Some smelters use Au- and Ag-bearing siliceous material as converter flux. The Au and Ag dissolve in the matte and proceed with copper to the electrolytic refinery where they are profitably recovered. These smelters tend to maximize flux input. Most smelters, however, use just enough flux to obtain an appropriately fluid slag. This minimizes flux cost, slag handling and Cu-from-slag recovery expense.

9.2.6 Slag formation rate

Flux is added through chutes above the converter mouth or via a high pressure air gun ('Garr Gun') at one end of the converter. It is added at a rate that matches the rate of Fe oxidation (usually after an initial several-minute delay while the converter heats up). The flux is commonly crushed to 1-5 cm diameter. Sand (0.1 cm) is used in some smelters.

Rapid reaction between O₂, matte and flux to form liquid slag is encouraged by:

- (a) high operating temperature
- (b) steady input of small and evenly sized flux (Schonewille *et al.*, 1993)
- (c) deep tuyere placement in the matte (to avoid overoxidation of the slag)
- (d) the vigorous mixing provided by the Peirce-Smith converter
- (e) reactive flux.

Casley *et al.* (1976) and Schonewille *et al.* (1993) report that the most reactive fluxes are those with a high percentage of quartz (rather than tridymite or feldspar).

9.2.7 End point determinations

Slag blow

The slag-forming stage is terminated and slag is poured from the converter when there is about 1% Fe left in the matte. Further blowing causes excessive Cu and solid magnetite in slag. The blowing is terminated when:

- (a) metallic copper begins to appear in matte samples or when X-Ray fluorescence shows 76 to 79% Cu in matte (Mitarai *et al.*, 1993)
- (b) the converter flame turns green from Cu vapor in the converter offgas
- (c) PbS vapor (from Pb in the matte feed) concentration decreases and PbO vapor concentration increases (Persson *et al.*, 1999).

Copper blow

The coppermaking stage is terminated the instant that copper oxide begins to appear in copper samples. Copper oxide attacks converter refractory so it is avoided as much as possible.

The copper blow is ended and metallic copper is poured from the converter when:

- (a) copper oxide begins to appear in the samples
- (b) SO₂ concentration in the offgas falls because S is nearly gone from the matte (Shook *et al.*, 1999)
- (c) PbO concentration in the offgas falls and CuOH concentration increases (H from moisture in the air blast, Persson, *et al.*, 1999).

9.3 Oxygen Enrichment Of Peirce-Smith Converter Blast

An increasing number of smelters enrich their converter blast during part or all of the converting cycle. The advantages of O₂-enrichment are:

- (a) oxidation rate is increased for a given blast input rate
- (b) SO₂ concentration in offgas is increased, making gas handling and acid making cheaper
- (c) the amount of N₂ 'coolant' entering the converter per kg of O₂-in-blast is diminished.

The diminished amount of N₂ 'coolant' is important because it permits:

- (a) generation of high temperatures even with high Cu grade – low FeS 'fuel' mattes

- (b) rapid heating of the converter and its contents
- (c) melting of valuable 'coolants' such as Cu-bearing reverts and copper scrap.

The only disadvantage of high-O₂ blast is that it gives a high reaction temperature at the tuyere tip. This leads to rapid refractory erosion in the tuyere area. This erosion is discouraged by blowing at a high velocity which promotes tubular accretion formation and pushes the reaction zone away from the tuyere tip (Bustos *et al.*, 1988).

On balance, the advantages of O₂-enrichment outweigh the refractory erosion disadvantages, especially in smelters which wish to:

- (a) convert high Cu grade – low FeS 'fuel' matte
- (b) maximize converting rate, especially if converting is a production bottleneck
- (c) maximize melting of solids, e.g. flux, reverts and scrap.

The present upper practical limit of oxygen-enrichment seems to be about 29 vol% O₂. Above this level, refractory erosion becomes excessive. This is because strong tubular accretions do not form in front of the tuyeres above 29 vol% O₂ – causing the O₂-matte reactions to take place flush with the tuyere tip and refractory. Sonic high-pressure blowing is expected to permit higher oxygen levels, Section 9.5.

9.4 Maximizing Converter Productivity

The production rate of a converter, tonnes of copper produced per day, is maximized by:

- (a) charging high Cu grade (low FeS) matte to the converter, Fig. 9.4
- (b) blowing the converter blast at its maximum rate (including avoidance of tuyere blockages)
- (c) enriching the blast to its maximum feasible O₂ level
- (d) maximizing O₂ utilization efficiency
- (e) maximizing campaign life, Section 9.4.3.

High grade matte contains little FeS so that it requires little O₂ (and time) to convert, Fig. 9.4. Rapid blowing of blast, a high %O₂ in blast and a high O₂ utilization efficiency all lead to rapid oxidation.

High O₂ utilization efficiency is obtained by ensuring that the tuyeres are submerged as deeply as possible in the matte. This gives maximum O₂-in-matte residence time.

9.4.1 Maximizing solids melting

An important service of the Peirce-Smith converter is melting of valuable solids with the heat from the converting reactions. The most usual solids are (i) Cu-bearing revert materials; (ii) scrap copper and (iii) Au and Ag flux. Cu concentrate is also melted in several smelters.

Melting of solids is maximized by:

- (a) maximizing blast O_2 enrichment
- (b) blowing the converter at a rapid rate with the tuyeres deep in the matte. This maximizes reaction rate, hence heat production rate (at an approximately constant heat loss rate from the converter).

The solids are added steadily to avoid excessive cooling of the converter liquids. This is easily done with flux and reverts which can be crushed and added at controlled rates from storage bins above the converter.

Scrap copper, on the other hand, is often large and uneven in shape. It is usually added in batches by crane with the converter in charging position (Fig. 1.6). This has the disadvantages that (i) blowing must be stopped and (ii) the large batch of scrap may excessively cool the converter liquids.

Several converters have conveyor systems which feed large pieces of copper (e.g. scrap anodes and purchased blister copper) at a steady rate during blowing (Fukushima *et al.*, 1988, Maruyama *et al.* 1998). This avoids excessive cooling and maximizes the converter's scrap melting capability.

Up to 30% of a converter's blister copper product comes from copper scrap (Fukushima *et al.*, 1988; Pannell, 1987).

9.4.2 Smelting concentrates in the converter

Melting of scrap copper and solid reverts in the Peirce-Smith converter is done in most smelters. Several smelters also smelt dried concentrates in their converters by injecting the concentrates through several tuyeres (Godbehere *et al.*, 1993, Oshima and Igarashi, 1993, Mast *et al.*, 1999).

The process has the advantage that:

- (a) it can increase smelter capacity without major investment in a larger smelting furnace
- (b) it can lengthen the converting blow and improve impurity removal, especially bismuth and antimony (Godbehere *et al.*, 1993).

The technology is well-proven (Godbehere *et al.*, 1993, Mast *et al.*, 1999).

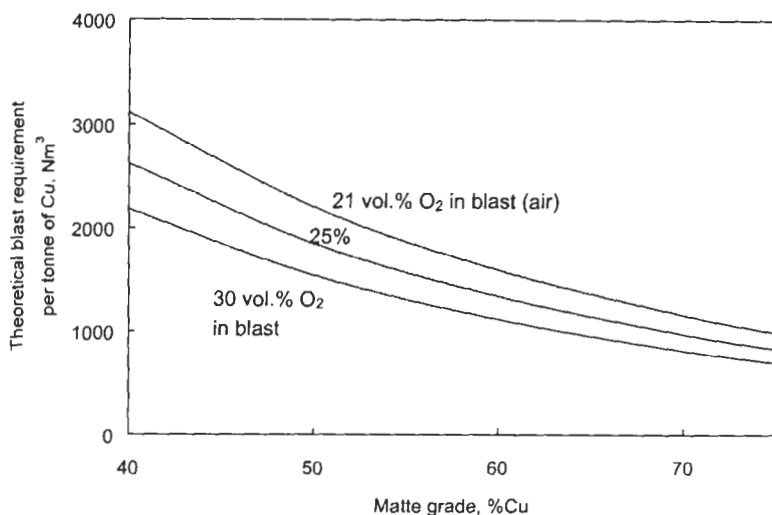


Fig. 9.4. Theoretical air and oxygen-enriched air blast requirements for converting Cu_2S - FeS mattes to copper. Blast requirement decreases with increasing matte grade and % O_2 -in-blast. 100% O_2 efficiency is assumed.

9.4.3 Maximizing campaign life

Converters produce 20 000 – 50 000 tonnes of blister copper before they must be taken out of service for tuyere-refractory replacement. The replacement takes about two weeks and it is done many times before the converter must be completely relined ('shelled'). Several Chilean smelters remove and replace segments of the tuyere line refractories from the outside of the converter (Campos and Torres, 1993). This lowers converter off-line time to several days but it may weaken the converter shell.

Copper production per tuyere-refractory replacement period (campaign life) increased markedly during the late 20th Century due to:

- (a) improved refractories
- (b) higher Cu-grade matte feeds (requiring less blowing per tonne of Cu)
- (c) better temperature measurement and control.

The most durable refractories in 2002 are burned or direct bonded chrome-magnesite bricks.

Industrial evidence suggests that oxygen-enrichment up to 25% O_2 enhances converter productivity without shortening campaign life. This is especially true if

converter blowing rates are high (Verney, 1987). Enrichment above this level should be tracked to determine the optimum from the points of view of converter productivity and campaign life.

9.5 Recent Developments In Converting - Shrouded Blast Injection

ALSI (*Air Liquide Shrouded Injector*) technology has been successfully demonstrated in Peirce-Smith converters which process copper-lead matte (45%Cu-25%Pb) and copper-nickel matte (13%Cu-22%Ni) (Bustos *et al.*, 1995, Bustos *et al.*, 1999). The objectives of the ALSI process are to:

- (a) oxidize matte using 30%-60% O₂ blast – thereby increasing the converter's productivity and its ability to melt solids
- (b) eliminate the need to “punch” the converter, Section 9.2.1
- (c) minimize refractory wear in tuyere area.

The tuyere used to achieve these objectives is shown in Fig. 9.5a. It consists of two concentric pipes – the inner pipe for oxygen-enriched air ‘blast’ (30-60% O₂) and the annulus for nitrogen ‘coolant’.

The purpose of the nitrogen is:

- (a) to cool the circumference of the tuyere tip
- (b) to protect the refractory around the tuyere by building up an accretion of solidified matte/slag, Fig. 9.5b.

The blast and nitrogen are blown in at high pressure, ~6 atmospheres gage. This prevents the accretion from bridging across the tuyere and it eliminates the need for ‘punching’.

ALSI technology has been successfully implemented on a Peirce-Smith converter at the Falconbridge nickel smelter near Sudbury, Ontario. It has yet to be fully tested in a copper smelter, perhaps because it requires installation of high pressure blowing equipment.

9.6 Alternatives to Peirce-Smith Converting

Peirce-Smith converting accounts for over 90% of Cu matte converting. This is due to its simplicity and high chemical efficiency. It suffers, however, from the problems that:

- (a) it leaks SO₂-bearing gas into the workplace during charging and pouring
- (b) it leaks air into its offgas between its mouth and gas-collection hood, producing a relatively weak SO₂ gas

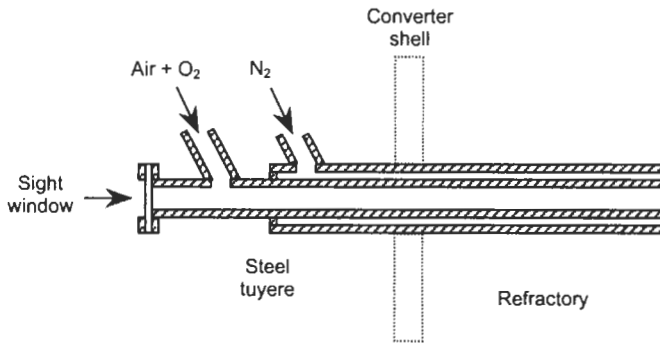


Fig. 9.5a. ALSI shrouded injector tuyere detail. Oxygen enriched air is blown through the center pipe. Nitrogen is blown through the annulus.

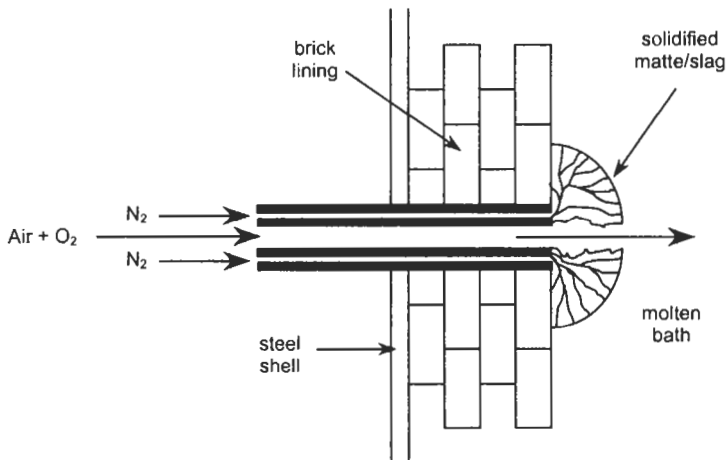


Fig. 9.5b. ALSI schematic of accretion growth mechanism with shrouded tuyere. The accretion at the tip of the tuyere protects the adjacent refractory from wear.

- (c) it operates batchwise, giving uneven flow of SO_2 offgas into the sulfuric acid plant.

These deficiencies are attacked by several different alternative converters:

- (a) Hoboken or siphon converter which is a Peirce-Smith converter with an improved gas-collection system, ~10 units operating, 2002
- (b) Mitsubishi top-blown converter which blows oxygen enriched blast onto the molten matte surface via vertical lances, 5 units operating, 2002
- (c) Outokumpu flash converting which oxidizes solidified crushed matte in a small Outokumpu flash furnace, one unit operating, 2002
- (d) Noranda continuous converting which uses submerged tuyeres to blow oxygen-enriched air into matte in a Noranda-type furnace, one unit operating, 2002.

Hoboken converting is discussed next, the others in Chapter 10.

9.6.1 Hoboken converter

The Hoboken converter collects its offgas through an axial flue at one end of the converter (Gomez, 1979, Coelho and Morais, 1993, Binegar and Tittes, 1993). A 'goose neck' is provided to allow the offgas (but not the liquids) to enter the flue. The offgas is collected efficiently.

Considerable care must be taken to prevent buildup of splash and dust in the goose-neck. This appears to have prevented wider adoption of the process.

9.7 Summary

Converting is the second half of the smelting/converting sequence by which most of the world's Cu-Fe-sulfide concentrates are made into metallic copper. The process oxidizes the Fe and S from molten smelting furnace matte with oxygen-enriched air or air to produce molten metallic copper. It is most often carried out in the cylindrical Peirce-Smith converter.

The products of the process are:

- (a) molten blister copper (99% Cu, 0.02% S and 0.6% O) which is sent forward to fire refining for final S and O removal, then anode casting
- (b) molten Fe-silicate slag (4 to 8% Cu) which is sent to Cu recovery, then discard
- (c) SO_2 -bearing offgas which is treated for heat, dust and SO_2 capture.

All of the heat for converting comes from Fe and S oxidation.

Peirce-Smith converting is a batch process. It produces SO₂ intermittently and captures it somewhat inefficiently. Alternatives are:

- (a) Hoboken converting, which is Peirce-Smith converting with an improved gas collection system
- (b) Mitsubishi continuous downward lance converting
- (c) Outokumpu continuous flash converting
- (d) Noranda continuous submerged tuyere converting.

(b), (c) and (d) are described in Chapter 10.

Suggested Reading

Díaz, C., Landolt, C., Luraschi, A. and Newman, C.J. (1991) *Copper 91/Cobre 91, Volume IV, Pyrometallurgy of Copper*, Pergamon Press, New York.

Johnson, R.E. (1979) *Copper and Nickel Converters*, TMS, Warrendale, PA.

Lehner, T. Ishikawa, O., Smith, T., Floyd, J., Mackey, P. and Landolt, C. (1993) The 1993 survey of worldwide copper and nickel converter practice. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 1 58.

Marcuson, S.W. (1993) Copper converting – an historical perspective. *CIM Bulletin*, 86(966), 92 96.

Taylor, J.C. and Traulsen, H.R. (1987) *World Survey of Nonferrous Smelters*, TMS, Warrendale, PA.

Verney, L.R. (1987) Peirce-Smith copper converter operations and economics. In *Copper 87, Vol. 4, Pyrometallurgy of Copper*, ed. Díaz, C., Landolt, C. and Luraschi, A., Alfabet Impresores, Lira 140, Santiago, Chile, 55 75.

References

Binegar, A.H. and Tittes, A.F. (1993) Cyprus Miami Mining Corporation siphon converter operation, past and present. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 297 310.

Bustos, A.A., Brimacombe, J.K. and Richards, G.G. (1988) Accretion growth at the tuyeres of a Peirce-Smith copper converter. *Canadian Metallurgical Quarterly*, 27(1), 7 21.

Bustos, A.A., Brimacombe, J.K., Richards, G.G., Vahed, A. and Pelletier, A. (1987) Developments of punchless operation of Peirce-Smith converters. In *Copper 87, Vol. 4, Pyrometallurgy of Copper*, ed. Díaz, C., Landolt, C. and Luraschi, A., Alfabet Impresores, Lira 140, Santiago, Chile, 347 373.

Bustos, A., Cardoen, M. and Janssens, B. (1995) High oxygen enrichment at UM-Hoboken converters. In *Copper 95-Cobre95 Proceedings of the Third International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Chen, W.J., Diaz, C., Luraschi, A. and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 255 269.

Bustos, A.A., Kapusta, J.P., Macnamara, B.R. and Coffin, M.R. (1999) High oxygen shrouded injection at Falconbridge. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. VI Smelting, Technology Development, Process Modelling and Fundamentals*, ed. Diaz, C., Landolt, C. and Utigard, T., TMS, Warrendale, PA, 93 106.

Bustos, A.A., Richards, G.G., Gray, N.B., and Brimacombe, J.K. (1984) Injection phenomena in nonferrous processes. *Metallurgical Transactions B*, **15B**, 77 79.

Campos, R. and Torres, L. (1993) Caletones Smelter: two decades of technological improvements. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Vol. II: Copper and Nickel Smelter Operations*, ed. Landolt, C., TMS, Warrendale, PA, 1441 1460.

Casley, G. E., Middlin, J. and White D. (1976) Recent developments in reverberatory furnace and converter practice at the Mount Isa Mines copper smelter. In *Extractive Metallurgy of Copper, Volume I, Pyrometallurgy and Electrolytic Refining*, ed. Yannopoulos, J.C. and Agarwal, J.C., TMS, Warrendale, PA, 117 138.

Coelho, A.C. and Morais, S.N. (1993) Syphon type converters operation and improvements. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 69 78.

Dutton, W. and Simms, D. (1988) Automated Gaspé puncher. In *Process Control and Automation in Extractive Metallurgy*, ed. Partelpoeg, E.H. and Himmesoete, D.C., TMS, Warrendale, PA, 131 137.

Eltringham, G.A. (1993) Developments in converter fluxing. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 323 331.

Fukushima, K., Baba, K., Kurokawa, H. and Yamagiwa, M. (1988) Development of automation systems for copper converters and anode casting wheel at Toyo smelter. In *Process Control and Automation in Extractive Metallurgy*, ed. Partelpoeg, E.H. and Himmesoete, D.C., TMS, Warrendale, PA, 113 130.

Godbehere, P.W., Cloutier, J.P., Carissimi, E. and Vos, R.A. (1993) Recent developments and future operating strategies at the Horne smelter. Paper presented at TMS annual meeting, Denver Colorado, February 1993.

Gomez, J.D. (1979) Paipote smelter: seven years operating Hoboken converters. In *Copper and Nickel Converters*, ed. Johnson, R. E., TMS, Warrendale, PA, 291 311.

Johnson, R.E., Themelis, N.J., and Eltringham, G.A. (1979) A survey of worldwide copper converter practices. In *Copper and Nickel Converters*, ed. Johnson, R.E., TMS, Warrendale, PA, 1 32.

- Lehner, T., Ishikawa, O., Smith, T., Floyd, J. Mackey, P. and Landolt, C. (1993) The 1993 survey of worldwide copper and nickel converter practices. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 1 58.
- Maruyama, T., Saito, T. and Kato, M. (1998) Improvements of the converter's operation at Tamano smelter. In *Sulfide Smelting '98*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 219 227.
- Mast, E.D., Arrian V., J., Benavides V., J. (1999) Concentrate injection and oxygen enrichment in Peirce-Smith converters at Noranda's Altonorte smelter. In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., Weddick, A.J., TMS, Warrendale, PA, 433 445.
- Mendoza, H. and Luraschi, A. (1993) Impurity elimination in copper converting. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 191 202.
- Mitarai, T., Akagi, S. and Masatoshi, M. (1993) Development of the technique to determine the end point of the slag-making stage in copper converter. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 169 180.
- Oshima, E. and Igarashi, T. (1993) Recent Operation and Improvements at Onahama Smelter. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Vol. II: Copper and Nickel Smelter Operations*, ed. Landolt, C., TMS, Warrendale, PA, 1319 1333.
- Pannell, D.G. (1987) A survey of world copper smelters. In *World Survey of Nonferrous Smelters*, ed. Taylor, J.C. and Traulsen, H.R., TMS, Warrendale, PA, 3 118.
- Pasca, O., Bryant, J., Safe, P. and Wiggins, B. (1999) Peirce-Smith converter hood improvements at BHP copper. In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., Weddick, A.J., TMS, Warrendale, PA, 149 159.
- Pelletier, A., Lucas, J.M., and Mackey, P.J. (1987) The Noranda tuyere pyrometer, a new approach to furnace temperature measurement. In *Copper 87, Vol. 4, Pyrometallurgy of Copper*, ed. Díaz, C., Landolt, C. and Luraschi, A., Alfabeta Impresores, Lira 140, Santiago, Chile, 375 391.
- Peretti, E.A. (1948) An analysis of the converting of copper matte. *Discuss. Faraday Soc.*, 4, 179 184.
- Persson, W., Wendt, W. and J. Demetrio, S. (1999) Use of optical on-line production control in copper smelters. In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., Weddick, A.J., TMS, Warrendale, PA, 491 503.
- Richards, G.G., Legeard, K.J., Bustos, A.A., Brimacombe, J.K. and Jorgensen, D. (1986) Bath slopping and splashing in the copper converter. In *The Reinhardt Schuhmann International Symposium on Innovative Technology and Reactor Design in Extraction Metallurgy*, ed. Gaskell, D.R., Hager, J.P., Hoffmann, J.E. and Mackey, P.J., TMS, Warrendale, PA, 385 402.

Schonewille R.H., O'Connell, G.J. and Toguri, J.M. (1993) A quantitative method for silica flux evaluation. *Metallurgical Transactions B*, **24B**, 63 73.

Sharma, R.C. and Chang Y.A. (1980) A thermodynamic analysis of the copper sulfur system. *Metallurgical Transactions B*, **11B**, 575 583.

Sharma, S.N., Jimenez, R.A., Ogilvie, K.M. and Hanssen, A.H. (1979) Control of secondary emissions from copper converters. In *Copper and Nickel Converters*, ed. Johnson, R.E., TMS, Warrendale, PA, 312 335.

Shibasaki, T. and Hayashi, M. (1991) Top blowing injection smelting and converting - the Mitsubishi process. In *International Symposium on Injection in Process Metallurgy*, ed. Lehner, T., Koros, P.J. and Ramachandran, V., TMS, Warrendale, PA, 199 213.

Shook, A.A., Pasca, O. and Eltringham, G.A. (1999) Online SO₂ analysis of copper converter off-gas. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., Weddick, A.J., TMS, Warrendale, PA, 465 475.

Tenmaya, Y., Inoue, H., Matsumoto, M. and Watanabe, K. (1993) Current operation of converter and anode furnace in Kosaka smelter. In *Converting, Fire Refining and Casting*, ed. McCain, J.D. and Floyd, J.M., TMS, Warrendale, PA, 363 370.

Verney, L.R. (1987) Peirce-Smith copper converter operations and economics. In *Copper 87, Vol. 4, Pyrometallurgy of Copper*, ed. Díaz, C., Landolt, C. and Luraschi, A., Alfabeta Impresores, Lira 140, Santiago, Chile, 375 391.

Vogt, J.A., Mackey, P.J. and Balfour, G.C. (1979) Current converter practice at the Horne smelter. In *Copper and Nickel Converters*, ed. Johnson, R.E., TMS, Warrendale, PA, 357 390.

CHAPTER 10

Continuous Converting

Chapter 9 indicates that most converting is done in rotary Peirce-Smith converters. Peirce-Smith converting is a 'batch' process which blows oxygen-enriched air or air through submerged tuyeres into molten matte. It produces molten blister copper and molten slag.

A disadvantage of the Peirce-Smith converter is that it is fed and emptied by rotating its mouth out of its blowing position, Fig. 1.6b. This makes the converting vessel strong and simple but it:

- (a) makes converting discontinuous
- (b) makes SO_2 -offgas capture somewhat inefficient.

These inefficiencies have led to the development of three continuous converting processes:

- (a) downward lance Mitsubishi converting
- (b) solid matte Outokumpu flash converting
- (c) submerged tuyere Noranda continuous converting.

All convert continuously and collect offgas continuously.

This chapter describes these processes in terms of their principles of operation, their 2002 industrial applications and their potential.

10.1 Common Features of Continuous Converting

Continuous converters always contain molten metallic copper, $\sim 1220^\circ\text{C}$. They also contain highly oxidized slag with considerable Cu, Fe^{+++} and sometimes solid Fe_3O_4 (magnetite).

The continuous presence of metallic copper in a furnace requires that special care be taken with:

- (a) refractories, to avoid copper penetration, solidification and floating of the refractory by the dense, fluid copper
- (b) taphole construction and maintenance, to avoid rapid erosion of the tapholes.

This necessity for special care probably explains the century-plus longevity of batch, Peirce-Smith style converting. Metallic copper resides in the Peirce-Smith converter for only 30% of its cycle and it avoids tapholes by mouth pouring.

10.1.1 Continuous converting impurity behavior

Copper metal always tends to absorb impurities from a converter's feed materials. Batch converting avoids some of this by removing impurities from the converter in slag and offgas before metallic copper appears.

Continuous converters, on the other hand, always contain molten metallic copper – which is always available to absorb impurities. Continuous converter smelters have minimized this effect by:

- (a) lowering the impurity content of their feed matte by not recycling some smelting and converting dusts (Gabb *et al.*, 1995)
- (b) providing impurity removal processes after continuous converting (Prevost *et al.*, 1999; Newman *et al.*, 1991).

Potential users should, therefore, test for impurity behavior before adopting a continuous converting process.

10.1.2 Avoidance of foaming

Copper converters tend to form slag-gas foams. In extreme cases, the foam can fill and overflow the converter, endangering workers and damaging the converter and its auxiliary apparatus.

The main cause of slag foaming is over-oxidizing Fe to solid magnetite under the highly oxidizing conditions of converting. This solid magnetite makes the slags viscous and susceptible to foaming.

Slag foaming is avoided by:

- (a) avoiding slag over-oxidation
- (b) avoiding gas formation beneath the slag.

The methods by which Mitsubishi, Outokumpu and Noranda converting avoid foaming are described in Sections 10.2.4, 10.3.2 and 10.4.5.

10.1.3 Choice of matte grade for continuous converting

The matte that continuous converters receive from smelting is 68-75% Cu. Production of this high-Cu matte:

- (a) generates most of the Fe and S oxidation heat in the smelting furnace where it is needed for heating and melting
- (b) gives maximum impurity removal before continuous converting
- (c) minimizes slag production in the converting furnace.

Minimization of converter slag is important because continuous converting slags:

- (a) contain 10 to 20% Cu
- (b) are usually recycled to smelting to recover this Cu (at extra cost).

10.2 Downward Lance Mitsubishi Continuous Converting (See also Chapter 13)

Mitsubishi converting blows oxygen-enriched air downwards through lances onto a molten slag/matte/copper bath, Figure 10.1. Tables 10.1, 13.1 and 13.2 give operating data.

The Mitsubishi converter is used mostly as part of the Mitsubishi continuous smelting/converting system (Chapter 13, four operating systems in 2002). It is used in one case to convert the matte from a Noranda smelting furnace, Table 10.1.

10.2.1 Description

The Mitsubishi continuous converter consists of:

- (a) a wall opening for continuously feeding molten matte into the furnace
- (b) vertical lances for blowing oxygen-enriched air and limestone flux continuously into the incoming matte
- (c) a siphon for continuously underflowing the converter's molten copper product
- (d) an overflow hole for continuously overflowing molten slag.

It also has an enclosed 'push-chute' for periodically pushing scrap anodes, purchased scrap and large reverts through its roof (Oshima, *et al.*, 1998).

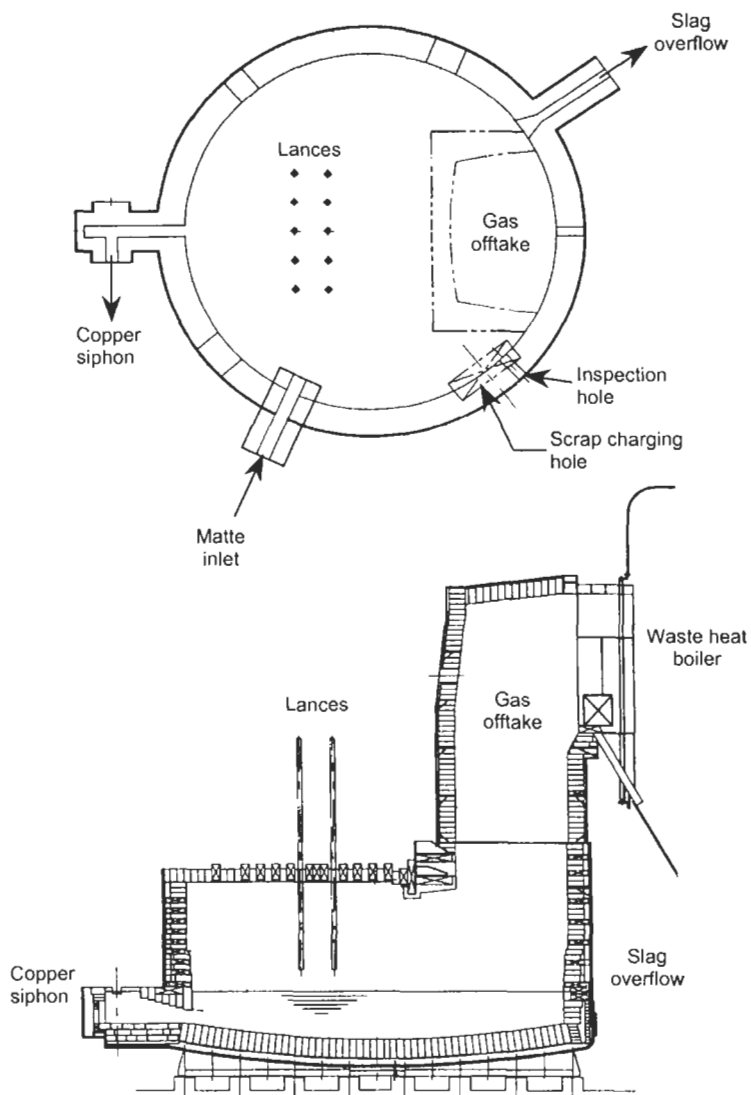


Fig. 10.1. Mitsubishi downward lance continuous converter, 12.5 m diameter. It converts up to 1500 tonnes of matte per day. The 10 rotating vertical lances are notable.

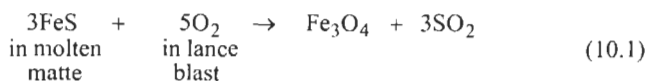
During operation, the converter contains:

a molten copper layer	~1 m thick
a molten slag layer	~0.15 m thick.

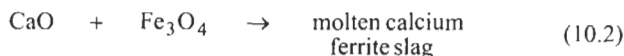
The converter's matte feed is completely consumed as it pours in and passes under the oxygen-air lances. This is shown by the 0.7 to 0.9% S of its product copper – which is lower than would be at equilibrium with a Cu_2S layer (~1% S, Fig. 9.2a).

10.2.2 Reaction mechanism

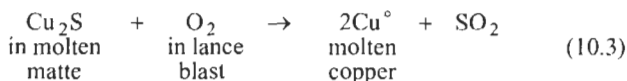
The Mitsubishi converter's molten matte feed, O_2 and flux by the reactions:



and:



then:



giving:

- (a) droplets of copper which descend to the copper layer causing it to underflow through the siphon
- (b) droplets of slag which rise to the slag layer, causing it to overflow the slag hole.

Some copper is inadvertently oxidized to Cu_2O – which joins the calcium ferrite slag, Section 13.4.1.

10.2.3 Industrial details (Table 10.1)

Molten matte continuously enters the converter through a sidewall opening. It continuously spreads out across the molten copper bath – pushing slag towards its overflow notch.

Oxygen-enriched air, CaCO_3 flux and reverts are blown into the matte through 5 to 10 vertical lances through the roof of the converter. Each lance consists of two concentric pipes – a central pipe for air-blown solids and an annulus for

Table 10.1. Physical and operating details of Port Kembla's Mitsubishi continuous converter, 2001.

Smelter	Port Kembla Copper
Mitsubishi converter startup date	2000
Converting furnace details	
shape	circular
diameter × height inside, m	8.05 × 3.6
lances	
number	5
outside pipe diameter, cm	10.2
rotations per minute	6.5
inside pipe diameter, cm	8.9
slag layer thickness, m	0.15
copper layer thickness, m	0.88
active copper tapholes	1 continuous siphon
active slag tapholes	1 continuous overflow hole
number of auxiliary burners	5 available
Feeds, tonnes/day	
molten matte from Noranda smelting furnace	460-480 (70% Cu)
CaCO ₃ flux	20-35
copper anode scrap	60-80
reverts	40-45
Blast	
volume% O ₂	32-40
input rate, thousand Nm ³ /hour	9-14
oxygen input rate, tonnes/day	
Products	
copper, tonnes/day	400-420
%S in copper	0.7
%O in copper	0.2
temperature, °C	1225
slag, tonnes/day	60-70
%Cu in slag	12-16
%CaO/%Fe	0.42
temperature, °C	1240
Cu-from-slag recovery method	recycle to smelting furnace
offgas, thousand Nm ³ /hour	13-15
volume% SO ₂ in offgas	28
temperature, °C	1200
dust production, tonnes/day	25-40
Fuel inputs	0 (autothermal)

oxygen-enriched air blast. The central pipes terminate about roof level, the outside pipes 0.5 – 0.8 m above the liquids (Majumdar *et al.*, 1997). The outside pipes are rotated to keep them from becoming stuck in the roof (by metal/slag splashes). They are also slowly lowered as their tips burn back. New sections are welded on top.

The flux and reverts mix with oxidizing gas at the end of the inner pipe. The mixture jets onto the molten bath to form a gas/slag/matte/copper emulsion in which the gas, liquids and solids react to form new copper and new slag at the expense of the molten matte feed.

The copper underflows continuously through its siphon – then down a launder into one of two anode furnaces (Goto *et al.*, 1998).

The slag (14% Cu) travels 4 or 5 m from the lances to its overflow notch where it flows continuously to water-granulation. The slag granules are recycled to smelting (for Cu recovery) or to converting (for temperature control).

The offgas (25 to 30 volume% SO₂) is drawn up a large gas uptake. It passes through a waste heat boiler, electrostatic precipitators and wet gas cleaning system before being blown into a sulfuric acid plant. The offgas contains ~0.06 tonnes of dust per tonne of molten matte feed. It is captured and recycled to smelting for Cu recovery.

A Mitsubishi converter produces 400 to 900 tonnes of copper per day. This is equivalent to 2 or 3 Peirce-Smith converters.

10.2.4 Calcium ferrite slag

The Mitsubishi converter uses CaO-based (rather than SiO₂-based) slag (Goto and Hayashi, 1998). Early in the development of the process, it was found that blowing O₂-rich blast onto the surface of SiO₂-based slag made a crust of solid magnetite. This made further converting impossible. CaO, on the other hand, reacts with magnetite, molten Cu and O₂ to form a molten Cu₂O-CaO-Fe₃O₄ slag, Fig. 13.3. The slag typically contains:

14 to 16% Cu
40 to 55% Fe (mostly Fe⁺⁺⁺)
15 to 20% CaO.

This slag has a low viscosity (~0.1 kg/m·s, Wright *et al.*, 2000) and it avoids solid magnetite formation. It minimizes the potential for slag foaming.

10.2.5 Mitsubishi converting summary

Mitsubishi continuous smelting/converting has been in operation since 1974.

Independent use of a Mitsubishi converter with a Noranda smelting furnace began in 2000. Its applicability for independent use is now being evaluated.

Mitsubishi has developed measurement and control systems which give continuous stable converting. Refractories and water-cooling have also been improved. These improvements have greatly increased the durability of the process. Campaigns in excess of two years are now expected (Lee *et al.*, 1999).

10.3 Solid Matte Outokumpu Flash Converting

Flash converting uses a small Outokumpu flash furnace to convert *solidified/crushed matte* (50 μm) to molten metallic copper (Newman *et al.*, 1999; Davenport *et al.*, 2001). Flash converting entails:

- tapping molten 70% Cu matte from a smelting furnace
- granulating the molten matte to ~ 0.5 mm granules in a water torrent
- crushing the matte granules to 50 μm followed by drying
- continuously feeding the dry crushed matte to the flash converter with 80 volume% O_2 blast and CaO flux, Fig. 10.2

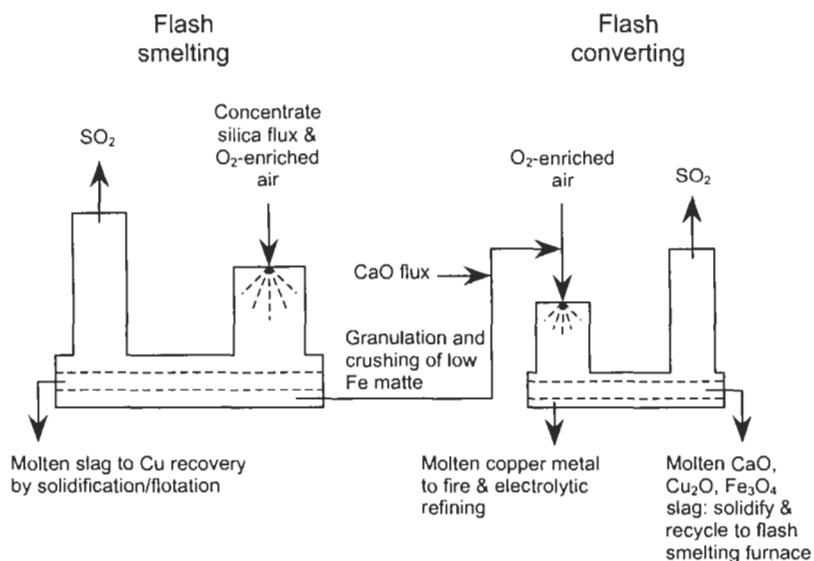


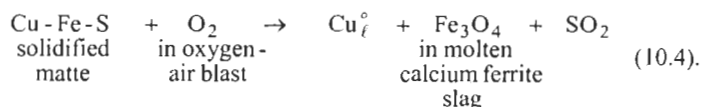
Fig. 10.2. Sketch of Outokumpu flash smelting/flash converting operated by Kennecott Utah Copper. The smelting furnace is 24 m long. The converting furnace is 19 m long. Operating data for the two furnaces are given in Tables 5.1 and 10.2.

- (e) continuously collecting offgas
- (f) periodically tapping molten blister copper and molten calcium ferrite slag.

The uniqueness of the process is its use of particulate solid matte feed. Preparing this feed involves extra processing, but it is the only way that a flash furnace can be used for converting. A benefit of the solid matte feed is that it unlocks the time dependency of smelting and converting. A stockpile of crushed matte can be (i) built while the converting furnace is being repaired and then (ii) depleted while the smelting furnace is being repaired.

10.3.1 Chemistry

Flash converting is represented by the (unbalanced) reaction:



Exactly enough O_2 is supplied to make metallic copper rather than Cu_2S or Cu_2O .

The products of the process (Table 10.2) are:

- (a) molten copper, 0.2% S, 0.3% O
- (b) molten calcium ferrite slag (~16% CaO) containing ~20% Cu
- (c) sulfated dust, ~0.1 tonnes per tonne of matte feed
- (d) 35-40 volume% SO_2 offgas.

The molten copper is periodically tapped and sent forward to pyro- and electrorefining. The slag is periodically tapped, water-granulated and sent back to the smelting furnace. The offgas is collected continuously, cleaned of its dust and sent to a sulfuric acid plant. The dust is recycled to the flash converter and flash smelting furnace.

10.3.2 Choice of calcium ferrite slag

The Kennecott flash converter uses the CaO slag described in Section 10.2.4. This slag is fluid and shows little tendency to foam. It also absorbs some impurities (As, Bi, Sb, but not Pb) better than SiO_2 slag. It is, however, somewhat corrosive and poorly amenable to controlled deposition of solid magnetite on the converter walls and floor.

Table 10.2. Physical and operating details of Kennecott's Outokumpu flash converter, 2001.

Smelter	Kennecott Utah Copper
Flash converter startup date	1995
Size, inside brick, m	
hearth: $w \times l \times h$	$6.5 \times 18.75 \times 3$
reaction shaft	
diameter	4.25
height above settler roof	6.5
gas uptake	
diameter	3
height above settler roof	8.7
slag layer thickness, m	0.3
copper layer thickness, m	0.46
active copper tapholes	6 tapholes + 2 drain holes
active slag tapholes	3
particulate matte burners	1
Feeds, tonnes/day	
granulated/crushed matte	1344 (70% Cu)
matte particle size, μm	
CaO flux	50
recycle flash converter dust	90
Blast	
blast temperature, $^{\circ}\text{C}$	ambient
volume% O_2	75-85
input rate, thousand Nm^3/hour	
oxygen input rate, tonnes/day	307
Products	
copper, tonnes/day	900
%S in copper	0.2
%O in copper	0.3
slag, tonnes/day	290
%Cu in slag	20
%CaO/%Fe	0.35
Cu-from-slag recovery method	granulate and recycle to smelting furnace
offgas, thousand Nm^3/hour	26
volume% SO_2 in offgas	35-40
dust production, tonnes/day	130
copper/slag/offgas temperatures, $^{\circ}\text{C}$	1220/1250/1290
Fuel inputs	
hydrocarbon fuel burnt in reaction shaft	125 Nm^3/hour natural gas
hydrocarbon fuel into settler burners	0

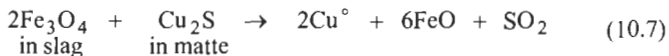
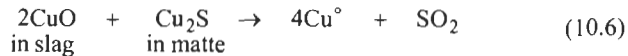
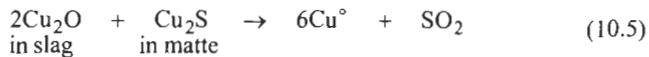
10.3.3 No matte layer

There is no matte layer in the flash converter. This is shown by the 0.2% S content of its blister copper— far below the 1% S that would be in equilibrium with Cu₂S matte. The layer is avoided by keeping the converter's:

$$\frac{\text{O}_2 \text{ input rate}}{\text{matte feed rate}}$$

slightly towards Cu₂O formation rather than Cu₂S formation.

The matte layer is avoided to minimize the possibility of SO₂ formation (and slag foaming) by the reactions:



beneath the slag (Davenport *et al.*, 2001).

10.3.4 Productivity

Kennecott's flash converter in Magna, Utah treats ~1300 tonnes of 70% Cu matte and produces ~900 tonnes of blister copper per day. It is equivalent to 2 or 3 Peirce-Smith converters.

10.3.5 Flash converting summary

Flash converting is an extension of the successful Outokumpu flash matte-smelting process. Kennecott helped Outokumpu develop the process and in 1995 installed the world's first commercial furnace.

The process has the disadvantages that:

- (a) it must granulation-solidify and crush its matte feed, which requires extra energy
- (b) it is not well adapted to melting scrap copper.

On the other hand, it has a simple, efficient matte oxidation system and it efficiently collects its offgas and dust.

10.4 Submerged-Tuyere Noranda Continuous Converting

Noranda continuous converting developed from Noranda submerged tuyere smelting, Chapter 7. It uses a rotary furnace (Fig. 10.3) with:

- (a) a large mouth for charging molten matte and large pieces of scrap
- (b) an endwall slinger and hole for feeding flux, revert pieces and coke
- (c) a second large mouth for drawing offgas into a hood and acid plant
- (d) tuyeres for injecting oxygen-enriched air into the molten matte, Fig. 9.1b
- (e) tapholes for separately tapping molten matte and slag
- (f) a rolling mechanism for correctly positioning the tuyere tips in the molten matte.

The converter operates continuously and always contains molten copper, molten matte (mainly Cu_2S) and molten slag. It blows oxygen-enriched air continuously through its tuyeres and continuously collects $\sim 18\%$ SO_2 offgas. It taps copper and slag intermittently.

10.4.1 Industrial Noranda converter

Noranda has operated its continuous converter since late 1997. It produces ~ 800 tonnes of copper per day. This is equivalent to two or three Peirce-Smith converters.

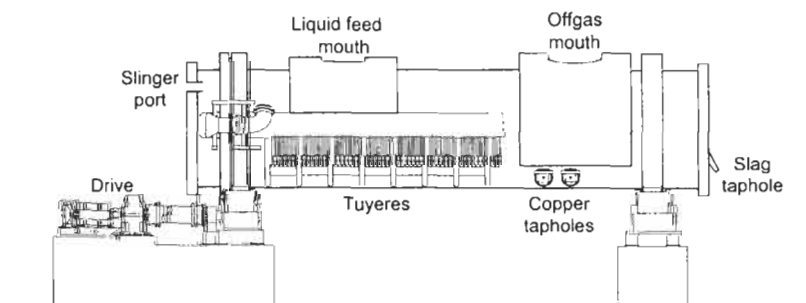


Fig. 10.3. Sketch of Noranda continuous submerged tuyere converter. The furnace is 20m long and 4.5m diameter. It converts matte from a Noranda smelting furnace.

Table 10.3. Physical and operating details of Noranda continuous submerged tuyere converting, 2001.

Smelter	Noranda (Horne)
Noranda converter startup date	1997
Noranda converter details	
shape	horizontal rotating cylinder
diameter × length, inside, m	4.5 × 19.8
tuyeres	44
diameter, cm	6.35
slag layer thickness, m	~0.4
matte layer thickness, m	~0.9
copper layer thickness, m	~0.4
copper tapholes	2 on bottom
slag tapholes	1 on end opposite feed port
number of auxiliary burners	0
Feeds, tonnes/day	
molten matte from Noranda smelting furnace	830
silica flux	70
coke	21
'coolants', e.g. solid matte, smelting furnace slag concentrate, internal and external reverts	380
Blast	
volume% O ₂	27
total input rate, thousand Nm ³ /hour	30
oxygen input rate, tonnes/day	75
feed port air, thousand Nm ³ /hour	2.1
Products	
copper, tonnes/day	700
%Cu / %S / %Pb	98 / 1.3 / 0.15
slag, tonnes/day	370
%Cu in slag	10
mass% SiO ₂ /mass% Fe	0.85
Cu-from-slag recovery method	solidification/flotation
offgas leaving furnace, thousand Nm ³ /hour	35
volume% SO ₂	18.3
dust, tonnes/day (spray chamber + total dust to ESP)	30
copper/slag/offgas temperatures, °C	1210 / 1190 / 1175

10.4.2 Chemical reactions

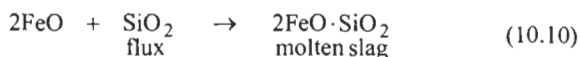
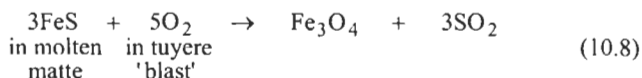
Noranda converting controls its matte and O₂ input rates to always have matte (mainly Cu₂S) in the furnace. It is this matte phase that is continuously oxidized by tuyere-injected O₂.

The constant presence of this matte is confirmed by the high S content, ~1.3%, in the converter's copper product.

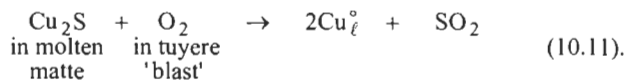
10.4.3 Reaction mechanisms

Reactions in the Noranda continuous converter are as follows:

- (a) a ladle of molten ~70% Cu matte (5 to 10% Fe, ~22% S) is poured into the furnace – it joins the molten matte layer between copper and slag.
- (b) this matte is oxidized by O₂ in the tuyere blast by the reactions:



then (Prevost *et al.*, 1999, page 277):



- (c) the matte phase is continuously consumed, drops of molten slag rise and drops of molten copper fall below the tuyeres to the molten copper layer.
- (d) the matte layer is replenished with Cu, Fe and S by the next ladle of matte feed.

Slag, matte, gas and copper are intimately mixed in emulsion form in the converter's tuyere zone so that the above reaction scheme is an oversimplification. Nevertheless, the concept of slag formation, copper formation, matte consumption and intermittent matte replenishment is probably correct.

10.4.4 Silicate slag

Noranda continuous converting uses SiO_2 slag rather than the Mitsubishi and Outokumpu continuous converting's CaO slag. This is because:

- (a) Noranda's Cu_2S layer tends to reduce magnetite by Reaction (10.7) so that magnetite solubility (in CaO -base slag) is not critical
- (b) SiO_2 slag is cheaper, less corrosive and more easily controlled than CaO slag.

10.4.5 Control

The critical control parameters in Noranda continuous converting are:

- (a) matte temperature
- (b) matte 'layer' position and thickness (to ensure that tuyere O_2 blows into matte rather than into slag or copper).

Matte temperature is measured continuously with a Noranda tuyere two wavelength optical pyrometer (Prevost *et al.*, 1999). It is adjusted by increasing or decreasing the rate at which solid 'coolants' (solid matte, slag concentrate, reverts, etc.) are charged to the converter. Natural gas combustion rate and coke addition rate are also used to control temperature.

Matte layer thickness is controlled by adjusting:

$$\frac{\text{total } \text{O}_2 \text{ input rate}}{\text{matte feed rate}}.$$

A high ratio decreases matte mass (hence matte layer thickness), a low ratio the opposite.

Matte layer position is controlled by adjusting the amount of copper below the matte. It is altered by adjusting the frequency at which copper is tapped from the furnace.

Blowing of O_2 into the slag is avoided. It tends to overoxidize the slag, precipitate magnetite and cause slag foaming. It is avoided by controlling copper and matte layer thicknesses as described above.

10.4.6 Noranda converting summary

The Noranda continuous converter is a compact, highly productive, submerged tuyere converting process. It charges its matte via ladle through a large mouth, which is also used for charging large pieces of scrap copper. It produces 1.3% S

molten copper which is sent to a desulfurizing furnace prior to pyro- and electrorefining.

10.5 %Cu-in-Slag

The slags from Noranda continuous submerged-tuyere converting contain ~10% Cu. This is high, but lower than the 14% and 20% Cu in the slags from Mitsubishi top blown converting and Outokumpu flash converting.

Continuous converting's Cu-in-slag is always high because the process's:

$$\frac{\text{O}_2 \text{ input rate}}{\text{concentrate feed rate}}$$

- (a) is set high enough to produce metallic copper rather than Cu_2S
- (b) this setting inadvertently produces some Cu_2O in slag.

Noranda's slag is lowest in Cu_2O . This is because the Noranda furnace always contains a Cu_2S layer which partially reduces Cu_2O to metallic copper, Reaction (10.5).

Flash converting's Cu_2O -in-slag is highest because it deliberately avoids a Cu_2S layer to avoid slag foaming.

Mitsubishi converting's Cu_2O -in-slag is intermediate.

10.6 Summary

In 2002, most converting of molten matte to molten copper metal is done by 'batch' Peirce-Smith submerged tuyere converting, Chapter 9. It is the most inefficient and environmentally difficult part of pyrometallurgical copper production. This has led engineers to develop three continuous converting processes:

downward lance Mitsubishi converting
solid matte Outokumpu flash converting
submerged tuyere Noranda converting.

All continuously oxidize matte to molten copper. All continuously collect SO_2 offgas and send it to a sulfuric acid plant.

Batch converting is inefficient and environmentally difficult. It is, on the other hand, simple and well understood. It is still resisting replacement.

Nevertheless, continuous converting is advantageous environmentally and it minimizes materials handling. These should lead to its gradual adoption.

Suggested Reading

Davenport, W.G., Jones, D.M., King, M.J. and Partelpoeg, E.H. (2001) *Flash Smelting: Analysis, Control and Optimization*, TMS, Warrendale, PA.

Goto, M. and Hayashi, M. (1998) *The Mitsubishi Continuous Process*, Mitsubishi Materials Corporation, Tokyo, Japan www-adm@mmc.co.jp

Newman, C.J., Collins, D.N. and Weddick, A.J. (1999) Recent operation and environmental control in the Kennecott smelter. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 29-45.

Prevost, Y., Lapointe, R., Levac, C.A. and Beaudoin, D. (1999) First year of operation of the Noranda continuous converter. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 269-282.

References

Davenport, W.G., Jones, D.M., King, M.J. and Partelpoeg, E.H. (2001) *Flash Smelting: Analysis, Control and Optimization*, TMS, Warrendale, PA.

Gabb, P.J., Howe, D.L., Purdie, D.J. and Woerner, H.J. (1995) The Kennecott smelter hydrometallurgical impurities process. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrorefining and Hydrometallurgy of Copper*, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G., The Metallurgical Society of CIM, Montreal, Canada, 591-606.

Goto, M. and Hayashi, M. (1998) *The Mitsubishi Continuous Process*, Mitsubishi Materials Corporation, Tokyo, Japan www-adm@mmc.co.jp

Goto, M., Oshima, I. and Hayashi, M. (1998) Control Aspects of the Mitsubishi Continuous Process, *JOM*, **50**(4), 60-65.

Lee, J.H., Kang, S.W., Cho, H.Y. and Lee, J.J. (1999) Expansion of Onsan Smelter. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 255-267.

Majumdar, A., Zuliani, P., Lenz, J.G. and MacRae, A. (1997) Converting furnace integrity project at the Kidd metallurgical copper smelter. In *Proceedings of the Nickel-Cobalt 97 International Symposium, Vol. III Pyrometallurgical Operations, Environment, Vessel Integrity in High-Intensity Smelting and Converting Processes*, ed. Diaz, C., Holubec, I. and Tan, C.G., Metallurgical Society of CIM, Montreal, Canada, 513-524.

Newman, C.J., Collins, D.N. and Weddick, A.J. (1999) Recent operation and environmental control in the Kennecott smelter. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 29 45.

Newman, C.J., MacFarlane, G., Molnar, K. and Storey, A.G. (1991) The Kidd Creek copper smelter - an update on plant performance. In *Copper 91-Cobre 91, Proceedings of the Second International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C., Luraschi, A. and Newman, C.J., Pergamon Press, New York, NY, 65 80.

Oshima, E., Igarashi, T., Hasegawa, N. and Kumada, H. (1998) Recent operation for treatment of secondary materials at Mitsubishi process. In *Sulfide Smelting '98*, ed. Asteljoki J.A. and Stephens, R.L., TMS, Warrendale, PA, 597 606.

Prevost, Y., Lapointe, R., Levac, C.A. and Beaudoin, D. (1999) First year of operation of the Noranda continuous converter. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 269 282.

Wright, S., Zhang, L., Sun, S. and Jahanshahi, S. (2000) Viscosity of calcium ferrite slags and calcium alumino-silicate slags containing spinel particles. In *Proceedings of the Sixth International Conference on Molten Slags, Fluxes and Salts*, ed. Seetharaman, S. and Sichen, D., Division of Metallurgy, KTH, Stockholm, Sweden, paper number 059.

CHAPTER 11

Copper Loss in Slag

Pyrometallurgical production of molten copper generates two slags, smelting and converting. Smelting furnace slag contains one or two percent Cu, Table 4.2. The percentage increases as matte grade increases. Converter slag contains four to eight percent Cu, Table 9.2. Its percentage increases as converting proceeds, i.e. as % Cu-in-matte increases.

Multiplying these percentages by the mass of each slag shows that a significant fraction of the Cu in the original concentrate is present in these slags. This fraction is increased by the production of higher-grade mattes in the smelting furnace. Because of this, the value of the Cu in these slags is usually too high to justify the old practice of simply discarding them.

This chapter discusses the nature of Cu in smelting and converting slags. It also describes strategies for minimizing the amount of Cu lost from their disposal. The main strategies include:

- (a) minimizing the mass of slag generated
- (b) minimizing the percentage of Cu in the slags
- (c) processing the slags to recover as much Cu as possible.

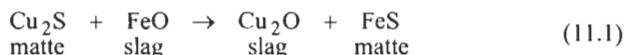
Slag processing can be divided into two types. The first is pyrometallurgical reduction and settling, performed in an electric or fuel fired slag-cleaning furnace. The second is minerals processing of solidified slag, including crushing, grinding and froth flotation, to recover Cu from the slag.

11.1 Copper in Slags

The Cu in smelting and converting slags is present in two forms:

- (a) dissolved Cu, present mostly as Cu^+ ions
- (b) entrained droplets of matte.

The dissolved Cu is associated either with O^{2-} ions (i.e. Cu_2O), or with S^{2-} ions (Cu_2S). Cu_2O becomes the dominant form of dissolved Cu at matte grades above 70% Cu_2S (Nagamori, 1974; Barnett, 1979), due to the increased activity of Cu_2S in the matte. Higher Cu_2S activity pushes the reaction:



to the right. The solubility of sulfur in slags is also lower in contact with higher-grade mattes (Matousek, 1995). As a result, dissolved Cu in *converter* slags is present mostly as Cu_2O .

Conversely, the dissolved Cu in *smelting furnace* slags is present mostly as Cu_2S . This is due to the smelting furnace's lower matte grades and oxygen potentials.

There are several sources of entrained matte in slags. The most obvious are droplets of matte that have failed to settle completely through the slag layer during smelting. Stokes' Law predicts the rate at which matte droplets will settle through molten slag, i.e.:

$$V = \frac{1}{18} g \frac{\rho_{\text{drop}} - \rho_{\text{slag}}}{\mu_{\text{slag}}} (\phi_{\text{drop}})^2 \quad (11.2).$$

In this expression V is the settling rate of the matte droplets (m/s), g the gravitational constant (9.8 m/s^2), ρ_{drop} matte density ($3900\text{--}5200 \text{ kg/m}^3$), ρ_{slag} slag density ($3300\text{--}3700 \text{ kg/m}^3$), μ_{slag} slag viscosity ($\sim 0.1 \text{ kg/m}\cdot\text{s}$) and ϕ_{drop} the diameter (m) of the settling matte droplet.

The expression is most accurate for systems with Reynolds numbers below 10 (i.e., droplet sizes below $\sim 1 \text{ mm}$). Larger matte droplets settle at slower rates than predicted by Stokes' Law. However, it is the settling rates of the smallest droplets that are of greatest concern, Table 11.1.

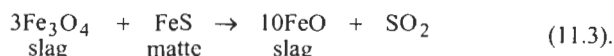
The table shows just how long the smallest matte droplets can take to settle. Besides droplet size, the biggest influences on settling rate are temperature and slag silica content. Higher temperatures and lower silica levels decrease slag viscosities, increasing settling rate. A more reducing environment also encourages settling, by decreasing the $\text{Fe}_3\text{O}_4(\text{s})$ content of the slag (Ip and Toguri, 2000).

Table 11.1. Calculated settling velocities and residence times of matte droplets settling through molten slag. Input data: matte density, 4500 kg/m³; slag density, 3500 kg/m³; slag viscosity, 0.1 kg/m·s.

Drop diameter (mm)	Settling velocity (m/s)	Time to settle through one meter of slag (s)
10	0.55	2
3	0.049	20
1	0.0055	183
0.3	0.00049	2039 (0.57 hr)
0.1	0.000055	18349 (5.1 hr)

In addition, matte grade has an impact on settling rates. Low Cu-grade mattes have lower densities than high-grade mattes and therefore settle at slower rates (Fagerlund and Jalkanen, 1999).

Matte droplets can become suspended in smelter slags by several other mechanisms. Some are carried upwards from the molten matte layer by gas bubbles generated by the reaction (Poggi, *et al.*, 1969):



Still others appear by precipitation from the slag in colder areas of the smelting furnace (Barnett, 1979). Converter slag returned to a smelting furnace also contains suspended matte droplets, which may not have time to completely settle. As a result, entrained matte can represent from 50% to 90% of total Cu-in-slag (Ajima *et al.*, 1995; Imriš *et al.*, 2000).

11.2 Decreasing Copper in Slag I: Minimizing Slag Generation

It seems logical to suggest that decreasing the amount of Cu lost in smelting and converting slags could be accomplished by decreasing slag production. However, methods to decrease slag mass may do more harm than good. Possibilities include the following:

- (a) *maximizing concentrate grades.* The less gangue in the concentrate, the less silica required to flux it and the less overall slag generated. However, increasing concentrate grades may come at the expense of decreasing Cu recoveries in the concentrator.

- (b) *adding less flux.* Adding less flux would decrease slag mass (desirable) and decrease its viscosity, making settling easier (also desirable). However, it would also increase the activity of FeO in the slag, leading to more dissolved Cu_2O by Reaction (11.1) (undesirable) and more magnetite (also undesirable).

11.3 Decreasing Copper in Slag II: Minimizing Cu Concentration in Slag

Cu-in-slag concentrations are minimized by:

- (a) maximizing slag fluidity, principally by avoiding excessive $\text{Fe}_3\text{O}_4(\text{s})$ in the slag and by keeping the slag hot
- (b) providing enough SiO_2 to form distinct matte and slag phases
- (c) providing a large quiet zone in the smelting furnace
- (d) avoiding an excessively thick layer of slag
- (e) avoiding tapping of matte with slag.

Metallurgical coke or coal may also be added to the smelting furnace to reduce $\text{Fe}_3\text{O}_4(\text{s})$ to $\text{FeO}(\ell)$.

11.4 Decreasing Copper in Slag III: Pyrometallurgical Slag Settling/Reduction

Conditions that encourage suspended matte droplets to settle to a matte layer are low viscosity slag, low turbulence, a long residence time and a thin slag layer.

These conditions are often difficult to obtain in a smelting vessel, particularly the necessary residence time. As a result, Cu producers have since the 1960's constructed separate furnaces specifically for 'cleaning' smelting and converting slags. These furnaces have two purposes:

- (a) allowing suspended matte droplets to finish settling to the molten matte layer
- (b) facilitating the reduction of dissolved Cu oxide to suspended Cu sulfide drops.

Inputs to these furnaces vary considerably. Slag cleaning furnaces associated with bath-smelting units like the Isasmelt or Mitsubishi smelting furnace accept an un-separated mixture of slag and matte and are required to do all the settling.

Others accept converter slag in addition to smelter slag, requiring more emphasis on reduction. Most commonly, these furnaces are fed only smelting-furnace slag and are used primarily as a 'final settling' furnace.

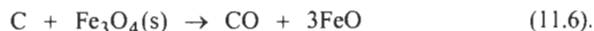
Fig. 11.1 illustrates a typical electric slag-cleaning furnace (Barnett, 1979; Higashi *et al.*, 1993; Kucharski, 1987). Heat is generated by passing electric current through the slag layer. AC power is used, supplied through three carbon electrodes. This method of supplying heat generates the least amount of turbulence, which improves settling rates. The furnace sidewalls are cooled by external water jackets to minimize refractory erosion.

Table 11.2 compares the operating characteristics of seven electric furnaces. Required capacities are set by the size of the smelting operation and the choice of input slags. Settling times are usually on the order of one to five hours. Typical energy use is 15–70 kWh per tonne of slag, depending upon furnace inputs, target % Cu, temperature and residence time.

While some electric slag-cleaning furnaces process only smelting furnace slag, others are fed a variety of materials. Several furnace operators input converter slag or solid reverts in addition to smelting slag. When this is done, a reducing agent is often required to reduce Cu oxide in the slag to Cu metal or Cu sulfide. Coal or coke is often added for this reduction. Pyrite may also be added if additional sulfur is needed to form matte (Ponce and Sánchez, 1999):



Carbon additions also reduce solid magnetite in the slag to liquid FeO:



This decreases slag viscosity and improves settling rates.

Ferrosilicon is occasionally used as a reducing agent (Shimpo and Toguri, 2000), especially in the Mitsubishi slag-cleaning furnace, Chapter 13. Recent initiatives in slag-cleaning furnace practice have involved lance injection of solid reductants or gaseous reducing agents such as methane, to improve reduction kinetics (Addemir, *et al.*, 1986; An, *et al.*, 1998; Sallee and Ushakov, 1999).

Fuel-fired slag cleaning furnaces are also used in a few smelters, Table 11.3. The foremost is the Teniente slag-cleaning furnace, which is similar in design to a rotary fire-refining furnace (Chapter 15, Campos and Torres, 1993; Demetrio *et al.*, 2000).

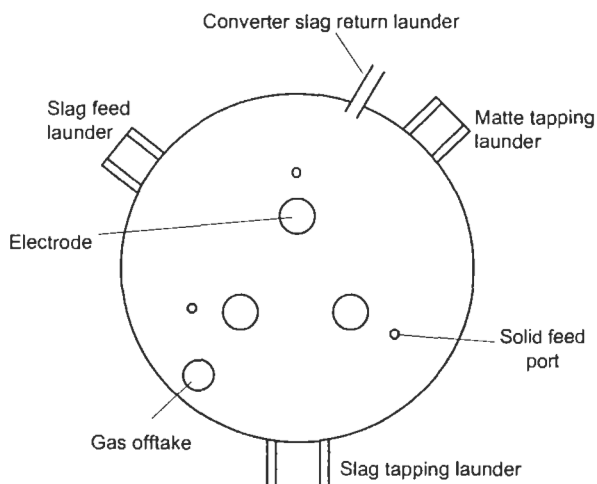
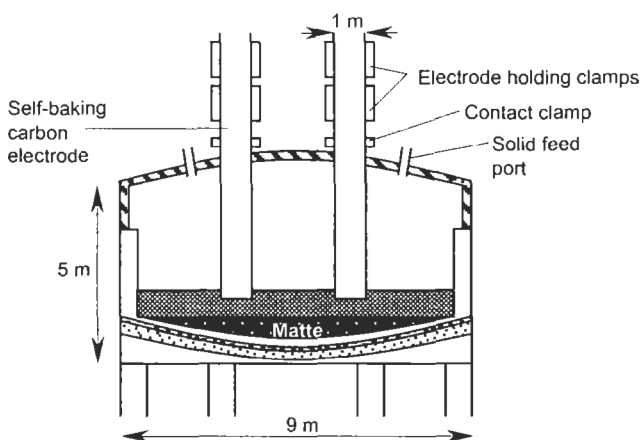


Fig. 11.1. Electric slag cleaning furnace. A furnace of this size 'cleans' 1000 to 1500 tonnes of slag per day.

Table 11.2. Details of electric slag cleaning furnaces, 2001.

Smelter	Caraiba Metais Dias d'Avila Brazil	Norddeutsche Affinerie Hamburg	Nippon Mining Saganoseki Japan	Sumitomo Toyo Japan	LG Nikko Onsan Korea	Mexicana de Cobre Mexico Furnace 1	Mexicana de Cobre Mexico Furnace 2
Slag details, tonnes/day							
smelting furnace slag	880 OK flash furnace	1600 OK flash furnace	1386 OK flash furnace	1212 OK flash furnace	609 OK flash furnace	900 OK flash furnace	740 Teniente furnace
% Cu	1.7	1-1.5	1-1.2	1.3	2	1.5 to 2.5	5
converter slag		0			260	113	184
% Cu					5	8	8
Products							
slag, % Cu	0.7	0.6-0.8	0.8	0.7	0.8	1.26	1.3
matte, % Cu	65-70	65-70	65.5	63	68-72	70.3	70.5
Furnace details							
shape	circular	circular	circular	ellipse	circular	circular	circular
diameter, m	11	10.2	9	5.1 x 13	8.1	10	10
power rating, MW	2-4	2-3	0.7-1.1	1.85	2-3	1.5-4.5	1.5-4.5
electrodes	3	3	3	5	3	3	3
material	self baking	self baking	self baking	self baking	self baking	self baking	self baking
diameter, m	1	1	0.68	3 x 0.72; 2 x 0.55	0.8	0.9	0.9
Operating details							
slag residence time, hours	2-3	5	1.5-3.0	2	2-5	0.25-1	0.25-1
energy use, kWh/tonne of slag	70	40-50	15	16	50	57	69
reductant, kg/tonne of slag	coke, 8.3	coke, 4-5	coke, 15	coal, 2	12.5 coke	7.17 coke	7.32 coke
slag layer thickness, m	0.97-1.4	1.5-1.8	0.5-0.9	0.6	1-1.3	0.8-1.5	0.8-1.5
matte layer thickness, m	0-0.45	0-0.4	0.4-0.8	0.8	0-0.3	0-0.2	0-0.2

Table 11.3. Details of Teniente rotary hydrocarbon-fired slag settling furnace at Caletones, Chile, 2001.

Smelter	Caletones, Chile
Slag details	
smelting furnace slag, tonnes/day	3000
% Cu	6 to 8
converting furnace slag, tonnes/day	0
% Cu	
Products	
slag, % Cu	1
matte, % Cu	72
matte destination	Peirce-Smith converters Teniente smelting furnace
% Cu recovery	85%
Furnace details	
number of slag cleaning furnaces	4
shape	horizontal cylinder
diameter inside refractory, m	4.6
length inside refractory, m	3 × 10.7; 1 × 12.7
number of reducing tuyeres	4
tuyere diameter, cm	6.35
Operating details	
slag residence time, hours	2
reductant	coal, oil or natural gas
kg per tonne of slag	6
slag layer thickness, m	1.4
matte layer thickness, m	0.4
fuel	bunker C fuel oil
kg per tonne of slag	8.8

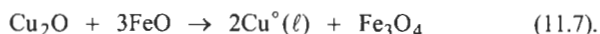
It features injection of powdered coal and air into molten slag. It operates on a batch basis, generating slag with 0.6–0.8% Cu (Achurra, *et al.*, 1999). Ausmelt has also developed a fuel-fired furnace (like Fig. 8.1) for cleaning slags and residues.

% Cu-in-slag after pyrometallurgical settling is 0.7 to 1.0% Cu, which is lost when the slag is discarded. Some effort has been made to recover this Cu by leaching (Das, *et al.*, 1987). The leaching was successful, but is likely to be too expensive on an industrial scale.

11.5 Decreasing Copper in Slag IV: Slag Minerals Processing

Several options are available for recovering Cu from converter slags. Pyrometallurgical 'cleaning' in electric furnaces is quite common. Molten converter slag is also recycled to reverberatory smelting furnaces and Inco flash furnaces. Outokumpu and Teniente smelting furnaces occasionally accept some molten converter slag (Warczok *et al.*, 2001).

Cu is also removed from converter slags by slow solidification, crushing/grinding and froth flotation. It relies on the fact that, as converter slags cool, much of their dissolved Cu exsolves from solution by the reaction (Victorovich, 1980):



Reaction (11.7) is increasingly favored at low temperatures and can decrease the dissolved Cu content of converter slag to well below 0.5% (Bérubé *et al.*, 1987; Imriš *et al.*, 2000). After the slag has solidified, the exsolved copper and suspended matte particles respond well to froth flotation. As a result, converter slags have long been crushed, ground and concentrated in the same manner as sulfide ores (Subramanian and Themelis, 1972).

The key to successful minerals processing of converter slags is ensuring that the precipitated grains of matte and metallic Cu are large enough to be liberated by crushing and grinding. This is accomplished by cooling the slag slowly to about 1000°C (Subramanian and Themelis, 1972), then naturally to ambient temperature. Once this is done, the same minerals processing equipment and reagents that are used to recover Cu from ore can be used to recover Cu from slag, Table 11.4.

Some smelting slags are also treated this way, Table 11.4 and Davenport *et al.*, (2001).

11.6 Summary

Cu smelters produce two slags: smelting furnace slag with one to two percent Cu and converter slag with four to eight percent Cu. Discard of these slags would waste considerable Cu, so they are almost always treated for Cu recovery.

Cu is present in molten slags as (i) entrained droplets of matte or metal and (ii) dissolved Cu^+ . The entrained droplets are recovered by settling in a slag-cleaning furnace, usually electric. The dissolved Cu^+ is recovered by hydrocarbon reduction and settling of matte.

Table 11.4. Details of four slag flotation plants, 2001. The 0.4 to 0.65 % Cu in slag tailings is notable.

Smelter	Noranda, Québec	Saganoski, Japan	Toyo, Japan	PASAR, Philippines
Slag inputs, tonnes/day				
smelting furnace slag	1700	0	0	0
%Cu	6 (average)			
converter slag	300	450	450	370
%Cu		8.33	6.5	10-15*
Products				
slag concentrate, %Cu	42	21.8	28	29-33
slag tailings, %Cu		0.65	0.4	0.5-0.6
Cu recovery, %	90-95	95	95	97-98
Operating details				
solidification method	ladle cooling with or without water sprays	~150 kg ingots on moving slag conveyor	~150 kg ingots on moving slag conveyor	
cooling description		cooled on slag conveyor	1 hour in air then immersion in H ₂ O	
Crushing/grinding				
equipment	80% semi autogenous grinding, 20% crushing & ball milling	jaw crusher; cone crusher (twice); ball mill (twice)	gyratory crusher; cone crusher (twice); ball mill	jaw crusher; cone crusher; ball mills (primary and regrind)
particle size after grinding	78% -44 µm	40-50% -44 µm	90% -44 µm	65-75% -45 µm
Flotation				
machinery	mechanically agitated cells	mechanically agitated cells	mechanically agitated cells	mechanical agitator Agitair 48, Jameson cell (Fig. 3.12)**
flotation residence time	60 minutes		30 minutes (rougher+scavenger)	
Flotation reagents				
promoter				NH ₄ & Na dibutyl dithiophosphate
collector	thionocarbamate, SIPX	Na isopropyl xanthate, UZ200	thionocarbamate, PAX	a) Danafloat 245, Penfloat TM3
frother	propylene glycol	pine oil, MF550	pine oil	b) K amyl xanthate
CaO?	no	no		pine oil NF 183
pH	8-9	7-8	7-8	yes
Energy use kWh/tonne slag	32.5	58.4	64	8.5-9.5
				40

*Non-magnetic 'white metal' (Cu₂S) pieces are isolated magnetically after crushing, leaving 5 to 6.5% Cu in the ball mill feed slag. ** Switching to all Jameson cells.

A second method of recovering this Cu from slag is slow-cooling/solidification, crushing/grinding and froth flotation. Slowly-cooled/solidified slag contains the originally entrained matte and Cu droplets plus matte and Cu which precipitate during cooling/solidification. These Cu-bearing materials are efficiently recovered from the solidified slag by fine grinding and froth flotation.

Electric furnace settling has the advantage that it can be used for recovering Cu from reverbs and miscellaneous materials around the smelter. Slag flotation has the advantages of more efficient Cu recovery and the possibility of using a company's existing crushing/grinding/flotation equipment.

Suggested Reading

Barnett, S.C.C. (1979) The methods and economics of slag cleaning. *Min. Mag.*, **140**, 408 417.

Demetrio, S., Ahumada, J., Ángel, D.M., Mast, E., Rosas, U., Sanhueza, J., Reyes, P. and Morales, E. (2000) Slag cleaning: The Chilean copper smelter experience. *JOM*, **52** (8), 20 25.

Imriš, I., Rebolledo, S., Sanchez, M., Castro, G., Achurra, G. and Hernandez, F. (2000) The copper losses in the slags from the El Teniente process. *Can. Metall. Q.*, **39**, 281 290.

References

Achurra, G., Echeverria, P., Warczok, A., Riveros, G., Díaz, C. M. and Utigard, T. A. (1999) Development of the El Teniente slag cleaning process. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. VI Smelting, Technology Development, Process Modeling and Fundamentals*, ed. Díaz, C., Landolt, C. and Utigard, T., TMS, Warrendale, PA, 137 152.

Addemir, O., Steinhäuser, J. and Wuth, W. (1986) Copper and cobalt recovery from slags by top-injection of different solid reductants. *Trans. Inst. Min. Metall., Sect. C*, **95**, C149 C155.

Ajima, S., Igarashi, T., Shimizu, T. and Matsutani, T. (1995) The Mitsubishi process ensures lower copper content in slag. In *Quality in Non-ferrous Pyrometallurgy*, ed. Kozłowski, M. A., McBean, R. W. and Argyropoulos, S. A., The Metallurgical Society of CIM, Montreal, Canada, 185 204.

An, X., Li, N. and Grimsey, E.J. (1998) Recovery of copper and cobalt from industrial slag by top-submerged injection of gaseous reductants. In *EPD Congress 1998*, ed. Mishra, B., TMS, Warrendale, PA, 717 732.

Barnett, S.C.C. (1979) The methods and economics of slag cleaning. *Min. Mag.*, **140**, 408 417.

Bérubé, M., Choquette, M. and Godbehre, P. W. (1987) Mineralogie des scories cuprifères. *CIM Bulletin*, **80** (898), 83 90.

- Campos, R. and Torres, L. (1993) Caletones Smelter: two decades of technological improvements. In *Paul E. Queneau International Symposium., Vol. II*, ed. Landolt, C. A., TMS, Warrendale, PA, 1441 1460.
- Das, R. P., Anand, S., Sarveswara Rao, K. and Jena, P. K. (1987) Leaching behaviour of copper converter slag obtained under different cooling conditions. *Trans. Inst. Min. Metall., Sect. C*, **96**, C156 C161.
- Davenport, W.G., Jones, D.M., King, M.J. and Partelpoeg, E.H. (2001) *Flash Smelting, Analysis, Control and Optimization*, TMS, Warrendale, PA, 22 25.
- Demetrio, S., Ahumada, J., Ángel, D.M., Mast, E., Rosas, U., Sanhueza, J., Reyes, P. and Morales, E. (2000) Slag cleaning: the Chilean copper smelter experience. *JOM*, **52** (8), 20 25.
- Fagerlund, K. O. and Jalkanen, H. (1999) Some aspects on matte settling in copper smelting. in *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. VI Smelting, Technology Development, Process Modeling and Fundamentals*, ed. Diaz, C., Landolt, C. and Utigard, T., TMS, Warrendale, PA, 539 551.
- Higashi, M., Suenaga, C. and Akagi, S. (1993) Process analysis of slag cleaning furnace. in *First Int. Conf. Proc. Mater. Prop.*, ed. Hencin, H. and Oki, T., TMS, Warrendale, PA, 369 372.
- Hughes, S. (2000) Applying Ausmelt technology to recover Cu, Ni and Co from slags. *JOM*, **52** (8), 30 33.
- Imriš, I., Rebolledo, S., Sanchez, M., Castro, G., Achurra, G. and Hernandez, F. (2000) The copper losses in the slags from the El Teniente process. *Can. Metall. Q.*, **39**, 281 290.
- Ip, S. W. and Toguri, J. M. (2000) Entrainment of matte in smelting and converting operations. In *J. M. Toguri Symp.: Fund. of Metall. Proc.*, ed. Kaiura, G., Pickles, C., Utigard, T. and Vahed, A., The Metallurgical Society of CIM, Montreal, Canada, 291 302.
- Kucharski, M. (1987) Effect of thermodynamic and physical properties of flash smelting slags on copper losses during slag cleaning in an electric furnace. *Arch. Metall.*, **32**, 307 323.
- Matousek, J. W. (1995) Sulfur in copper smelting slags. In *Copper 95-Cobre 95, Vol. IV—Pyrometallurgy of Copper*, ed. Chen W. J., Diaz C., Luraschi, A. and Mackey, P. J., The Metallurgical Society of CIM, Montreal, Canada, 532 545.
- Nagamori, M. (1974) Metal loss to slag. Part I: Sulfidic and oxidic dissolution of copper in fayalite slag from low-grade matte. *Metall. Trans.*, **5**, 531 538.
- Poggi, D., Minto, R. and Davenport, W. G. (1969) Mechanisms of metal entrapment in slags, *JOM*, **21**(11), 40 45.
- Ponce, R. and Sánchez, G. (1999) Teniente Converter slag cleaning in an electric furnace at the Las Ventanas smelter. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George D. B., Chen, W. J., Mackey, P. J. and Weddick, A. J., TMS, Warrendale, PA, 583 597.

Sallee, J. E. and Ushakov, V. (1999) Electric settling furnace operations at the Cyprus Miami Mining Corporation copper smelter. In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D. B., Chen, W. J., Mackey, P. J. and Weddick, A. J., TMS, Warrendale, PA, 629 643.

Shimpo, R. and Toguri, J.M. (2000) Recovery of suspended matte particles from copper smelting slags. In *J.M. Toguri Symposium: Fundamentals of Metallurgical Processing*, ed. Kaiura, G., Pickles, C., Utigard, T. and Vahed, A., The Metallurgical Society of CIM, Montreal, Canada, 481 496.

Subramanian, K. N. and Themelis, N. J. (1972) Copper recovery by flotation. *JOM*, **24** (4), 33 38.

Victorovich, G. S. (1980) Precipitation of metallic copper on cooling of iron silicate slags. In *Int. Symp. Metall. Slags*, ed. Masson, C. R., Pergamon Press, New York, NY, 31 36.

Warczok, A., Riveros, G., Mackay, R., Cordero, G. and Alvera, G. (2001) Effect of converting slag recycling into Teniente converter on copper losses. In *EPD Congress 2000*, ed. Taylor, P. R., TMS, Warrendale, PA, 431 444.

CHAPTER 12

Direct-To-Copper Flash Smelting

Previous chapters show that coppermaking from sulfide concentrates entails two major steps: smelting and converting. They also show that smelting and converting are part of the same chemical process, i.e.:

oxidation of Fe and S from a Cu-Fe-S phase.

It has long been the goal of metallurgical and chemical engineers to combine these two steps into one continuous direct-to-copper smelting process.

The principal advantages of this combining would be:

- (a) isolation of SO_2 emission to a single, continuous gas stream
- (b) minimization of energy consumption
- (c) minimization of capital and operating costs.

This chapter (i) describes direct-to-copper smelting in 2002 and (ii) examines the degree to which its potential advantages have been realized. The chapter indicates that the principal problems with the process are that:

- (a) about 25% of the Cu entering a direct-to-copper smelting furnace ends up dissolved in its slag
- (b) the cost of recovering this Cu will probably restrict future expansion of direct-to-copper smelting to low-Fe concentrates (e.g. chalcocite (Cu_2S) and bornite (Cu_5FeS_4) concentrates) rather than high-Fe chalcopyrite concentrates.

12.1 The Ideal Direct-to-Copper Process

Fig. 12.1 is a sketch of the ideal direct-to-copper process. The principal inputs to the process are:

concentrate, oxygen, air, flux and recycles.

The principal outputs are:

molten copper, low-Cu slag, high-SO₂ offgas.

The process is autothermal. With highly oxygen-enriched blast, there is enough excess reaction heat to melt all the Cu-bearing recycle materials from the smelter and adjacent refinery, including scrap anodes. The process is continuous.

The remainder of this chapter indicates how close we have come to this ideality.

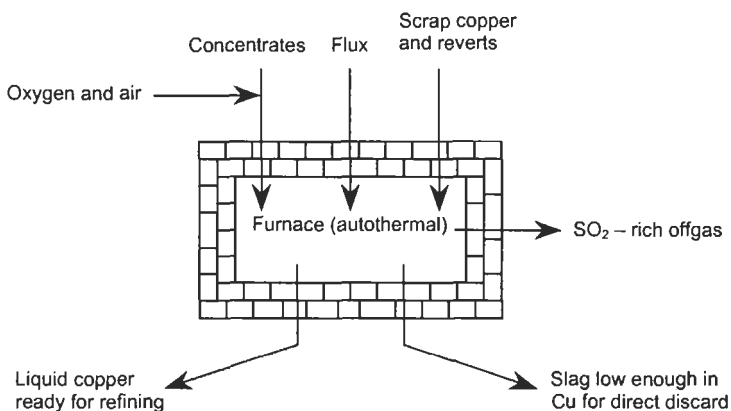


Fig. 12.1. Ideal single-furnace coppermaking process. Ideally the copper is low in impurities, the slag is discardable without Cu-recovery treatment and the offgas is strong enough in SO₂ for sulfuric acid manufacture.

12.2 Industrial Single Furnace Direct-to-Copper Smelting

In 2002, single furnace direct-to-copper smelting is done by only one process – Outokumpu flash smelting, Fig. 1.4. It is done in two locations; Glogow, Poland (Czernecki *et al.*, 1998, 1999a,b,c) and Olympic Dam Australia (Hunt *et al.*, 1999a,b). Both furnaces treat chalcocite-bornite concentrates.

For several years the Noranda submerged-tuyere process (Fig. 1.5) also produced copper directly (Mills *et al.*, 1976). It now produces high-grade matte, 72-75% Cu. The change was made to increase smelting rate and improve impurity elimination.

The products of direct-to-copper flash smelting (Table 12.1) are:

copper	99% Cu, 0.04 to 0.9% S, 0.01% Fe, 0.4% O, 1280°C
slag	14 to 24% Cu, ~1300°C
offgas	15 to 20 volume% SO ₂ , 1350°C.

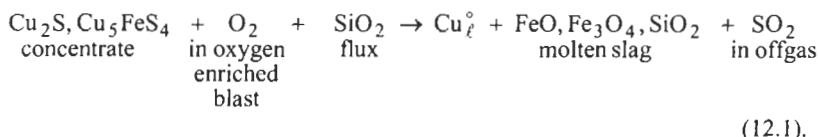
As with conventional matte flash smelting, the temperature of the furnace is controlled by adjusting;

- (a) the degree of oxygen enrichment of the blast, i.e. the amount of N₂ 'coolant' entering the furnace
- (b) the rate at which fossil fuel is burnt in the furnace.

The O₂ content of industrial direct-to-copper flash furnace blast is 50 to 90 volume% O₂, depending on the furnace's solid feed mixture. Considerable fossil fuel is burnt in the reaction shaft and in settler burners, Table 12.1.

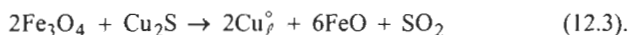
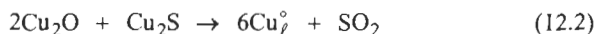
12.3 Chemistry

Direct-to-copper smelting takes place by the schematic (unbalanced) reaction:



Just enough O₂ is supplied to produce metallic copper rather than Cu₂S or Cu₂O.

In practice, the flash furnace reaction shaft product is a mixture of overoxidized (oxide) and underoxidized (sulfide) materials. Individual particles may be overoxidized on the outside and underoxidized on the inside. The overoxidized and underoxidized portions react like:



to produce molten copper, molten slag and SO₂.

Industrially, the overall extent of Reaction 12.1 is controlled by:

- (a) monitoring the Cu content of the product slag and the S content of the product copper
- (b) adjusting the:

$$\frac{\text{O}_2 - \text{in} - \text{blast input rate}}{\text{concentrate input rate}}$$

ratio based on these measured Cu-in-slag and S-in-copper values.

An increasing % Cu-in-slag is reversed by decreasing the O₂/concentrate ratio and vice versa. The % Cu-in-slag is kept between 14 and 24%.

12.4 Industrial Details

Operating details of the two direct-to-copper flash furnaces are given in Table 12.1. The furnaces are similar to conventional flash furnaces. Differences are:

- (a) the hearths are deeply 'bowl' shaped to prevent molten copper from contacting the furnace sidewalls
- (b) the hearths are more radically arched and compressed to prevent their refractory from being floated by the dense (7.8 tonnes/m³) molten copper layer (Hunt, 1999)
- (c) the furnace walls are extensively water cooled and the hearth extensively air cooled to prevent metallic copper from seeping too far into the refractories
- (d) the refractories are monolithic to prevent molten copper from seeping under the bricks, solidifying and lifting them.

Also, the copper tapholes are designed to prevent the out-flowing molten copper from enlarging the taphole to the point where molten copper contacts cooling water.

Olympic Dam's molten copper passes through magnesite-chrome brick (inside), a silicon carbide insert and a graphite insert (outside) (Hunt *et al.*, 1999b). The graphite insert is replaced after ~1200 tonnes of tapped copper and the silicon carbide insert is replaced after ~2400 tonnes. Excessive copper flow (i.e. an excessive taphole diameter) initiates earlier replacement.

12.5 Control

The compositions of the industrial furnace products are controlled by adjusting the ratios:

$$\frac{\text{O}_2 - \text{in} - \text{blast input rate}}{\text{concentrate input rate}}$$

and

Table 12.1. Details of Olympic Dam and Glogow direct-to-copper Outokumpu flash furnaces. Note the high product temperatures as compared to matte smelting, Table 5.1.

Smelter	WMC Resources Olympic Dam, Australia	KGHM Polska Miedz Glogow Poland
Startup date	1999	1978
Size, inside brick, m		
hearth: w × l × h	6.3 × 19.2 × 1.9	9.2 × 26.4 × 3.0
reaction shaft		
diameter	4.8	7.4
height, above settler roof	5.8	8.3
gas uptake		
diameter	3.7	6.7
height above settler roof	7.5	12.3
slag layer thickness, m	0-0.65	0.5
copper layer thickness, m	0.5-0.85	0.7
active slag tapholes	2	6
active copper tapholes	8	10
concentrate burners	1	4
settler burners	2	normally none
Feed details, tonnes/day		
new concentrate (dry)	1200-1600: 41-56% Cu	2000 (28% Cu)
oxygen	90-450	
silica flux	12-120 (95% SiO ₂)	self-fluxing
recycle flash furnace dust	0-144	270
other		100 desulfurizing dust
Blast details		
blast temperature, °C	ambient	140
volume% O ₂	50-90	75
flowrate, thousand Nm ³ /hour	22	32
Production details		
copper production, tonnes/day	390-680	392
composition	99% Cu, 0.7 to 0.85% S, 0.4% O	0.04% S, 0.45% O, 0.007% Fe, 0.25% Pb
temperature, °C	1280	1280
slag production, tonnes/day	620-883	1050
mass% Cu	24	14
mass% SiO ₂ /mass%Fe	0.5	5.7*
temperature, °C	1320	1290
Cu-from-slag recovery method	electric furnace	electric furnace
offgas, thousand Nm ³ /hour	25	35
volume% SO ₂ , leaving furnace	19	15
temperature, °C	1320-1400	1320
dust production, tonnes/day	boiler 65, ESP 55	260
Hydrocarbon fuel inputs, kg/hour		
burnt in reaction shaft	oil, 0-200	oil, 300
burnt in settler burners	oil, 900-1200	0

*32% SiO₂; 5.6% Fe; 10% Al₂O₃; 13.4% CaO; 6.9% MgO; 13.7% Cu; 3% Pb

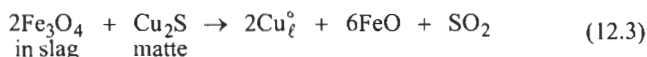
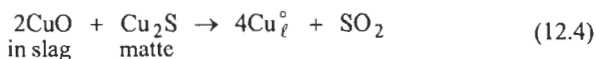
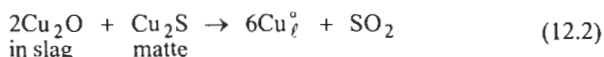
$$\frac{\text{flux input rate}}{\text{concentrate input rate}}$$

The temperatures of the products are controlled by adjusting the oxygen-enrichment level of the blast (as represented by the N_2/O_2 ratio) and the rate at which fossil fuel is burnt in the furnace.

12.5.1 Target: No Matte Layer to Avoid Foaming

The Glogow and Olympic Dam furnaces are operated with O_2 /concentrate ratios which are high enough to avoid forming a Cu_2S layer. This is done to avoid the possibility of foaming slag out the top of the furnace (Smieszek *et al.*, 1985; Asteljoki and Muller, 1987; Day, 1989; Hunt *et al.*, 1999a).

A molten Cu_2S layer, once built up between the molten copper and molten slag layers, has the potential to react with slag by reactions like:



all of which can produce SO_2 **beneath the slag layer**.

Foaming is particularly favored if the input O_2 /concentrate ratio is subsequently increased to shrink or remove an existing Cu_2S layer. This results in a highly oxidized slag, full of Fe_3O_4 , CuO and Cu_2O , which has great potential for producing SO_2 beneath the slag layer.

The foaming problem is avoided by ensuring that the O_2 /concentrate ratio is always at or above its set point, never below. This may lead to high copper oxide-in-slag levels but it avoids the potentially serious operational problems caused by foaming (Hunt *et al.*, 1999a). S-in-copper below ~1% S guarantee that a Cu_2S layer does not form (Fig. 9.2a)*.

*Glogow copper contains 0.04% S, i.e. much less than is necessary to prevent matte layer formation. This extra oxidation is done to oxidize Pb (from concentrate) to PbO , keeping Pb-in-copper below 0.3%.

12.5.2 High %Cu-in-slag from no-matte-layer strategy

An unfortunate side effect of the above no-matte-layer strategy is high %Cu-in-slag, mainly as dissolved Cu_2O . It arises because there is no permanent layer of Cu_2S in the furnace to reduce Cu_2O to metallic copper, Reaction (12.2).

Simply stated, direct-to-copper smelting is operated in a slightly over-oxidizing mode to prevent the foaming described in Section 12.5.1. The downside of operating this way is 14 to 24% Cu in slag, Table 12.1.

12.6 Cu-in-Slag: Comparison with Conventional Matte Smelting/Converting

A significant difference between direct-to-copper flash smelting and flash smelting/Peirce-Smith converting is the large amount of Cu in direct-to-copper slag. This extra Cu-in-slag arises because:

- (a) % Cu in direct-to-copper slags (14-24%, Table 12.1) is much greater than % Cu in conventional smelting slags (1-2% Cu) and converting slags (~6% Cu)
- (b) the amounts of slag produced by direct-to-copper smelting and conventional smelting/converting are about the same.

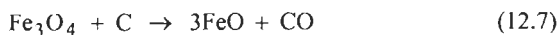
Also, direct-to-copper slags contain most of their Cu in oxidized form (i.e. copper oxide dissolved in the molten slag) – so they must be reduced with carbon to recover their Cu.

12.6.1 Electric furnace Cu recovery

Both direct-to-copper smelters reduce their flash furnace slag in an electric slag cleaning furnace. The slag flows from the flash furnace directly into an electric furnace where it is settled for about 10 hours under a 0.25 m blanket of metallurgical coke (Czernecki *et al.*, 1999b). This coke reduces the oxidized Cu from the slag by reactions like:



Magnetite (molten and solid) is also reduced:



and some FeO is inadvertently reduced to Fe by the reaction:



The Fe joins the newly reduced copper.

Glogow results

The Cu content of the Glogow direct-to-copper slag is lowered from ~14% Cu to ~0.6% Cu in an 18 000 kVA electric furnace. The metallic product is (Czernecki *et al.*, 1999b):

70-80% Cu

~5% Fe

15-25% Pb (from Pb in the concentrate).

This product is too impure to be sent directly to anode-making. It is oxidized in a Hoboken converter (Section 9.6.1) to remove its Fe and Pb, then sent to anode-making.

Olympic Dam results

Olympic Dam lowers its direct-to-copper slag from 24% to ~4% in its 15 000 kVA electric furnace (Hunt *et al.*, 1999a). It could lower it more by using more coke and a longer residence time, but the copper product would contain excessive radioactive ^{210}Pb and ^{210}Po , from the original concentrate.

Instead, the Cu-in-slag is lowered further by solidification/communion/flotation in its mine flotation circuit, Section 11.5.

12.7 Cu-in-Slag Limitation of Direct-to-Copper Smelting

The principal advantage of direct-to-copper smelting is isolation of SO_2 evolution to one furnace. The principal disadvantage of the process is its large amount of Cu-in-slag.

Balancing these factors, it appears that direct-to-copper smelting is best suited to Cu_2S , Cu_5FeS_4 concentrates. These concentrates produce little slag so that Cu recovery from slag is not too costly.

Direct-to-copper smelting will probably not, however, be suitable for most chalcopyrite concentrates, ~30% Cu. These concentrates produce about 2 tonnes of slag per tonne of Cu so that the energy and cost of recovering Cu from their slag is considerable. Only about 60% of new Cu in concentrate would report directly to copper, 40% being recovered from slag.

Davenport *et al.* (2001) confirm this view but Hanniala *et al.* (1999) suggest that direct-to-copper smelting may be economic even for chalcopyrite concentrates.

12.8 Direct-to-Copper Impurities

The compositions of the anode copper produced by the direct-to-copper smelters are given in Table 12.2. The impurity levels of the copper are within the normal range of electrorefining anodes, Chapter 15. The impurity levels could be reduced further by avoiding recycle of the flash furnace dust.

Impurities do not seem therefore, to be a problem in the two existing direct-to-copper smelters. However, metallic copper is always present in the direct-to-copper furnace, ready to absorb impurities. For this reason, concentrates destined for direct-to-copper smelting should always be carefully tested in a pilot furnace before being accepted by the smelter.

Table 12.2. Anode compositions from direct to copper smelters.

Impurity	Olympic Dam	Glogow II
	ppm in copper	ppm in copper
Ag	200-300	1500-3500
As	250-350	500-800
Au	10-20	
Bi	100-150	10-30
Fe	20-200	200-400
Ni	20-40	500-1000
Pb	10-50	2000-3000
S		20-30
Sb	5-15	50-200
Se	150-350	100
Te	30-50	

12.9 Summary

Direct-to-copper smelting is smelting of concentrate directly to molten copper in one furnace. In 1994, it is practiced in two smelters; Glogow II (Poland) and Olympic Dam (Australia). In both cases the smelting unit is an Outokumpu flash furnace.

The main advantage of the process is its restriction of SO₂ evolution to a single continuous source of high SO₂-strength gas. In principal, the energy, operating and capital costs of producing metallic copper are also minimized by the single-furnace process.

Metallic copper is obtained in a flash furnace by setting the ratio:

$$\frac{\text{O}_2 \text{ - in - blast input rate}}{\text{concentrate input rate}}$$

at the point where all the Fe and S in the input concentrate are oxidized. The ratio must be controlled precisely, otherwise Cu_2S or Cu_2O will also be produced. Avoidance of forming a molten Cu_2S layer in the furnace is particularly important. Reactions between Cu_2S layers and oxidizing slag have caused rapid SO_2 evolution and slag foaming.

Direct-to-copper flash smelting has proven effective for SO_2 capture. However, 15-35% of the Cu-in-concentrate is oxidized, ending up as copper oxide dissolved in slag. This copper oxide must be reduced back to metallic copper, usually with coke.

The expense of this Cu-from-slag recovery treatment will probably restrict future direct-to-copper smelting to concentrates which produce little slag. Chalcopyrite concentrates will probably continue to be treated by multi-furnace processes – either by conventional smelting/converting or by continuous multi-furnace processing, Chapter 13.

Suggested Reading

Czernecki, J., Smieszek, Z., Miczkowski, Z., Dobrzanski, J. and Warmuz, M. (1999) Copper metallurgy at the KGHM Polska Miedz S.A. – present state and perspectives. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey P.J. and Weddick, A.J., TMS, Warrendale, PA, 189 203.

Davenport, W.G., Jones, D.M., King, M.J. and Partelpoeg, E.H. (2001) *Flash Smelting, Analysis, Control and Optimization*, TMS, Warrendale, PA (especially Chapters 19-21).

Hunt, A.G., Day, S.K., Shaw, R.G. and West, R.C. (1999) Developments in direct-to-copper smelting at Olympic Dam. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 239 253.

References

Asteljoki, J.A. and Muller, H.B. (1987) Direct smelting of blister copper – flash smelting tests of Olympic Dam concentrate. In *Pyrometallurgy 87*, The Institution of Mining and Metallurgy, London, England, 265 283.

Czernecki, J., Smieszek, Z., Gizicki, S., Dobrzanski, J. and Warmuz, M. (1998) Problems with elimination of the main impurities in the KGHM Polska Miedz S.A. copper concentrates from the copper production cycle (shaft furnace process, direct blister smelting in a flash furnace). In *Sulfide Smelting '98*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 315-343.

(a) Czernecki, J., Smieszek, Z., Miczkowski, Z., Bas, W., Warmuz, M. and Szwanyber, G. (1999) Changes in the construction of the KGHM flash smelting furnace of Glogow II introduced in the years 1996-1998. In *Proceedings of 9th International Flash Smelting Congress*, Australia, June 6-12, 1999.

(b) Czernecki, J., Smieszek, Z., Miczkowski, Z., Dobrzanski, J., Bas, W., Szwanyber, G., Warmuz, M. and Barbacki, J. (1999) The process flash slag cleaning in electric furnace at the Glogow II copper smelter. In *Proceedings of 9th International Flash Smelting Congress*, Australia, June 6-12, 1999.

(c) Czernecki, J., Smieszek, Z., Miczkowski, Z., Dobrzanski, J. and Warmuz, M. (1999) Copper metallurgy at the KGHM Polska Miedz S.A. – present state and perspectives. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference. Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey P.J. and Weddick, A.J., TMS, Warrendale, PA, 189-203.

Davenport, W.G., Jones, D.M., King, M.J. and Partelpoeg, E.H. (2001) *Flash Smelting. Analysis, Control and Optimization*, TMS, Warrendale, PA (Chapter 19).

Day, B.E. (1989) Commissioning of the Olympic Dam smelter. Paper presented at the Non-Ferrous Smelting Symposium of the Australasian Institute of Mining and Metallurgy (Parkville, Victoria), held at Port Pirie, South Australia, September 1989, 57-60.

Hanniala, P., Helle, L. and Kojo, I.V. (1999) Competitiveness of the Outokumpu flash smelting technology now and in the Third Millennium. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference. Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey P.J. and Weddick, A.J., TMS, Warrendale, PA, 221-238.

(a) Hunt, A.G., Day, S.K., Shaw, R.G., Montgomerie, D. and West, R.C. (1999) Start up and operation of the #2 direct-to-copper flash furnace at Olympic Dam. In *Proceedings of 9th International Flash Smelting Congress*, Australia, June 6-12, 1999.

(b) Hunt, A.G., Day, S.K., Shaw, R.G. and West, R.C. (1999) Developments in direct-to-copper smelting at Olympic Dam. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference. Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 239-253.

Mills, L.A., Hallett, G.D. and Newman, C.J. (1976) Design and operation of the Noranda Process continuous smelter. In *Extractive Metallurgy of Copper. Vol. I Pyrometallurgy and Electrolytic Refining*, ed. Yannopoulos, J.C. and Agarwal, J.C., TMS, Warrendale, PA, 458-487.

Smieszek, Z., Sedzik, S., Grabowski, W., Musial, S. and Sobierajski, S. (1985) Glogow 2 copper smelter – seven years of operational experience. In *Extractive Metallurgy 85*, IMM Publications, London, 1049-1056.

CHAPTER 13

Mitsubishi Continuous Smelting/Converting

Chapter 12 indicates that single furnace coppermaking:

(a) successfully restricts SO_2 emission to a single continuous source
but:

(b) inadvertently sends ~25% of its input Cu to slag as copper oxide.

Reduction and recovery of this Cu from the slag is expensive. It will probably restrict future single-furnace smelting to concentrates which produce little slag - i.e. chalcocite (Cu_2S) and bornite (Cu_5FeS_4) concentrates rather than chalcopyrite (CuFeS_2) concentrates.

This Cu-in-slag problem and the significant potential benefits of continuous processing have led to the development of continuous coppermaking in connected smelting, slag cleaning and converting furnaces.

The potential benefits are:

- (a) ability to smelt all concentrates, including CuFeS_2 concentrates
- (b) elimination of Peirce-Smith converting with its SO_2 collection and air infiltration difficulties
- (c) continuous production of high SO_2 -strength offgas, albeit from two sources
- (d) relatively simple Cu-from-slag recovery
- (e) minimal materials handling.

The most advanced industrial manifestation of continuous smelting/converting is the Mitsubishi process with four systems operating in 2002 (Goto and Hayashi, 1998; Ajima *et al.*, 1999). Other manifestations are Outokumpu flash smelting/converting and Noranda submerged tuyere smelting/converting, Chapter 10.

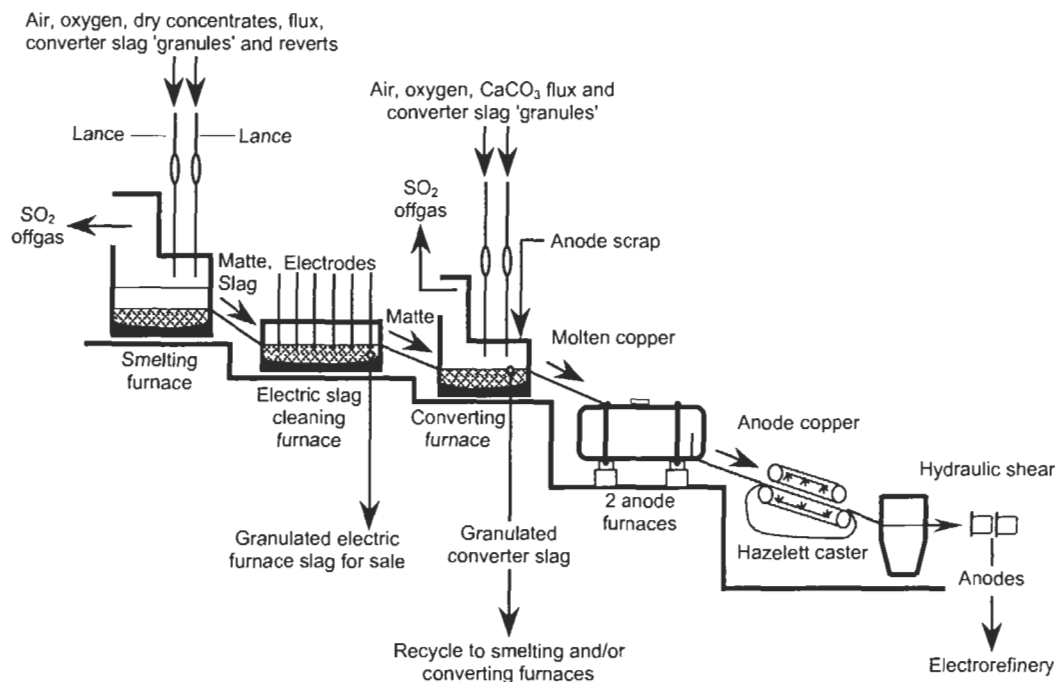


Fig. 13.1. Mitsubishi process flowsheet and vertical layout at Gresik, Indonesia (Ajima *et al.*, 1999). Note the continuous gravity flow of liquids between furnaces. The smelting furnace is about 15 m higher than the Hazelett caster. The smelting and converting furnaces each have 9 or 10 rotating lances, Figs. 10.1 and 13.2.

13.1 The Mitsubishi Process (Fig. 13.1, Tables 13.1 And 13.2)

The Mitsubishi process employs three furnaces connected by continuous gravity flows of molten material. They are:

smelting furnace

electric slag cleaning furnace

converting furnace

The **smelting** furnace blows oxygen-enriched air, dried concentrates, SiO_2 flux and recycles into the furnace liquids via vertical lances, Fig. 13.1. It oxidizes the Fe and S of the concentrate to produce ~68% Cu matte and Fe-silicate slag. Its matte and slag flow together into the electric slag cleaning furnace.

The **electric** slag-cleaning furnace separates the smelting furnace's matte and slag. Its matte flows continuously to the converting furnace. Its slag (0.7-0.9% Cu) flows continuously to water granulation and sale or stockpile.

The **converting** furnace blows oxygen-enriched air, CaCO_3 flux and granulated converter slag 'coolant' into the matte via vertical lances. It oxidizes the matte's Fe and S to make molten copper. The copper continuously exits the furnace into one of two holding furnaces for subsequent fire- and electrorefining. The slag (14% Cu) flows continuously into a water granulation system. The resulting slag granules are recycled to the smelting furnace for Cu recovery and the converting furnace for temperature control.

A major advantage of the process is its effectiveness in capturing SO_2 . It produces two continuous strong SO_2 streams, which are combined to make excellent feed gas for sulfuric acid or liquid SO_2 manufacture. Also, the absence of crane-and-ladle transport of molten material minimizes workplace emissions. These environmental advantages plus recent improvements in productivity make the Mitsubishi process well worth examining for new copper smelting projects.

13.2 Smelting Furnace Details

Fig. 13.2 shows details of the Mitsubishi smelting furnace. Solid particulate feed and oxidizing gas are introduced through 9 vertical lances in two rows across the top of the furnace. Each lance consists of two concentric pipes inserted through the furnace roof. The diameter of the inside pipe is 5 cm – the diameter of the outside pipe, 10 cm. Dried feed is air-blown from bins through the central pipe; oxygen-enriched air (55 volume% O_2) is blown through the annulus between the pipes. The outside pipes are continuously rotated (7-8 rpm) to prevent them from sticking to their water-cooled roof collars.

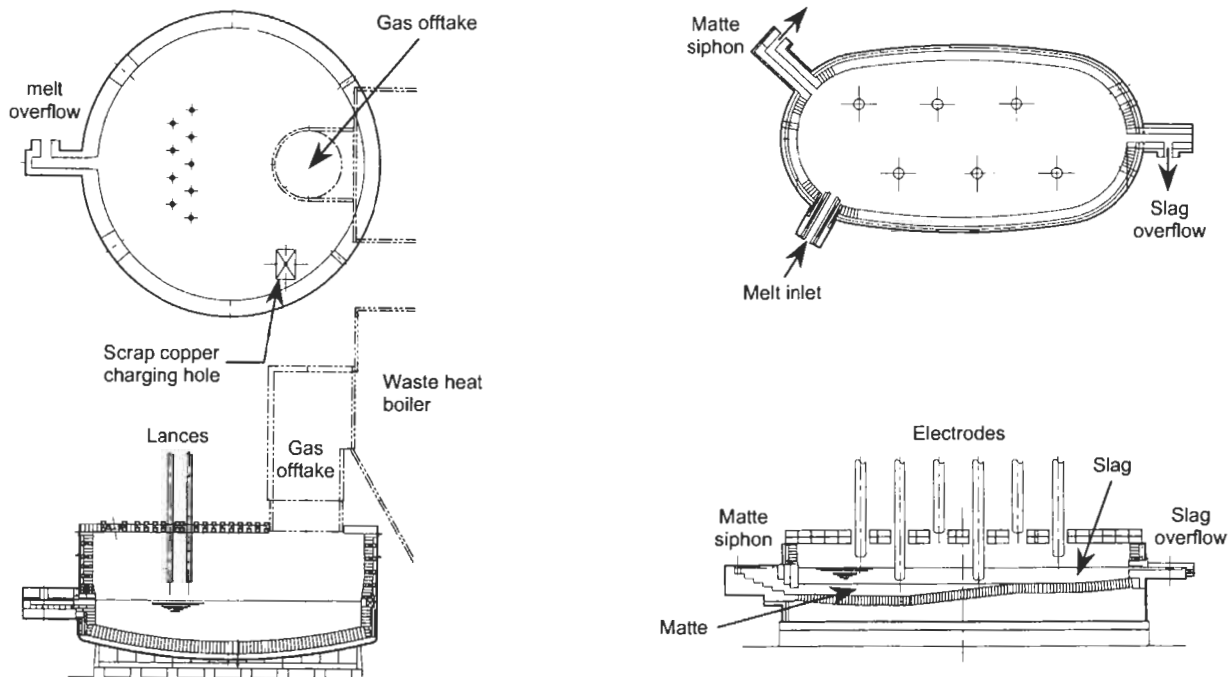


Fig 13.2. Details of Mitsubishi smelting and electric slag cleaning furnaces (Goto and Hayashi, 1998). Note particularly the siphon by which matte underflows the slag cleaning furnace. Most of the refractories are fused cast and direct-bonded magnesite chrome ($\text{MgO-Cr}_2\text{O}_3$). The Mitsubishi converting furnace is shown in Fig. 10.1.

The outside pipes extend downward to ~0.7 m above the molten bath – the inside pipes to the furnace roof or just above. The outside pipes are high chromium steel (27% Cr) – they burn back ~0.4 m per day and are periodically slipped downward to maintain their specified tip positions. New 3 m sections are welded to the top of the shortened pipes to maintain continuous operation. The inside pipes are 304 stainless steel. They do not wear back because their tips are high above the reaction zone.

Concentrate/flux/recycle feed meets oxidizing gas at the exit of the inside pipe. The mixture jets onto the molten bath to form a matte-slag-gas foam/emulsion in which liquids, solids and gas react with each other to form matte and slag. These continuously overflow together through a taphole and down a sloped launder into the electric slag-cleaning furnace.

The offgas (25-30 volume% SO₂) from the oxidation reactions is drawn up a large uptake. It passes through waste heat boilers, electrostatic precipitators and a wet gas cleaning system before being pushed into a sulfuric acid or liquid SO₂ plant.

13.3 Electric Slag Cleaning Furnace Details

The electric slag-cleaning furnace (3600 kW) is elliptical with three or six graphite electrodes in one or two rows along the long axis. It accepts matte and slag from the smelting furnace and separates them into layers.

Matte continuously underflows from its layer out of the electric furnace and into the converting furnace. A siphon and launder system is used. Slag continuously overflows through a taphole. It is granulated in flowing water and sold or stockpiled. Residence times in the furnace are 1 to 2 hours.

The purpose of the electrodes and electrical power is to keep the slag hot and fluid. Heat is obtained by resistance to electric current flow between the graphite electrodes in the slag – selectively heating the slag to 1250°C.

Only a tiny amount of offgas is generated in the electric furnace. It is collected from the slag taphole hood, drawn through an electrostatic precipitator and vented to atmosphere.

13.4 Converting Furnace Details

The converting furnace continuously receives matte from the electric slag-cleaning furnace. It blows oxygen-enriched air blast (30-35 volume% O₂), CaCO₃ flux and converter slag granules onto the surface of the matte. It also receives considerable copper scrap including scrap anodes.

Table 13.1. Physical details of three Mitsubishi coppermaking systems, 2001. Figs. 13.2 and 10.1 show diagrams of the furnaces.

Smelter	Mitsubishi Materials Corp. Naoshima, Japan	PT Smelting Co. Gresik, Indonesia	LG Nikko Onsan, Korea
Furnace commissioning date	1991	1998	1998
Copper production rate, tonnes/day	900 to 1000	~750	800
Smelting furnace			
shape	circular	circular	circular
diameter × height (inside brick), m	10 × 4	10.1 × 4	10 × 4
number of lances	9	9	9
outside pipe diameter, cm	ID: 10	10	8×10cm, 2×9cm
inside pipe diameter, cm	ID: 5	5	5
lance rotations per minute	7.7	6.5	7.8
slag layer thickness, m	0.1	0.1	0.1
matte layer thickness, m	1.4	1.4	1.4
liquids, offgas temperature, °C	1225-1240, 1225-1240	1240, 1240	1240, 1250
Electric slag cleaning furnace			
power rating, kW	3600	2100(No.1); 1500(No.2)	3600
shape	elliptical	elliptical	elliptical
width × length × height, m	6.0×12.5×2.0	5.9×12.5×2.0	6.0×12.5×2.0
electrodes			
material	graphite	graphite	graphite
number	6	6	6
diameter, m	0.4	0.4	0.4
immersion in slag, m	0.5	0.2 to 0.3	0.5 to 0.6
voltage between electrodes, V	90 to 120	90 to 120	80 to 100
current between electrodes, kA	10.5 to 12.0	6.5(No.1); 5.5(No.2)	5.5 to 7.0
applied power, kW	2400	3000	1700
slag layer thickness, m	0.6	0.45	0.60
matte layer thickness, m	0.45	0.65	0.45
matte, slag, offgas temperatures, °C	1210, 1250, -	1230, 1270, -	1220, 1250, 1000
estimated slag residence time, hours	~1	1 to 2	1 to 2
Converting furnace			
shape	circular	circular	circular
diameter × height, m	8.0 × 3.6	9.0 × 3.7	8.1 × 3.6
number of lances	10	10	10
outside pipe diameter, cm	ID: 10	10, 9	8×10cm, 2×8.2cm
inside pipe diameter, cm	ID: 5	5	5
lance rotations per minute	7.7	6.5	7.8
slag layer thickness, m	0.12	0.15	0.13
copper layer thickness, m	0.97	1.1	0.96
copper, slag, offgas temperature, °C	1220, 1235, 1235	1220, 1235, 1230	1220, 1240, 1250

Table 13.2. Operating data for three Mitsubishi coppermaking systems, 2001.

Smelter	Naoshima, Japan	Gresik, Indonesia	Onsan, Korea
Smelting furnace			
Inputs, tonnes/day			
concentrate	2300 (34% Cu)	2000 to 2300 (31.7% Cu)	2109 (33.2% Cu)
silica flux	340	300 to 400	386 (82% SiO ₂)
limestone flux	42	35	52
granulated converting furnace slag	240	160 to 180	96
smelting furnace dust	67	60	60
converting furnace dust	61	60	60
other:	5 compressed copper scrap	40 sludge from wastewater treatment plant	14 reverts
Blast			
volume% O ₂	56	50 to 55	45 to 55
input rate, Nm ³ /minute	540	600 to 650	600
oxygen, tonnes/day	500		450 (99% O ₂)
Hydrocarbon Fuel (coal, tonnes/day)	63	90	140
Output offgas			
volume% SO ₂ (entering boiler)	34	30	31
flowrate, Nm ³ /minute	560	600 to 650	570
dust tonnes/day	67	60	60
Electric Slag Cleaning Furnace			
Inputs	matte and slag from smelting furnace		
Outputs			
matte, tonnes/day	1400	1270	1018
matte %Cu	68	68	68.8
slag, tonnes/day	1300	1450	1331
slag %Cu	0.7	0.7	0.8
slag %SiO ₂ /%Fe	0.9	0.8	0.9
offgas, Nm ³ /minute (ppm SO ₂)			500 (<150 ppm)
kWh consumption/tonne of slag	42	55	30
Converting Furnace (autothermal)			
Inputs, tonnes/day			
matte from electric furnace	1400	1270	1018
limestone flux	50	30	69
granulated converting furnace slag	360	160 to 180	246
anode scrap copper	120	95 to 100	78
purchased scrap copper	34	0	44
Blast			
volume% O ₂	35	25 to 28	32 to 35
input rate, Nm ³ /minute	490	460 to 470	430
oxygen, tonnes/day	180		133 (99% O ₂)
Outputs			
copper, tonnes/day	900 to 1000	850 to 900	820
copper, %Cu	98.4	98.5	98.5
copper, %O	0.3	0.3	-
copper, %S	0.7	0.7	0.9
slag, tonnes/day	600	160 to 180	360
slag, %Cu	14	14	15
slag, mass% CaO/mass% Fe	0.4	0.4	0.34
offgas, Nm ³ /minute	480	450	410
volume% SO ₂	31	25	24
dust, tonnes/day	61	60	60

It produces:

- (a) molten copper, ~0.7% S
- (b) molten slag, 14% Cu
- (c) SO₂ bearing offgas, 25-30 volume% SO₂.

The molten copper continuously departs the furnace through a siphon and launder into one of two anode furnaces, Fig 13.1. The slag continuously overflows into a water-granulation system. The offgas is drawn through a large uptake, waste heat boiler, electrostatic precipitators and a wet gas cleaning system before being pushed into a sulfuric acid or liquid SO₂ plant. The smelting and converting offgases are combined prior to entering the electrostatic precipitators.

The oxygen-enriched air and solids are introduced into the furnace through 10 lances like the smelting furnace lances. The tips of the outside pipes are 0.3 to 0.8 m above the bath – the inside pipe tips above or just through the roof. The outer pipes are continuously rotated to prevent them from sticking to their roof collars. They are also slowly slipped downwards as they burn back.

13.4.1 Converting furnace slag

A unique feature of Mitsubishi converting is its CaO-based (rather than SiO₂ based) slag (Yazawa *et al.*, 1981; Goto and Hayashi, 1998). Early in the development of the process, it was found that blowing strong O₂ 'blast' onto the surface of SiO₂-based slag made a crust of solid magnetite. This made further converting impossible. CaO, on the other hand, reacts with solid magnetite, molten Cu and O₂ to form a liquid CaO-Cu₂O-FeO_n slag, Fig. 13.3. The slag typically contains:

12-16% Cu (~60% as Cu₂O, balance Cu)

40-55% Fe (~70% as Fe⁺⁺⁺, balance Fe⁺⁺)

15-20% CaO.

Its viscosity is ~10⁻¹ kg/m·s (Wright *et al.*, 2000).

13.4.2 Converting furnace copper

Mitsubishi copper contains more S than Peirce-Smith converter copper, ~0.7% vs. ~0.02%. The only disadvantage of this is a longer oxidation period in the anode furnace. The S content can be lowered in the Mitsubishi converter by supplying more O₂, but this increases the amount of Cu in slag. 0.7% - 0.8% S in copper seems optimum.

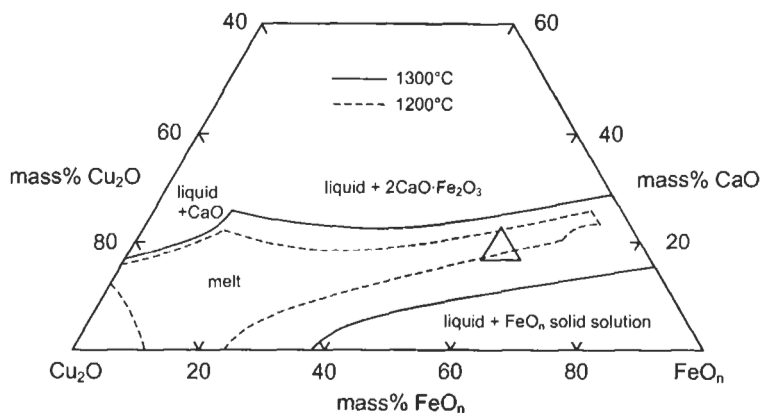


Fig. 13.3. Liquidus lines at 1200°C and 1300°C for CaO-Cu₂O-FeO_n slags in air, 1 atmosphere pressure (Yazawa and Eguchi, 1976; Goto and Hayashi, 1998). The triangle represents Mitsubishi converting furnace slag if all its Cu exists as Cu₂O. Slag compositions inside the solid line are fully liquid at 1300°C. Slag compositions inside the dashed lines are fully liquid at 1200°C.

13.5 Recent Mitsubishi Process Developments

The 1980's and 1990's saw a doubling of Mitsubishi smelting rates (Newman *et al.*, 1992, 1993). This has greatly improved the competitive position of the process. The changes that have enhanced productivity and competitiveness have been:

- increased oxygen enrichment of the smelting and converting furnace blasts
- improvements in furnace refractories and water-cooling, which have enhanced reliability and extended furnace campaign life (Majumdar *et al.*, 1997)
- better measurements of temperature and lance tip position plus improved computer control
- bending of recycle scrap anodes to prevent mechanical damage to the furnace hearth (Oshima *et al.*, 1998).

Converting furnace life was extended at the Timmins smelter by avoiding impingement of lance gas and solids on the furnace hearth (Majumdar *et al.*, 1997). Impingement was avoided by:

- increasing the lance diameter to reduce gas/solids velocity
- maintaining the lances at 0.6 or 0.7 m above the bath

- (c) feeding abrasive solids (e.g. converter slag granules) through low velocity bypass lances.

Innovations have also been made in the new Naoshima smelter to enable the smelting and converting furnaces to melt large quantities of scrap copper (Oshima *et al.*, 1998; Shibasaki *et al.*, 1991, 1992, 1993). This scrap melting capability has considerably enhanced the versatility of the process.

13.6 Reaction Mechanisms in Mitsubishi Smelting

13.6.1 Smelting furnace

The velocities of solids and gas leaving Mitsubishi smelting furnace lances are 130-150 m/second (Goto and Hayashi, 1998). Times of flight of the particles across the 0.7 m distance between lance tip and melt surface are, therefore, on the order of 10^{-3} to 10^{-2} seconds. The temperature rise of the gas/solid jet during this time is calculated to be $\sim 50^{\circ}\text{C}$. This is not enough to cause ignition of the concentrate. Consequently, melting and oxidation of concentrate particles occurs entirely after entry into the gas-slag-matte foam/emulsion beneath the lances (Goto and Hayashi, 1998; Asaki *et al.*, 2001).

Industrial evidence indicates that the smelting furnace contains mainly matte (1.2-1.5 m deep) with a gas/slag/matte foam/emulsion beneath the lances (Goto and Echigoya, 1980, Shibasaki and Hayashi, 1991). Away from the lances, SO_2/N_2 gas disengages from the foam and the matte and slag begin to separate. Newly formed slag (~ 0.05 m thick and containing some entrained matte) flows toward the taphole where it overflows. Matte also continuously overflows as new matte is made under the lances.

13.6.2 Electric slag cleaning furnace

The electric slag cleaning furnace accepts molten matte and slag from the smelting furnace. These liquids separate and form two layers in the furnace – a bottom layer of matte 0.5 - 0.8 m thick, and a top layer of slag ~ 0.5 m thick. The residence times of the liquids are 1 or 2 hours. These times, plus electromagnetic stirring in the furnace allow the slag and matte to approach equilibrium. Passage of electricity through the slag ensures that the slag is hot and fluid. This, in turn, creates conditions for efficient settling of matte droplets from the slag.

The slag is the main route of Cu loss from the smelter. It is important, therefore, that the total amount of Cu-in-slag be minimized. This is done by:

- (a) maximizing slag residence time in the electric furnace (to maximize matte settling)

- (b) keeping the slag hot, fluid and quiescent
- (c) minimizing slag mass (per tonne of Cu) by smelting high Cu grade concentrates and minimizing fluxing
- (d) optimizing slag composition to minimize slag viscosity and density.

13.6.3 Converting furnace

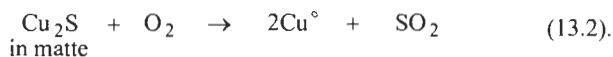
The converting furnace blows oxygen-enriched air, CaCO_3 flux and recycle converter slag granules through ten roof lances. The velocity of the gas/solid mix is typically 120 m/second. O_2 is supplied to the furnace at the exact rate which will produce metallic copper from the incoming matte.

The furnace contains a thin (~ 0.1 m) layer of slag on top of about 1 m of molten copper. The solids and gas from the lance penetrate through the slag and deep into the copper.

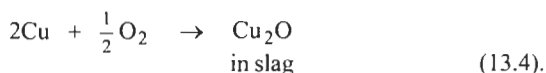
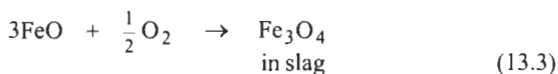
The furnace is operated with an excess of O_2 to avoid the presence of a permanent molten matte layer in the furnace. This reduces the risk of slag foaming, Section 12.5.1. The absence of a permanent matte layer is indicated by 0.7% S in the converter's copper rather than 1% S which would be at equilibrium with a Cu_2S layer.

Likely converting mechanisms are:

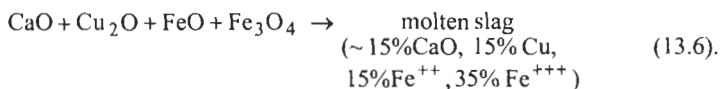
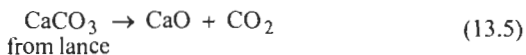
- (a) matte flows continuously into the furnace and spreads out on the furnace's permanent layer of molten copper
- (b) it reacts with O_2 under the lances to make FeO and molten copper by the reactions:



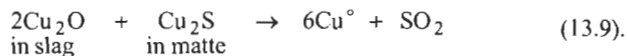
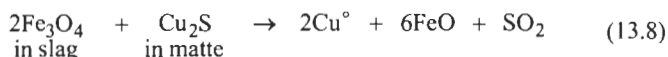
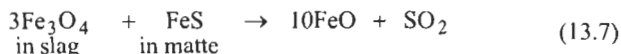
- (c) the above mentioned excess O_2 leads to over-oxidation of Cu and FeO by the reactions:



(d) Cu_2O , FeO and Fe_3O_4 are slagged by the reactions:



This slag probably reacts with matte by reactions like:



The relative importance of direct oxidation (by O_2) and indirect oxidation (by slag) is a matter of conjecture.

13.7 Optimum Matte Grade

The Cu grade of the matte being produced by the smelting furnace (and flowing into the converting furnace) is chosen as a balance between:

- the amount of Cu lost in the discard slag from the electric furnace, Fig. 4.6
- the amount of granulated high-Cu slag which must be recycled back from the converting furnace to the smelting furnace
- the amount of coal which must be added to the smelting furnace and the amount of coolant which must be added to the converting furnace.

The optimum matte grade for the Mitsubishi process is 68% Cu. With this matte grade, the discard slag from the electric slag cleaning furnace contains 0.7-0.9% Cu and converter slag recycle is 0.1 to 0.3 tonnes per tonne of concentrate feed, Table 13.2.

13.8 Impurity Behavior in Mitsubishi Smelting/Converting

Table 13.3 quantifies impurity behavior at the Naoshima and Timmins smelters.

It shows that Mitsubishi copper contains a significant fraction of impurities (except Zn), but that the fraction can be decreased by not recycling electrostatic precipitator dust.

Table 13.3. Distribution of impurities to anodes during Mitsubishi smelting/converting. The Naoshima data are from Shibasaki and Hayashi, 1991, Nagano, 1985 and Goto and Hayashi, 1998. The Timmins data are from Newman *et al.*, 1991.

Process	% of impurity-in-feed reporting to anode copper					
	As	Bi	Pb	Se	Sb	Zn
Naoshima Mitsubishi smelting/converting with complete dust recycle	21	34	42	87	45	0.2
Naoshima Mitsubishi smelting/converting, electrostatic precipitator dust not recycled	4	15	15		15	0
Timmins Mitsubishi smelting/converting, electrostatic precipitator dust sent to Zn plant			11	55		

13.9 Process Control in Mitsubishi Smelting/Converting (Goto and Hayashi, 1998)

Bath temperature is the most important control parameter in the Mitsubishi process. Maintaining an optimum temperature ensures good slag and matte fluidity while at the same time minimizing refractory erosion. Typical operating temperatures at the Naoshima smelter are shown in Table 13.4.

Table 13.4 shows that the electric slag cleaning furnace slag is operated hotter than the smelting furnace matte/slag. This is done to avoid precipitation of solid Fe_3O_4 and/or SiO_2 .

Precipitation of Fe_3O_4 has been found to cause formation of a “muddy layer” between molten matte and molten slag. This layer prevents good matte/slag separation. It results in high matte entrainment in the discard slag, hence high Cu-in-slag losses.

Precipitation of SiO_2 produces SiO_2 rich “floating solids”. These solids (~10% Cu) do not settle into the matte layer and result in high Cu-in-slag losses.

13.9.1 Mitsubishi process control

Process control at Naoshima combines quantitative and qualitative process information, Tables 13.5 and 13.6. The quantitative information is continuously inputted into an expert type computer control system.

Table 13.4. Maximum, minimum and optimum operating temperatures in the Mitsubishi smelter at Naoshima.

	minimum (°C)	maximum (°C)	optimum (°C)
Smelting furnace – matte/slag outlet	1200	1240	1220
Electric slag cleaning furnace – slag outlet	1220	1260	1240
Converting furnace – slag outlet	1210	1250	1230

The overall state of the process is best represented by the following quantitative variables. They are:

- (a) smelting furnace matte/slag outlet temperature
- (b) converting furnace slag temperature
- (c) matte grade
- (d) %SiO₂ in electric slag cleaning furnace slag
- (e) %CaO in electric slag cleaning furnace slag
- (f) %Cu in converting furnace slag
- (g) %CaO in converting furnace slag.

Table 13.7 shows how each parameter is controlled.

Control of the Mitsubishi process is a challenge for its operators. The difficulty lies in the fact that (i) there are many process variables to control and (ii) they all interact with each other. When one variable goes out of control the rest of the process is affected. For example, the solution to the problem of high viscosity slags, “floating solids” and “muddy layers” has typically been to increase furnace temperature. Unfortunately, this increases refractory erosion, ultimately decreasing smelter availability.

However, recent development of sophisticated continuous melt temperature devices coupled with the use of an expert type computer control system has helped minimize process excursions. This has greatly increased Mitsubishi process availability.

13.10 Summary

The Mitsubishi continuous coppermaking system consists of smelting and converting furnaces with an electric slag cleaning furnace in between. It produces two continuous, high SO₂ strength offgas streams excellent for efficient sulfuric acid and liquid SO₂ manufacture.

Table 13.5. Quantitative process parameters in Mitsubishi smelting/converting. Process control has been improved by the use of immersion thermocouples to continuously measure smelting furnace matte/slag temperature and converting furnace slag temperature. Molten copper temperature is measured with an optical fiber pyrometer.

Information	Adjustable or Result	Comments
Smelting furnace		
Melt temperature	Result	Continuous measurement by submerged K-type thermocouple at smelting furnace melt outlet.
Feedrate	Adjustable	Continuous monitoring of blended concentrate, silica, CaCO_3 , coal, converter slag granules, Cu scrap and dust input rates.
Blowing rate	Adjustable	Continuous monitoring of oxygen and air input rates.
Matte composition	Result	Hourly analysis by X-ray fluorescence analyzer (Cu and Pb). Samples are taken at electric slag cleaning furnace outlet.
Slag composition	Result	Hourly analysis by X-ray fluorescence analyzer (Cu, Fe, SiO_2 , CaO and Al_2O_3). Samples are taken at electric slag cleaning furnace outlet.
Converting furnace		
Slag temperature	Result	Hourly manual measurement by disposable K-type thermocouples.
Copper temperature	Result	Automatic measurement by submerged glass fiber optical pyrometer – every 15 minutes.
Feedrate	Adjustable	Continuous monitoring of CaCO_3 , recycled converter slag granules and Cu scrap input rates.
Matte flowrate	Result	Continuous measurement by infrared scanner at electric slag cleaning furnace matte siphon.
Blowing rate	Adjustable	Continuous measurement of oxygen and air input rates.
Slag composition	Result	Hourly sample and analysis (Cu, SiO_2 , CaO, S and Pb) by X-ray fluorescence analyzer.

Table 13.6. Qualitative process parameters in Mitsubishi smelting/converting.

Information	Adjustable or Result	Comments
Smelting furnace		
Melt flowrate and melt surface condition	Result	Visual inspection by remote camera and at the furnace.
Converting furnace		
Slag flowrate and slag surface condition	Result	Visual inspection by remote camera and at the furnace.
Matte inflow rate	Result	Visual inspection by remote camera and at the furnace.

Table 13.7. Mitsubishi process variables and their respective control actions. The first named actions act to increase the operating parameters, e.g. smelting furnace melt temperature is increased by decreasing converter slag granule feed rate.

Operation parameter	Corrective action
Smelting furnace melt temperature	decrease/increase recycle converter slag granule feedrate
Converting furnace slag temperature	decrease/increase recycle converter slag granule feedrate
Smelting furnace matte grade	{ decrease/increase concentrate feedrate decrease/increase coal feedrate increase/decrease oxygen feedrate increase/decrease air flowrate
%SiO ₂ in electric slag cleaning furnace slag	increase/decrease SiO ₂ feedrate to smelting furnace
%CaO in electric slag cleaning furnace slag	increase/decrease CaCO ₃ feedrate to smelting and converting furnace
%Cu in converting furnace slag	{ increase/decrease oxygen flowrate increase/decrease air flowrate decrease/increase concentrate feedrate
%CaO in converting furnace slag	increase/decrease CaCO ₃ feedrate

Its advantage over single furnace coppermaking is that its Cu-from-slag recovery system is simple and efficient. This makes it suitable for all concentrates, not just those which produce small amounts of slag. Its main disadvantage compared to single-furnace coppermaking is that it has two offgas streams rather than one.

The productivity of the Mitsubishi process doubled during the 1980's and 1990's due mainly to:

- (a) increased oxygen-enrichment of smelting and converting furnace 'blasts'
- (b) increased hearth life due to better refractories, increased water cooling and improved lance tip positioning
- (c) improved process control through the use of continuous melt temperature measurements and an expert control system.

This doubled productivity and Mitsubishi's excellent SO₂ capture performance make the Mitsubishi process well-worth examining for new smelting projects.

Suggested Reading

Ajima, S., Koichi, K., Kanamori, K., Igarashi, T., Muto, T. and Hayashi, S. (1999) Copper smelting and refining in Indonesia. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., Weddick, A.J., TMS, Warrendale, PA, 57-69.

Goto, M. and Hayashi, M. (1998) *The Mitsubishi Continuous Process – A Description and Detailed Comparison Between Commercial Practice and Metallurgical Theory*. Mitsubishi Materials Corporation, Tokyo, Japan.

Oshima, E., Igarashi, T., Hasegawa, N. and Kiyotani, K. (1998) Naoshima smelter operation – present and future. In *Sulfide Smelting '98*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 549 558.

References

Ajima, S., Koichi, K., Kanamori, K., Igarashi, T., Muto, T. and Hayashi, S. (1999) Copper smelting and refining in Indonesia. In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., Weddick, A.J., TMS, Warrendale, PA, 57 69.

Asaki, Z., Taniguchi, T. and Hayashi, M. (2001) Kinetics of the reactions in the smelting furnace of the Mitsubishi process, *JOM*, **53**(5), 25 27.

Goto, M. and Echigoya, T. (1980) Effect of injection smelting jet characteristics on refractory wear in the Mitsubishi process, *JOM*, **32**(11), 6 11.

Goto, M. and Hayashi, M. (1998) *The Mitsubishi Continuous Process – A Description and Detailed Comparison Between Commercial Practice and Metallurgical Theory*. Mitsubishi Materials Corporation, Tokyo, Japan.

Majumdar, A., Zuliani, P., Lenz, J.G., MacRae, A. (1997) Converting furnace integrity project at the Kidd metallurgical copper smelter. In *Proceedings of the Nickel-Cobalt 97 International Symposium, Vol. III Pyrometallurgical Operations, Environment, Vessel Integrity in High-Intensity Smelting and Converting Processes*, ed. Diaz, C., Holubec, I. and Tan, C.G., Metallurgical Society of CIM, Montreal, Canada, 513 524.

Nagano, T. (1985) Progress of copper sulfide continuous smelting. In *Physical Chemistry of Extractive Metallurgy*, ed. Kudryk, V. and Rao, Y. K., TMS, Warrendale, PA, 311 325.

Newman, C.J., MacFarlane, G., Molnar, K. and Storey, A.G. (1991) The Kidd Creek Copper smelter – an update on plant performance. In *Copper 91–Cobre 91 Proceedings of the Second International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C., Luraschi, A. and Newman, C. J., Pergamon Press, New York, NY, 65 80.

Newman, C.J., MacFarlane, G., and Molnar, K.E. (1993) Increased productivity from Kidd Creek Copper operations. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Vol. II: Copper and Nickel Smelter Operations*, ed. Landolt, C., TMS, Warrendale, PA, 1477 1496.

Newman, C.J., Storey, A.G., Macfarlane, G. and Molnar, K. (1992) The Kidd Creek Copper smelter – an update on plant performance, *CIM Bulletin*, **85**(961), 122 129.

Oshima, E., Igarashi, T., Hasegawa, N. and Kumada, H. (1998) Recent operation for treatment of secondary materials at Mitsubishi process. In *Sulfide Smelting '98*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 597 606.

- Shibasaki, T. and Hayashi, M. (1991) Top blowing injection smelting and converting – the Mitsubishi process. In *International Symposium on Injection in Process Metallurgy*, ed. Lehner, T., Koros, P. J. and Ramachandran, V., TMS, Warrendale, PA, 199 213.
- Shibasaki, T., Hayashi, M. and Nishiyama, Y. (1993) Recent operation at Naoshima with a larger Mitsubishi furnace line. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Volume II: Copper and Nickel Smelter Operations*, ed. Landolt, C., TMS, Warrendale, PA, 1413 1428.
- Shibasaki, T., Kanamori, K. and Hayashi, M. (1992) Development of large scale Mitsubishi furnace at Naoshima. In *Savard/Lee International Symposium on Bath Smelting*, ed. Brimacombe, J.K., Mackey, P.J., Kor, G.J.W., Bickert, C. and Ranade, M.G., TMS, Warrendale, PA, 147 158.
- Shibasaki, T., Ohichi, K., Kanamori, K. and Kawai, T. (1991) Construction of new Mitsubishi furnaces for modernization of Naoshima smelter and refinery. In *Copper 91-Cobre 91 Proceedings of the Second International Conference, Volume IV Pyrometallurgy of Copper*, ed. Díaz, C., Landolt, C., Luraschi, A. and Newman, C.J., Pergamon Press, New York, NY, 3 14.
- Wright, S., Zhang, L., Sun, S. and Jahanshahi, S. (2000) Viscosity of calcium ferrite slags and calcium alumino-silicate slags containing spinel particles. In *Proceedings of the Sixth International Conference on Molten Slags, Fluxes and Salts*, ed. Seetharaman, S. and Sichen, D., Division of Metallurgy, KTH, Stockholm, Sweden, paper number 059.
- Yazawa, A. and Eguchi, M. (1976) Equilibrium studies on copper slags used in continuous converting. In *Extractive Metallurgy of Copper, Vol. I Pyrometallurgy and Electrolytic Refining*, ed. Yannopoulos, J.C. and Agarwal, J.C., TMS, Warrendale, PA, 3 20.
- Yazawa, A., Takeda, Y. and Wascda, Y. (1981) Thermodynamic properties and structure of ferrite slags and their process implications, *Can. Met. Quart.*, **20**(2), 129 134.

CHAPTER 14

Capture and Fixation of Sulfur

About 85% of the world's primary copper originates in sulfide minerals. Sulfur is, therefore, evolved by most copper extraction processes. The most common form of evolved sulfur is SO_2 gas from smelting and converting.

SO_2 is harmful to fauna and flora. It must be prevented from reaching the environment. Regulations for ground level SO_2 concentrations around copper smelters are presented in Table 14.1. Other regulations such as maximum total SO_2 emission (tonnes per year), percent SO_2 capture and SO_2 -in-gas concentration at point-of-emission also apply in certain locations.

In the past, SO_2 from smelting and converting was vented directly to the atmosphere. This practice is now prohibited in most of the world so most smelters capture a large fraction of their SO_2 . It is almost always made into sulfuric acid, occasionally liquid SO_2 or gypsum. Copper smelters typically produce 2.5 – 4.0 tonnes of sulfuric acid per tonne of product copper depending on the S/Cu ratio of their feed materials.

This chapter describes:

- (a) offgases from smelting and converting
- (b) manufacture of sulfuric acid from smelter gases
- (c) future developments in sulfur capture.

14.1 Offgases From Smelting and Converting Processes

Table 14.2 characterizes the offgases from smelting and converting processes. SO_2 strengths in **smelting furnace** gases vary from about 70 volume% in Inco flash furnace gases to 1 volume% in reverberatory furnace gases. The SO_2 strengths in **converter** gases vary from about 40% in flash converter gases to 8 to 12 volume% in Peirce-Smith converter gases.

Table 14.1. Standards for maximum SO₂ concentration at ground level outside the perimeters of copper smelters.

Country	Time period	Maximum SO ₂ + SO ₃ concentration (parts per million)
U.S.A. (EPA, 2001)	Yearly mean	0.03
	daily mean	0.14
	3-hour mean	0.5
Ontario, Canada (St. Eloi <i>et al.</i> , 1989)	Yearly mean	0.02
	daily mean	0.10 recommendation
	1-hour mean	0.25
	0.5 hour average	0.3 (regulation)
Japan (Inami <i>et al.</i> , 1990)	Daily average	0.04
	hourly average	0.1

The offgases from most smelting and converting furnaces are treated for SO₂ removal in sulfuric acid plants. The exception is offgas from reverberatory furnaces. It is too dilute in SO₂ for economic sulfuric acid manufacture. This is the main reason reverberatory furnaces continue to be shut down.

The offgases from electric slag cleaning furnaces, anode furnaces and gas collection hoods around the smelter are dilute in SO₂, <0.1%. These gases are usually vented to atmosphere. In densely populated areas, they may be scrubbed with basic solutions before being vented (Inami *et al.*, 1990; Shibata and Oda, 1990; Tomita *et al.*, 1990).

14.1.1 Sulfur capture efficiencies

Table 14.3 shows the S capture efficiencies of 4 modern smelters. Gaseous emissions of S compounds are ≤ 1% of the S entering the smelter.

14.2 Sulfuric Acid Manufacture (Table 14.4)

Fig. 14.1 outlines the steps for producing sulfuric acid from SO₂-bearing smelter offgas. The steps are:

- (a) cooling and cleaning the gas

Table 14.2. Characteristics of offgases from smelting and converting processes. The data are for offgases as they enter the gas-handling system.

Furnace	SO ₂ concentration (volume%)	Temperature (°C)	Dust loading (kg/Nm ³)	Destination
Inco flash furnace	50-75	1270-1300	0.2-0.25	H ₂ SO ₄ occasionally liquid SO ₂ plant
Outokumpu flash furnace	25-50	1270-1350	0.1-0.25	H ₂ SO ₄ plant, occasionally liquid SO ₂ plant
Outokumpu flash converter	35-40	1290	0.2	H ₂ SO ₄ plant
Outokumpu direct-to-copper	43	1320-1400	0.2	H ₂ SO ₄ plant
Mitsubishi smelting furnace	30-35	1240-1250	0.07	H ₂ SO ₄ , occasionally liquid SO ₂ plant
Mitsubishi converting furnace	25-30	1230-1250	0.1	H ₂ SO ₄ , occasionally liquid SO ₂ plant
Noranda process	15-25	1200-1240	0.015-0.02	H ₂ SO ₄ plant
Teniente furnace	12-25	1220-1250		H ₂ SO ₄ plant
Isasmelt furnace	20-25	1150-1220	~0.01	H ₂ SO ₄ plant
Electric furnace	2-5	400-800		H ₂ SO ₄ or liquid SO ₂ plant or vented to atmosphere
Reverberatory furnace	1	1250	~0.03	Vented to atmosphere (made into gypsum in one plant, scrubbed with flotation tailings in another)
Peirce-Smith converter	8-15	1200		H ₂ SO ₄ plant or vented to atmosphere
Hoboken converter	12	1200		H ₂ SO ₄ plant
Electric slag cleaning furnaces	0.1	800		Vented to atmosphere (occasionally scrubbed with basic solution)
Anode furnaces	<0.1	1000		Vented to atmosphere (occasionally scrubbed with basic solution)
Gas collection hoods around the smelter	<0.1	50		Vented to atmosphere (occasionally scrubbed with basic solution)

Table 14.3. Distribution of sulfur in four copper smelters.

	Toyco, Japan (Inami <i>et al.</i> , 1990) Outokumpu flash furnace Peirce-Smith converters	Timmins, Canada (Newman <i>et al.</i> , 1993) Mitsubishi smelting/ converting	Tamano, Japan (Shibata and Oda, 1990) Outokumpu flash furnace Peirce-Smith converters	Norddeutsche, Germany (Willbrandt, 1993) Outokumpu flash furnace Peirce-Smith converters
Percent of incoming S in: Sulfuric acid	96.6	95	96	96.2
Gypsum	2.7		1.0	
Slag	1.2	1.4	1.2	1.2
Dust	0.2	2.0 (to Zn plant)		
Other				1.0
Neutralized liquid effluent	0.3	0.6	1.8	0.8
Gaseous emissions	0.2	1.0 (0.6*; 0.4 [†])	0.1	0.8

* from dryer, anode furnace and ventilation stacks

[†] from acid plant tail gas

- (b) drying the gas with 93% H₂SO₄-7% H₂O sulfuric acid
- (c) catalytically oxidizing the gas's SO₂ to SO₃
- (d) absorbing this SO₃ into 98% H₂SO₄-2% H₂O sulfuric acid.

The strengthened acid from step (d) is then blended with diluted acid from step (b) and sent to market or used for internal leach operations, Chapter 17.

The acid plant tail gas is cleaned of its acid mist and discharged to the atmosphere. Tail gases typically contain less than 0.5% of the S entering the gas treatment system. Several smelters scrub the remaining SO₂, SO₃ and H₂SO₄ mist with Ca/Na carbonate hydroxide solutions before releasing the gas to atmosphere (Bhappu *et al.* 1993; Chatwin and Kikumoto, 1981; Inami *et al.*, 1990; Shibata and Oda, 1990; Tomita *et al.* 1990). Basic aluminum sulfate solution is also used (Oshima *et al.*, 1997).

The following sections describe the principal sulfuric acid production steps and their purposes.

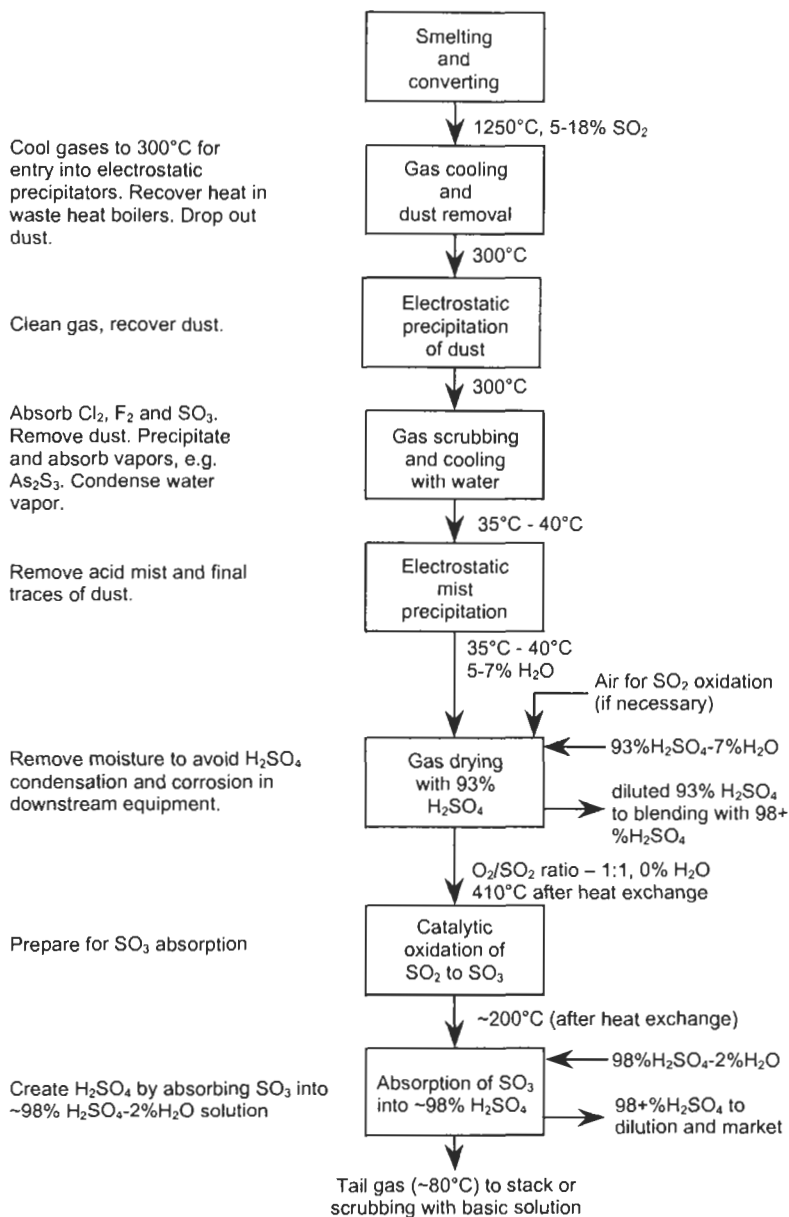


Fig. 14.1. Flowsheet for producing sulfuric acid from smelting and converting gases.

14.3 Smelter Offgas Treatment

14.3.1 Gas cooling and heat recovery

The first step in smelter offgas treatment is cooling the gas in preparation for electrostatic precipitation of its dust. Electrostatic precipitators operate at about 300°C. Above this temperature their steel structures begin to weaken. Below this temperature there is a danger of corrosion by condensation of sulfuric acid from SO₃ and H₂O(g) in the offgas.

Gas cooling is usually done in waste heat boilers, Fig. 14.2 – which not only cool the gas but also recover the heat in a useful form – steam (Peippo, *et al.*, 1999). The boilers consist of:

- (a) a radiation section in which the heat in the gas is transferred to pressurized water flowing through 4 cm diameter tubes in the roof and walls of a large (e.g. 25 m long × 15 m high × 5 m wide) rectangular chamber
- (b) a convection section (e.g. 20 m long × 10 m high × 3 m wide) in which heat is transferred to pressurized water flowing through 4 cm diameter steel tubes suspended in the path of the gas.

The product of the boiler is a water/steam mixture. The water is separated by gravity and re-circulated to the boiler. The steam is superheated above its dew point and used for generating electricity. It is also used without superheating for concentrate drying and for various heating duties around the smelter and refinery.

Dust falls out of waste heat boiler gases due to its low velocity in the large boiler chambers. It is collected and usually recycled to the smelting furnace for Cu recovery. It is occasionally treated hydrometallurgically (Chadwick, 1992). This avoids impurity recycle to the smelting furnace and allows the furnace to smelt more concentrate (Davenport *et al.*, 2001).

An alternative method of cooling smelter gas is to pass it through sprays of water. Spray cooling avoids the investment in waste heat recovery equipment but it wastes the heat in the gases. It is used primarily for Teniente, Inco, Noranda and Peirce-Smith gases.

14.3.2 Electrostatic precipitation of dust

After cooling, the furnace gases are passed through electrostatic precipitators (Parker, 1997, Conde *et al.*, 1999, Ryan *et al.*, 1999) for more dust removal. The dust particles are caught by (i) charging them in the corona of a high voltage

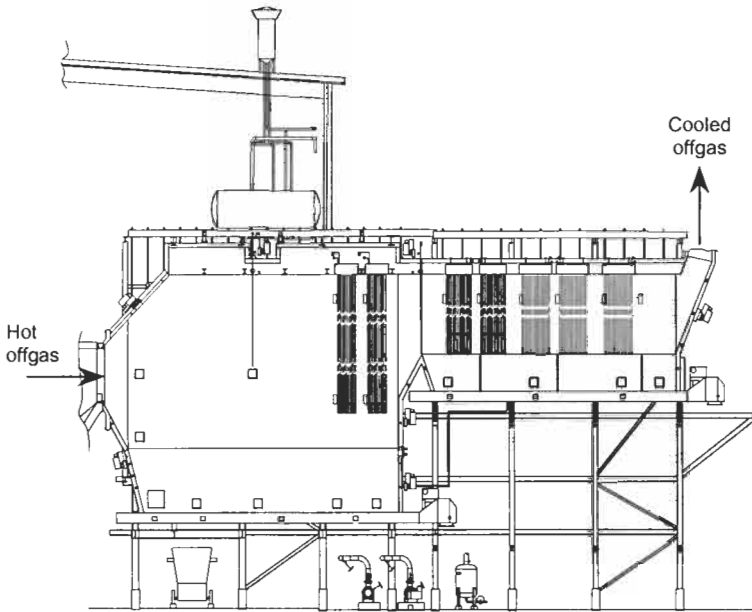


Fig. 14.2. Waste heat boiler for the Rönnskär flash furnace (Peippo *et al.*, 1999). Note, left to right, (i) flash furnace gas offtake; (ii) radiation section with tubes in the walls; (iii) suspended tube baffles in the radiation section to evenly distribute gas flow; (iv) convection section with hanging tubes. Note also water tank above radiation section and dust collection conveyors below the radiation and convection sections.

electric field; (ii) catching them on a charged plate or wire; (iii) collecting them by neutralizing the charge and shaking the wires or plates. The precipitators remove 99+% of the dust from their incoming gas (Conde *et al.*, 1999). The dust is usually re-smelted to recover its Cu.

About 70% of the dust is recovered in the cooling system and 30% in the electrostatic precipitators.

14.3.3 Water quenching and cooling

After electrostatic precipitation, the gas is quenched with water in an open or venturi tower. This quenching:

- (a) removes the remaining dust from the gas (to 1 or 2 mg/Nm³ of gas) to avoid fouling of downstream acid plant catalyst
- (b) absorbs Cl₂, F₂, SO₃ and vapor impurities (e.g. As₂S₃).

The gas is then cooled further (to 35 or 40°C) by direct contact with cool water in a packed tower or by indirect contact with cool water in a heat exchanger.

The gas leaves the cooling section through electrostatic mist precipitators to eliminate fine droplets of liquid remaining in the gas after quenching and cooling. Mist precipitators operate similarly to the electrostatic precipitators described in Section 14.3.2. They must, however, be:

- (a) constructed of acid-resistant materials such as fiber-reinforced plastic, alloy steels or lead
- (b) periodically turned off and flushed with fresh water to remove collected solids.

14.3.4 The quenching liquid, 'acid plant blowdown'

The water from quenching and direct-contact cooling is passed through water-cooled heat exchangers and used again for quenching/cooling. It becomes acidic (from SO_3 absorption) and impure (from dust and vapor absorption).

A bleed stream of this impure solution ('acid plant blowdown') is continuously withdrawn and replaced with fresh water. The amount of bleed and water replacement is controlled to keep the H_2SO_4 content of the cooling water below about 10% - to avoid corrosion. The quantity of bleed depends on the amount of SO_3 in the offgas as it enters the water-quench system.

Several smelters have found that SO_3 formation is inhibited by recycling some cooled offgas to the entrance of the waste heat boiler. This has the effect of slowing $\text{SO}_2 \rightarrow \text{SO}_3$ oxidation and decreasing 'blowdown' production rate.

The 'acid plant blowdown' stream is acidic and impure. It is neutralized and either stored or treated for metal recovery (Terayama *et al.*, 1981; Inami *et al.*, 1990; Trickett 1991, Newman *et al.*, 1999). Fig. 14.3 shows the Toyo smelter's flowsheet for 'blowdown' treatment.

14.4 Gas Drying

The next step in offgas treatment is $\text{H}_2\text{O}(\text{g})$ removal (drying). It is done to prevent unintentional H_2SO_4 formation and corrosion in downstream ducts, heat exchangers and catalyst beds.

The H_2O is removed by contacting it with 93% H_2SO_4 -7% H_2O (occasionally 96 or 98%) acid. H_2O reacts strongly with H_2SO_4 molecules to form hydrated acid molecules.

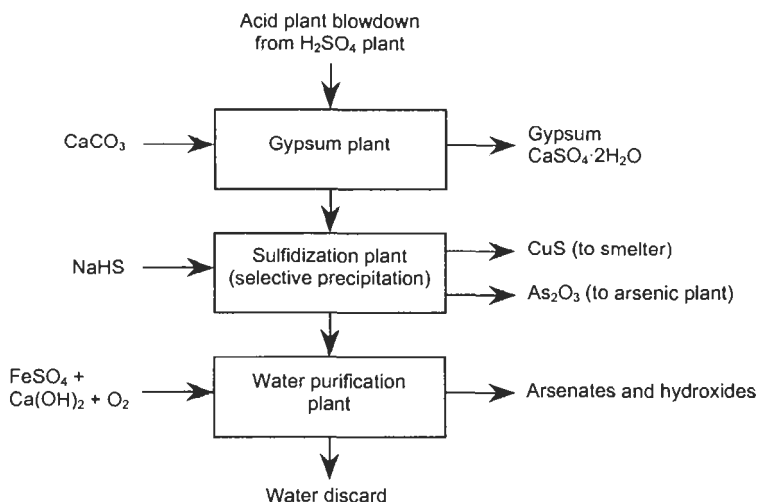


Fig. 14.3. Acid plant 'blowdown' treatment system at Toyo smelter (Inami, *et al.*, 1990). The plant treats 300 m³ of blowdown per day. The blowdown analysis is:

Item	Concentration, kg/m ³
H ₂ SO ₄	80 – 150
Cu	0.5 – 1
As	2 – 5
Zn	0.5 – 2
Cl	1 – 5

The contacting is done in a counter-current packed tower filled with 5 to 10 cm ceramic 'saddles', Fig. 14.4. The sulfuric acid flows down over the 'saddles'. The gas is drawn up by the main acid plant blowers.

The liquid product of gas drying is slightly diluted 93% H₂SO₄ acid. It is strengthened with the 98+% acid produced by subsequent SO₃ absorption (Section 14.5.2). Most of the strengthened acid is recycled to the absorption tower. A portion is sent to storage and then to market.

The gas product of the drying tower contains typically 50-100 milligrams H₂O/Nm³ of offgas. It also contains small droplets of 'acid mist' which it picks up during its passage up the drying tower. This mist is removed by passing the dry gas through stainless steel or fiber mist eliminator pads or candles.

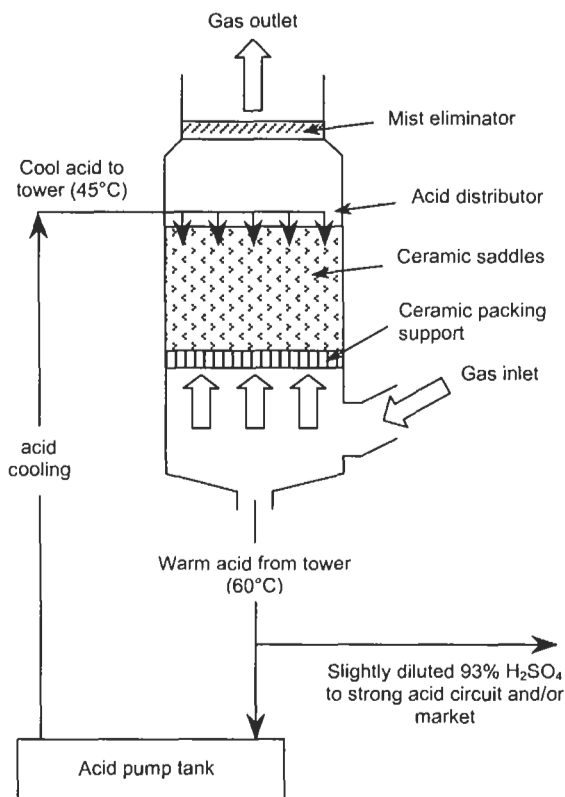


Fig. 14.4. Drying tower and associated acid circulation and cooling equipment. Acid is pumped around the tubes of the acid-water heat exchanger to the top of the tower where it is distributed over the packing. It then flows by gravity downward through the packing and returns to the pump tank. The mist eliminator in the top of the tower is a mesh 'pad'. In most SO₃ absorption towers this 'pad' is usually replaced with multiple candle type mist eliminators.

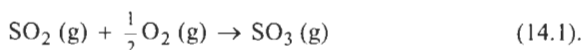
14.4.1 Main acid plant blowers

The now-dried gas is drawn into the main acid plant blowers – which push it on to SO₂ → SO₃ conversion and acidmaking. Two centrifugal blowers, typically 3000 kW, are used. They move 100 to 200 thousand Nm³ of gas per hour. The gas handling system is under a slight vacuum before the blowers (typically -0.07 atmospheres gage at the smelting furnace) and under pressure (0.3 to 0.5 atmospheres gage) after.

14.5 Acid Plant Chemical Reactions

14.5.1 Oxidation of SO_2 to SO_3

The SO_2 in the offgas is oxidized to SO_3 in preparation for absorption in the water component of 98% H_2SO_4 -2% H_2O acid. The oxidation reaction is:



This reaction is very slow without a catalyst so the offgas is always passed through V_2O_5 - K_2SO_4 catalyst 'beds'. The volumetric O_2/SO_2 ratio entering the catalyst beds is set at ~ 1 or above (by adding air, if necessary) to ensure near complete conversion of SO_2 to SO_3 .

Catalyst reactions

Typical V_2O_5 - K_2SO_4 based catalyst contains the following (mass%):

5 - 10%	V_2O_5
10 - 20%	K_2SO_4
1 - 5%	Na_2SO_4
55 - 70%	SiO_2 .

It may also contain 5-15% cesium sulfate (Cs_2SO_4) substituted for K_2SO_4 .

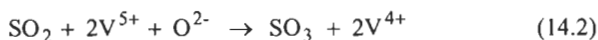
The active components of the catalyst are V_2O_5 , K_2SO_4 , Na_2SO_4 and Cs_2SO_4 (if present). The inactive material is SiO_2 , which acts as a support for the active components.

V_2O_5 - K_2SO_4 catalyst is supported liquid phase catalyst (Livbjerg, *et al.*, 1978). At the catalyst operation temperature, $\sim 400^\circ\text{C}$, the active catalyst components (V_2O_5 , K_2SO_4 , Na_2SO_4 , Cs_2SO_4) exist as a film of molten salt solution on the solid inactive SiO_2 support. Oxidation of SO_2 to SO_3 in the presence of oxygen takes place by homogeneous reactions in this liquid film. Pores on the surface of the silica substrate provide the large surface area necessary for rapid SO_2 oxidation.

The most widely cited SO_2 conversion reaction mechanism is that proposed by Mars and Maessen (1964, 1968). It is based on the experimental observation that, during SO_2 conversion, the valency of the catalyst's vanadium ions changes between the tetravalent and the pentavalent states. This observation suggests that the reaction involves:

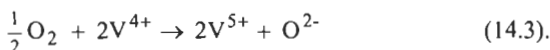
- (a) absorption of SO_2 , reduction of vanadium ions from V^{5+} to V^{4+} and

formation of SO_3 from SO_2 and O^{2-} ions, i.e.:



and:

- (b) absorption of oxygen, re-oxidation of the vanadium ions and formation of O^{2-} ions



The main reaction steps involved during catalytic oxidation of SO_2 to SO_3 are (King, 1999):

- (a) diffusion of SO_2 and O_2 from the feed gas to the surface of the supported liquid phase
- (b) absorption of SO_2 and O_2 into the liquid phase
- (c) oxidation of SO_2 to SO_3 in the melt accompanied by O^{2-} formation/reaction and reduction/re-oxidation of V^{5+} and V^{4+} species (Equations 14.2 and 14.3)
- (d) diffusion of SO_3 through the melt to its surface
- (e) desorption of SO_3 back into the gas phase
- (f) diffusion of SO_3 from the liquid surface into the gas stream.

Industrial V_2O_5 - K_2SO_4 catalysts

Catalyst is manufactured by mixing together the active components and substrate to form a paste which is extruded and baked at $\sim 530^\circ\text{C}$ into solid cylindrical pellets or rings. Ring-shaped (or 'star ring') catalyst is the most commonly used shape because (i) it gives a small pressure drop in a catalyst bed and (ii) its catalytic activity is only slowly affected by dust in the acid plant feed gas. A typical catalyst ring is 10 mm in diameter by 10 mm in length.

Catalyst ignition and degradation temperatures

The ignition temperature at which the $\text{SO}_2 \rightarrow \text{SO}_3$ conversion reaction begins with V_2O_5 - K_2SO_4 catalyst is $\sim 360^\circ\text{C}$. The reaction rate is relatively slow at this ignition temperature. Therefore, the gases entering the catalyst beds are heated to temperatures in the range of 400 – 440°C to ensure rapid $\text{SO}_2 \rightarrow \text{SO}_3$ conversion.

Above 650°C thermal deactivation of the catalyst begins. Several mechanisms for high temperature thermal deactivation have been proposed.

- (a) Silica in the substrate partly dissolves in the catalytic melt. This causes the thickness of the melt film to increase, which, in turn, blocks the pore structure, preventing gas access to the liquid phase inside the pores.
- (b) Sintering of the silica substrate closes pores restricting gas access to liquid phase inside the pores.

Thermal deactivation proceeds slowly. Most V_2O_5 - K_2SO_4 catalyst can be subjected to temperatures of 700-800°C for short periods without causing significant deactivation. Long times at these temperatures, however, reduce catalyst activity and decrease $SO_2 \rightarrow SO_3$ conversion rate.

Cs-promoted catalyst

Substituting Cs_2SO_4 for K_2SO_4 in the active liquid component of the catalyst lowers the melting point of the liquid providing higher reaction rates at lower temperatures. Lowering of the melting point by cesium allows the V^{4+} species to remain in solution at a lower temperature. This increases its low temperature catalytic activity. Cs-promoted catalyst has an ignition temperature of ~320°C. Its typical operating temperature range is 370-500°C.

Cs-promoted catalyst costs nearly 2 to 2.5 times that of non Cs-promoted catalyst. Therefore, its use is typically optimized by installing it only in the top half of the first and/or last catalyst beds.

Dust accumulation in catalyst beds

Over time, dust, which inadvertently passes through the gas cleaning section, begins to build up in the catalyst beds. It blocks gas flow through the catalyst and increases the pressure that must be applied to achieve the acid plant's required gas flowrate.

When the pressure drop in the catalyst beds becomes excessive, the acid plant must be shut down and the catalyst screened to remove the accumulated dust. Keeping offgas cleaning apparatus in optimum operating condition is critical to maintaining acid plant availability.

$SO_2 \rightarrow SO_3$ conversion equilibrium curve

Oxidation of SO_2 to SO_3 proceeds further towards completion at lower temperatures. Fig. 14.5 shows the equilibrium curve for a gas containing 12% SO_2 , 12% O_2 , balance N_2 at a total pressure of 1.2 atmospheres. The equilibrium curve on the graph represents the maximum attainable conversion of SO_2 to SO_3 at a given temperature. This curve is also shown in Fig. 14.8 with reaction heat-up paths for each catalyst bed.

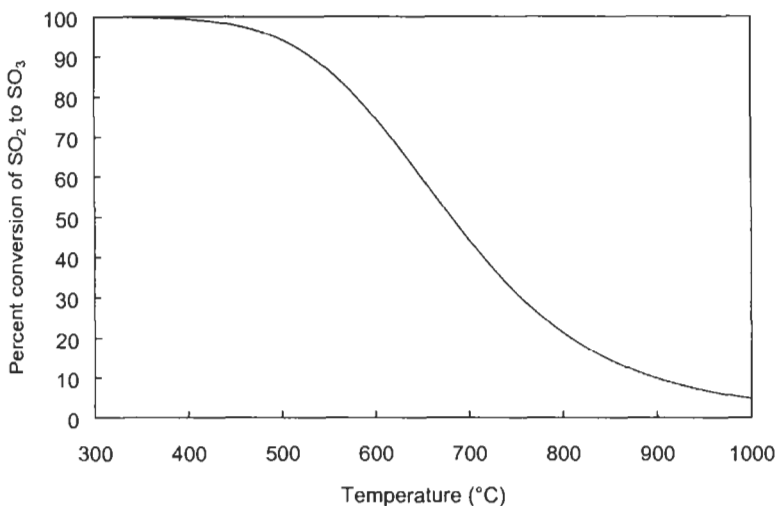


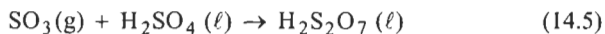
Fig. 14.5. Equilibrium curve for $\text{SO}_2 \rightarrow \text{SO}_3$ conversion for an initial gas composition of 12 volume% SO_2 , 12 volume% O_2 and 76 volume% N_2 at a total pressure of 1.2 atmospheres. The curve shows that higher SO_2 conversions are possible at lower temperatures.

14.5.2 Absorption of SO_3 into $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solution

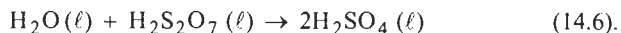
The SO_3 formed by the above-described catalytic oxidation of SO_2 is absorbed into 98% $\text{H}_2\text{SO}_4\text{-2% H}_2\text{O}$ acid. The process occurs in a packed tower of similar design to a drying tower, Fig. 14.4. In absorption, SO_3 laden gas and sulfuric acid flow counter currently. The overall absorption reaction is:



It is not possible to manufacture sulfuric acid by absorbing sulfur trioxide directly into water. Sulfur trioxide reacts with water vapor to form H_2SO_4 vapor. This sulfuric acid vapor condenses as a mist of fine, sub-micron, droplets, which are practically impossible to coalesce. However, the theoretical vapor pressure of water over 98% H_2SO_4 is low ($< 2 \times 10^{-5}$ atmospheres at 80°C), avoiding this water vapor problem. The most likely absorption reactions are:



followed by:



Some SO_3 is undoubtedly absorbed directly by water according to Equation 14.4. Because of the preponderance of H_2SO_4 molecules in the absorbent, however, absorption by Equations 14.5 and 14.6 probably predominates. SO_3 absorption is exothermic so that the strengthened acid must be cooled before it is (i) recycled for further absorption or (ii) sent to storage.

Optimum absorbing acid composition

The optimum absorbing acid composition is 98 to 99% H_2SO_4 . This is the composition at which the sum of the equilibrium partial pressures of H_2O , SO_3 and H_2SO_4 over sulfuric acid is at its minimum.

Below this optimum, H_2O vapor pressure increases and sulfuric acid mist may form by the reaction of $\text{H}_2\text{O}(\text{g})$ and SO_3 . This mist is difficult to coalesce so it tends to escape the acid plant into the environment. Above this optimum, SO_3 and H_2SO_4 partial pressures increase. This also increases the release of sulfur compounds into the environment.

Acid plant flowrates and compositions are controlled to keep the absorbing acid in the 98 to 99% range before and after SO_3 absorption.

14.6 Industrial Sulfuric Acid Manufacture (Tables 14.4 and 14.5)

Fig. 14.6 shows a typical flowsheet for $\text{SO}_2 \rightarrow \text{SO}_3$ conversion and SO_3 absorption. The plant is a 3:1 double absorption plant; i.e. the gases pass through three catalyst beds before intermediate absorption and then one catalyst bed before final absorption. Figs. 14.8 and 14.9 describe the process thermodynamically. The steps are:

- (a) heating of the incoming gas to the minimum continuous catalyst operating temperature ($\sim 430^\circ\text{C}$) by heat exchange with the hot gases from $\text{SO}_2 \rightarrow \text{SO}_3$ oxidation
- (b) passing the hot gas through a first bed of catalyst where partial $\text{SO}_2 \rightarrow \text{SO}_3$ conversion takes place and where the gases are heated by the heat of the $\text{SO}_2 \rightarrow \text{SO}_3$ reaction
- (c) cooling the gas back down by heat exchange with cool incoming gas
- (d) passing the cooled gas through a second bed of catalyst where more $\text{SO}_2 \rightarrow \text{SO}_3$ conversion takes place and where the gases again become hot
- (e) repeating steps (c) and (d) with a third catalyst bed.

The gas from the third catalyst bed is cooled and its SO_3 absorbed into 98% H_2SO_4 -2% H_2O acid.

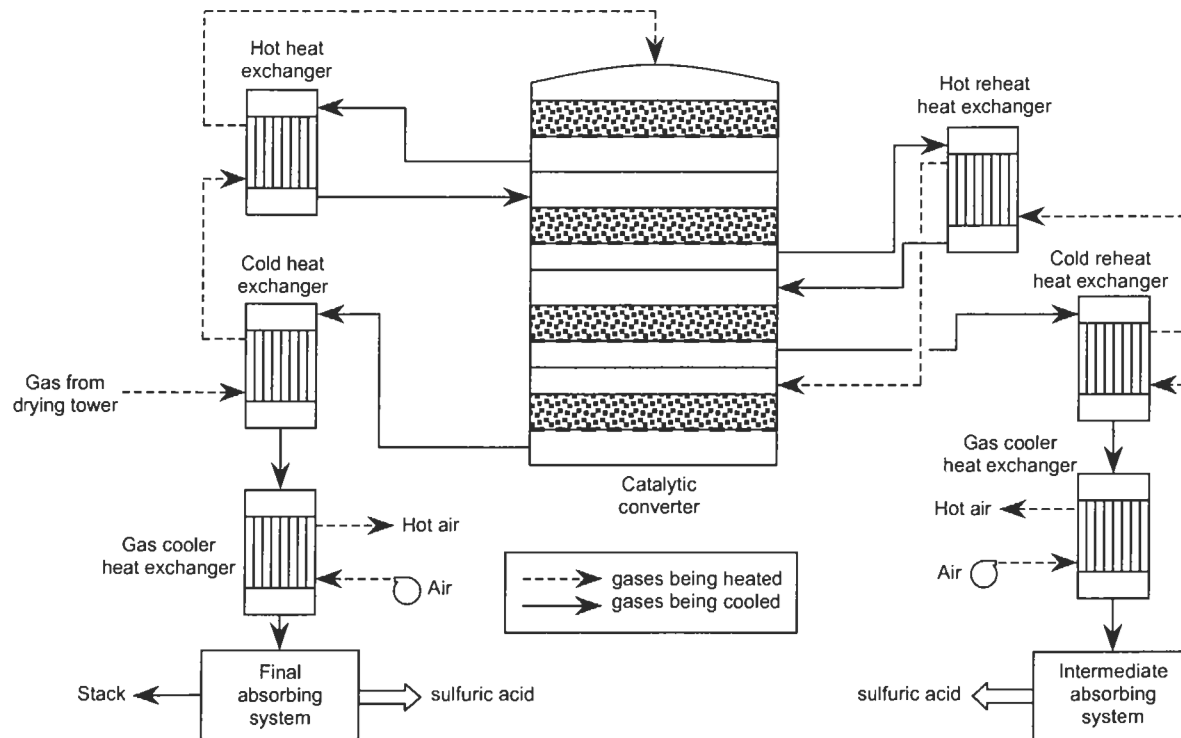


Fig 14.6. Flowsheet for a typical 3:1 metallurgical sulfuric acid plant. Catalyst beds with gas cooling between (to avoid overheating the catalyst) are notable. A hydrocarbon fuel-fired heat exchanger (not shown) is used to heat the feed gas during acid plant startup.

The exit gas from this absorption is then passed through a second set of heat exchangers, a fourth catalyst bed and a second absorption tower. In some plants, initial absorption takes place after the gas passes through two catalyst beds and final absorption after the remaining two catalyst beds.

The above description is for a 'double absorption' plant which converts and absorbs >99.5% of the SO_2 entering the acid plant. Single absorption acid plants convert SO_2 to SO_3 in three or four catalyst beds followed by single absorption of SO_3 , Table 14.5. Their conversion of SO_2 to SO_3 is less complete with consequentially lower sulfur capture efficiencies (97.5-98%).

14.6.1 Catalytic converter

A catalytic converter typically houses 3 to 5 catalyst beds. It is usually made of stainless steel. Fig. 14.7 shows the cross section of a typical catalyst bed.

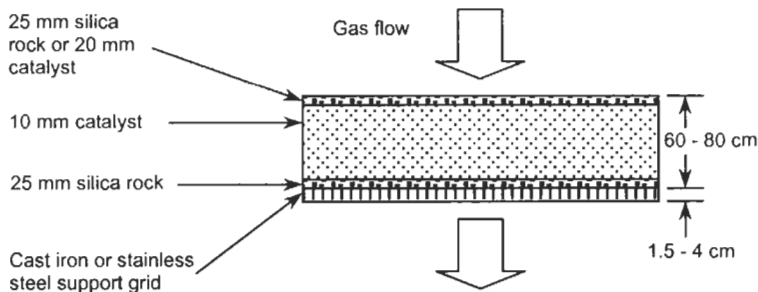


Fig 14.7. Catalyst bed showing steel support, catalyst and silica rock. The bed is typically 8 – 12 m in diameter. The silica rock on the top of the bed distributes the gas into the catalyst, preventing localized channeling and short-circuiting through the bed.

14.6.2 SO_2 to SO_3 conversion reaction paths

Figs. 14.8 and 14.9 show the schematic steady state % SO_2 conversion/temperature reaction path for a 12 volume% SO_2 , 12 volume% O_2 gas flowing through a double absorption 3:1 sulfuric acid plant.

The gas enters the first catalyst bed of the converter at about 410°C. SO_2 is oxidized to SO_3 in the bed – heating the gas to about 630°C. About 64% of the input SO_2 is converted to SO_3 .

The gas from bed 1 is then cooled to 430°C in a heat exchanger (Fig. 14.6) and is passed through the second catalyst bed.

Table 14.4. Operating details of five double absorption sulfuric verting gases are diluted to the input levels in this table by adding

Smelter	WMC, Olympic Dam, Australia	Norddeutsche Affinerie, Hamburg (lines 1 and 2)	Norddeutsche Affinerie, Hamburg (line 3)
Startup date	1998	1972	1991
Manufacturer	Lurgi wet gas/Monsanto strong acid	Lurgi	Lurgi
Gas source	Direct-to-copper flash furnace and anode furnace oxidation gases	Outokumpu flash furnace and Peirce-Smith converters	Outokumpu flash furnace and Peirce-Smith converters
Single or double absorption	double	double	double
number of catalyst beds	4	4	5
intermediate SO ₃ absorption after ? bed	3 rd	2 nd	3 rd
Converter diameter, m			
first pass	10	8	8.5
others	10	8	8.5
Thickness of catalyst beds, m			
bed 1	0.76	0.99	0.8
bed 2	0.81	0.94	0.87
bed 3	0.99	0.94	0.91
bed 4	1.12	0.94	0.87
bed 5			1.02
Catalyst			
bed 1	Monsanto LP 120	BASF+0.19 m Cs ring type catalysts	BASF+0.19 m Cs ring type catalysts
bed 2	Monsanto LP 120	BASF ring type	BASF ring type
bed 3	Monsanto LP 110	BASF ring type	BASF ring type
bed 4	Monsanto LP 110	BASF Cs ring type	BASF ring type
bed 5			BASF ring type
Gas into converter			
flowrate, Nm ³ /minute	2166	1830 (maximum)	
volume% SO ₂	12	11	
volume% O ₂	>12	>12.1	
H₂SO₄ production rate	900-1400	2500	
tonnes 100% H₂SO₄/day			
Products, mass% H₂SO₄	98.5	94, 96, 98 and 20% SO ₃ oleum	

acid manufacturing plants, 2001. Smelting and continuous con-
air through filters just before the acid plant's drying tower.

PT Smelting Co. Gresik, Indonesia	Sumitomo Mining Co. Toyo, Japan	Mexicana de Cobre, Nacozari Mexico (Plant 1)	Mexicana de Cobre, Nacozari Mexico (Plant 2)
1998	1971	1988	1996
Lurgi	Sumitomo Chemical Engineering	Monsanto	Monsanto
Mitsubishi process and anode furnace (oxidation stage only) double	Outokumpu flash furnace & Peirce- Smith converters double	Outokumpu flash + Teniente furnaces + Peirce-Smith converters double	Outokumpu flash + Teniente furnaces + Peirce-Smith converters double
4 3 rd	5	4 3 rd	4 3 rd
12	12.5	12.5	12.3
12	12.5	12.5	12.3
0.715	0.35	0.824	0.715
0.67	0.23	0.938	0.757
0.75	0.67	0.946	0.799
1.185	1.04	0.946	0.952
	1.04		
VK38&59 daisy type catalyst	Nihonshokubai 7S	split: Cs-K-V ₂ O ₅ input side, K-V ₂ O ₅ output side	split: Cs-K-V ₂ O ₅ input side, K-V ₂ O ₅ output side
VK38 daisy type	Monsanto T-516	K-V ₂ O ₅	K-V ₂ O ₅
VK48 daisy type	Topsoe VK38	split: Cs-K-V ₂ O ₅ input side, K-V ₂ O ₅ output side	K-V ₂ O ₅
VK38 daisy type	Nihonshokuhai R10	split: Cs-K-V ₂ O ₅ input side, K-V ₂ O ₅ output side	split: Cs-K-V ₂ O ₅ input side, K-V ₂ O ₅ output side
	Nihonshokubai R10		
3100 (max)	2917 (max)	3766	3283
12	13	11.05	11
>13	11.1	11.88	11
2400	1900	2614	2130
98.5	98, 70	98.5	98.5

Table 14.5. Physical and operating of two single absorption sulfuric acid manufacturing plants, 2001. Design of the Mt. Isa plant is discussed by Daum, 2000.

Smelter	Mt. Isa, Queensland Australia	Altonorte, Chile
Start-up date	1999	2003 (design data)
Manufacturer	Lurgi	Lurgi
Gas source	Isasmelt, 4 Peirce-Smith converters and sulfur burner	Noranda smelting furnace
Single or double absorption	single	single
number of catalyst beds	3	4
intermediate SO ₃ absorption after ? bed	no	no
Converter diameter, m		
first pass	15	11.7 with 4 m diameter internal heat exchanger
others	same	same
Thickness of catalyst beds, m		
bed 1	0.68	0.67
bed 2	0.8	0.87
bed 3	0.95	0.98
bed 4	no	1.42
Catalyst type		
bed 1	K-V ₂ O ₅	BASF 04-110 Low ignition
bed 2	K-V ₂ O ₅	BASF 04-111 V ₂ O ₅
bed 3	Cs-K-V ₂ O ₅	BASF 04-111 V ₂ O ₅
bed 4		BASF 04-111 V ₂ O ₅
Gas into converter		
flowrate, Nm ³ /minute	6333	2917
volume% SO ₂	11.2 maximum 10.6 normal operating	12
volume% O ₂	not measured	14
H₂SO₄ production rate tonnes 100% H₂SO₄/day	3300	2290 (capacity)
Products, mass% H₂SO₄	98.5	96 to 98.5

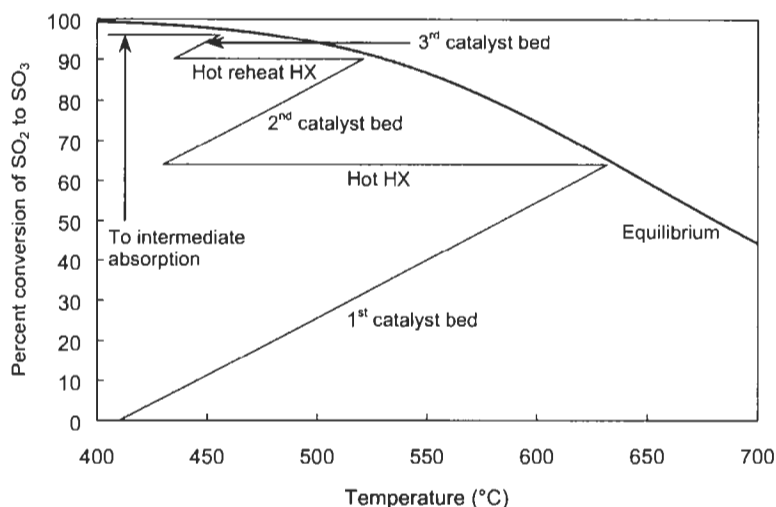


Fig. 14.8. Equilibrium curve and first through third catalyst bed reaction heat-up paths. The horizontal lines represent cooling between the catalyst beds in the heat exchangers. The feed gas contains 12 volume% SO_2 , 12 volume% O_2 , balance N_2 (1.2 atmospheres, gage, overall pressure).

There, a further 26% of the SO_2 is converted to SO_3 (to a total of 90%) and the gas is heated to about 520°C by the oxidation reaction.

This gas is then cooled to 435°C in a heat exchanger and is passed through the third catalyst bed. A further 6% of the initial SO_2 is oxidized to SO_3 (to 96% conversion) while the temperature increases to about 456°C .

At this point, the gas is cooled to $\sim 200^\circ\text{C}$ and sent to the intermediate absorption tower where virtually all (99.99%) of its SO_3 is absorbed into 98% $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ sulfuric acid.

After this absorption, the gas contains about 0.5 volume% SO_2 . It is heated to 415°C and passed through the last catalyst bed in the converter, Fig. 14.9. Here about 90% of its SO_2 is converted to SO_3 , leaving only about 0.025 volume% SO_2 in the gas. This gas is again cooled to $\sim 200^\circ\text{C}$ and sent to the final SO_3 absorption tower.

Overall conversion of SO_2 is approximately:

$$\frac{[12\% \text{SO}_2 \text{ (in initial gas)} - 0.025\% \text{SO}_2 \text{ (in final gas)}]}{12\% \text{SO}_2 \text{ (in initial gas)}} \times 100 = 99.8\%.$$

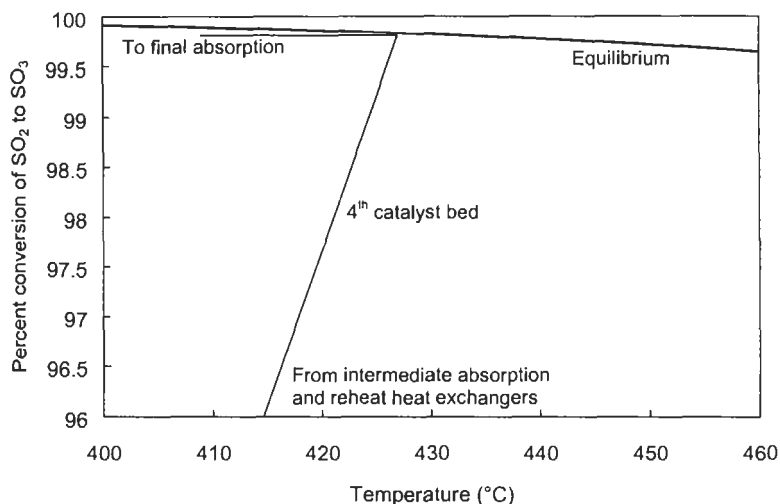


Fig. 14.9. Equilibrium curve and fourth catalyst bed reaction heat-up path. Almost all of the SO_3 in the gas leaving the third catalyst bed has been absorbed into sulfuric acid in the intermediate absorption tower.

14.6.3 Reaction path characteristics

Figs. 14.8 and 14.9 show some important aspects of $\text{SO}_2 \rightarrow \text{SO}_3$ conversion.

- Conversion to SO_3 is maximized by a low conversion temperature, consistent with meeting the minimum continuous operating temperature requirement of the catalyst.
- The maximum catalyst temperature is reached in the first catalyst bed where most of the $\text{SO}_2 \rightarrow \text{SO}_3$ conversion takes place. This is where a low ignition temperature Cs catalyst can be useful. Catalyst bed temperature increases with increasing SO_2 concentration in the gas because $\text{SO}_2 \rightarrow \text{SO}_3$ conversion energy release has to heat less N_2 . Cs catalyst is expensive, so it is only used when low temperature catalysis is clearly advantageous.
- Conversion of SO_2 to SO_3 after intermediate absorption is very efficient, Fig. 14.9. This is because (i) the gas entering the catalyst contains no SO_3 (driving Reaction (14.1) to the right) and because (ii) the temperature of the gas rises only slightly due to the small amount of SO_2 being oxidized to SO_3 .
- Maximum cooling of the gases is required for the gases being sent to SO_3

absorption towers (-440°C to 200°C), hence the inclusion of air coolers in Fig. 14.6.

- (e) Maximum heating of the gases is required for initial heating and for heating after intermediate absorption, hence the preheater and passage through several heat exchangers in Fig. 14.6.

14.6.4 Absorption towers

Double absorption sulfuric acid plants absorb SO_3 twice: after partial $\text{SO}_2 \rightarrow \text{SO}_3$ oxidation and after final oxidation. The absorption is done counter-currently in towers packed with 5 to 10 cm ceramic 'saddles' which present a continuous descending film of 98% H_2SO_4 -2% H_2O acid into which rising SO_3 absorbs. Typical sulfuric acid irrigation rates, densities and operating temperatures for absorption towers are shown in Table 14.6.

The strengthened acid is cooled in water-cooled shell and tube type heat exchangers. A portion of it is sent for blending with 93% H_2SO_4 from the gas drying tower to produce the grades of acid being sent to market. The remainder is diluted with blended acid and recycled to the absorption towers.

These cross-flows of 98+ and 93% H_2SO_4 allow a wide range of acid products to be marketed.

Table 14.6. Typical sulfuric acid design irrigation rates and irrigation densities for drying and absorption towers (Guenkel and Cameron, 2000).

Tower	Sulfuric acid irrigation rate (m^3/tonne of 100% H_2SO_4 produced)	Sulfuric acid irrigation density (m^3/min per m^2 of tower cross section)	Sulfuric acid temperature ($^{\circ}\text{C}$) inlet / outlet
Drying tower	0.005	0.2 - 0.4	45 / 60
Intermediate absorption tower	0.01	0.6 - 0.8	80 / 110
Final absorption tower	0.005	0.4	80 / 95

14.6.5 Gas to gas heat exchangers and acid coolers

Large gas-to-gas heat exchangers are used to transfer heat to and from gases entering and exiting a catalytic converter. The latest heat exchanger designs are radial shell and tube. Acid plant gas-to-gas heat exchangers typically transfer heat at 10,000 to 80,000 MJ/hr. They must be sized to ensure that a range of gas flowrates and SO_2 concentrations can be processed. This is especially significant for smelters treating offgases generated by batch type Peirce-Smith converters.

The hot acid from SO₃ absorption and gas drying is cooled in indirect shell and tube heat exchangers. The water flows through the tubes of the heat exchanger and the acid through the shell. The warm water leaving the heat exchanger is usually cooled in an atmospheric cooling tower before being recycled for further acid cooling.

Anodic protection of the coolers is required to minimize corrosion by the hot sulfuric acid. A non-anodically protected acid cooler has a lifetime on the order of several months whereas anodically protected coolers have lifetimes on the order of 20 - 30 years.

14.6.6 Grades of product

Sulfuric acid is sold in grades of 93 to 98% H₂SO₄ according to market demand. The principal product in cold climates is 93% H₂SO₄ because of its low freezing point, -35°C (DuPont, 1988).

Oleum, H₂SO₄ into which SO₃ is absorbed, is also sold by several smelters. It is produced by diverting a stream of SO₃-bearing gas and contacting it with 98+ H₂SO₄ in a small absorption tower.

14.7 Recent and Future Developments in Sulfuric Acid Manufacture

14.7.1 Maximizing feed gas SO₂ concentrations

The 1980's and 1990's saw significant shifts in smelting technology – from reverberatory and electric furnace smelting to flash furnace and other intensive smelting processes. Oxygen enrichment of furnace blasts also increased significantly. An important (and desired) effect of these changes has been an increased SO₂ strength in the gases that enter smelter sulfuric acid plants.

SO₂ offgases entering their drying tower now average 6 to 18 volume% SO₂. The low concentrations come from smelters using Peirce-Smith converters. The high concentrations come from direct to copper smelting and continuous smelting/converting smelters (St Eloi *et al.*, 1989; Ritschel, *et al.*, 1998).

High SO₂ gases contain little N₂. They heat up more than conventional smelter gas during passage through SO₂ → SO₃ catalyst beds. This can lead to overheating and degradation of the V₂O₅-K₂SO₄ catalyst (650°C) and to weakening of the steel catalyst bed support structure (630°C). These two items limit the maximum strength of sulfuric acid plant feed gas to ~13 volume% SO₂ (with conventional flow schemes).

Two approaches have been used to raise permissible SO_2 strength entering a sulfuric acid plant.

- (a) Installation of Cs-promoted catalyst in the first pass catalyst bed. This allows the bed inlet temperature to be operated at $\sim 370^\circ\text{C}$, i.e. about 40°C cooler than conventional catalysts. This allows a larger temperature rise (i.e. more SO_2 conversion) in the first bed without exceeding the bed outlet temperature limit.
- (b) Installation of a pre-converter to lower the SO_2 concentration entering the first catalyst bed of the main converter (Ritschel, *et al.*, 1998). This approach allows Olympic Dam to process 18 volume% SO_2 feed gas (Ritschel, *et al.*, 1998).

14.7.2 Maximizing heat recovery

Heat is generated during $\text{SO}_2 \rightarrow \text{SO}_3$ conversion. In sulfur burning sulfuric acid plants this heat is usually recovered into a useful form – steam. The hot gases exiting the catalyst beds are passed through boiler feed water economizers and steam superheaters. Several metallurgical plants also capture $\text{SO}_2 \rightarrow \text{SO}_3$ conversion and SO_3 absorption heat (Puricelli *et al.*, 1998) but most remove their excess heat in air coolers.

14.8 Alternative Sulfur Products

The SO_2 in Cu smelter gases is almost always captured as sulfuric acid. Other SO_2 -capture products have been:

- (a) liquid SO_2
- (b) gypsum
- (c) elemental sulfur (several plants built, but not used)

The processes for making these products are described briefly in Biswas and Davenport, 1994.

14.9 Future Improvements in Sulfur Capture

Modern smelting processes collect most of their SO_2 at sufficient strength for economic sulfuric acid manufacture. These processes continue to displace reverberatory smelting.

Peirce-Smith converting remains a problem for SO_2 collection especially during charging and skimming (Fig. 1.6b) when gas leaks into the workplace and at ground level around the smelter. Adoption of continuous converting processes such as Mitsubishi, flash and Noranda continuous converting will alleviate this problem.

14.10 Summary

This chapter has shown that most copper is extracted from sulfide minerals so that sulfur, in some form, is a byproduct of most copper extraction processes. The usual byproduct is sulfuric acid, made from the SO_2 produced during smelting and converting.

Sulfuric acid production entails:

- (a) cleaning and drying the furnace gases
- (b) catalytically oxidizing their SO_2 to SO_3 (with O_2 in the gas itself or in added air)
- (c) absorbing the resulting SO_3 into a 98% $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ sulfuric acid solution.

The process is autothermal when the input gases contain about 4 or more volume% SO_2 . The double absorption acid plants being installed in the 1990's recover 99.5% of their input SO_2 . SO_2 recovery can be increased even further by scrubbing the acid plant tail gas with basic solutions.

Some modern smelting processes produce extra-strong SO_2 gases, 13+ volume% SO_2 . These strong gases tend to overheat during $\text{SO}_2 \rightarrow \text{SO}_3$ oxidation causing catalyst degradation and inefficient SO_2 conversion. This problem is leading to the development of catalysts which have low ignition temperatures and high degradation temperatures. Thought is also being given to the use of O_2 -enriched air or industrial oxygen for $\text{SO}_2 \rightarrow \text{SO}_3$ conversion. This would minimize (i) the size (hence capital cost) of the acid plant and (ii) the amount of gas being blown through the plant (hence energy cost).

The Peirce-Smith converter is the major environmental problem remaining in the Cu smelter. It tends to spill SO_2 -bearing gas into the workplace and it produces gas discontinuously for the acid plant.

Adoption of replacement converting processes began in the 1980's (Mitsubishi converter) and is continuing in the 2000's (flash converter, Noranda converter). Replacement is slow because of the excellent chemical and operating efficiencies of the Peirce-Smith converter.

Suggested Reading

Friedman, L.J. (1999) Analysis of recent advances in sulfuric acid plant systems and designs (contact area). In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 95–117.

Holm, H.J., Chidester, S.H. and Polk, P. (2001) Sulfuric acid catalyst sizes and shapes, Haldor Topsoe A/S, Haldor Topsoe Inc. Presented at the AIChE Clearwater Conference June 14, 2001, Clearwater, FL.

Humphris, M.J., Liu, J. and Javor, F. (1997) Gas cleaning and acid plant operations at the Inco Copper Cliff smelter. In *Proceedings of the Nickel-Cobalt 97 International Symposium, Vol. III Pyrometallurgical Operations, Environment, Vessel Integrity in High-Intensity Smelting and Converting Processes*, ed. Diaz, C., Holubec, I. and Tan, C.G., Metallurgical Society of CIM, Montreal, Canada, 321–335.

Puricelli, S.M., Grendel, R.W. and Fries, R.M. (1998) Pollution to power: a case study of the Kennecott sulfuric acid plant. In *Sulfide Smelting '98*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 451–462.

References

Bhappu, R.R., Larson, K.H. and Tunis, R.D. (1993) Cyprus Miami Mining Corporation smelter modernization project: summary and status. Paper prepared for 1994 TMS Annual Meeting, San Francisco, February 27–March 4, 1994.

Biswas, A.K. and Davenport, W.G. (1994) *Extractive Metallurgy of Copper, 3rd Edition*, Elsevier Science Press, New York, NY, 298–299.

Chadwick, J. (1992) Magma from the ashes. *Mining Magazine*, 167(4), 221–237.

Chatwin, T.D. and Kikumoto, N. (1981) *Sulfur Dioxide Control in Pyrometallurgy*. TMS, Warrendale, PA.

Conde, C.C., Taylor, B. and Sarma, S. (1999) Philippines Associated Smelting electrostatic precipitator upgrade. In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 685–693.

Daum, K.H. (2000) Design of the world's largest metallurgical acid plant. In *Sulphur 2000 Preprints*, British Sulphur, London, UK, 325–338.

Davenport, W.G., Jones, D.M., King, M.J., Partelpoeg, E.H. (2001) *Flash Smelting: Analysis, Control and Optimization*. TMS, Warrendale, PA.

DuPont (1988) Sulfuric acid storage and handling. Brochure from E.I. du Pont de Nemours & Co. (Inc.), Wilmington, Delaware.

- Evans, C.M., Lawler, D.W., Lyne, E.G.C. and Drexler, D.J. (1998) Effluents, emissions and product quality. In *Sulphur 98 Preprints – Volume 2*, British Sulphur, London, UK, 217 241.
- Environmental Protection Agency (U.S.) (2001) *Regulations on National Primary and Secondary Ambient Air Quality Standards*, The Bureau of National Affairs Inc., Washington, DC 20037.
- Friedman, L.J. (1981) Production of liquid SO₂, sulfur and sulfuric acid from high strength SO₂ gases. In *Sulfur Dioxide Control in Pyrometallurgy*, ed. Chatwin, T.D. and Kikumoto, N., TMS, Warrendale, PA. 205 220.
- Friedman, L.J. (1983) Sulfur dioxide control system arrangements for modern smelters. In *Advances in Sulfide Smelting Vol. 2, Technology and Practice*, ed. Sohn, H.Y., George, D.B. and Zunkel, A.D., TMS, Warrendale, PA, 1023 1040.
- Friedman, L.J. (1999) Analysis of recent advances in sulfuric acid plant systems and designs (contact arca). In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 95 117.
- Guenkel, A.A. and Cameron, G.M. (2000) Packed towers in sulfuric acid plants - review of current industry practice. In *Sulphur 2000 Preprints*, British Sulphur, London, UK, 399 417.
- Humphris, M.J., Liu, J. and Javor, F. (1997) Gas cleaning and acid plant operations at the Inco Copper Cliff smelter. In *Proceedings of the Nickel-Cobalt 97 International Symposium, Vol. III Pyrometallurgical Operations, Environment, Vessel Integrity in High-Intensity Smelting and Converting Processes*, ed. Díaz, C., Holubec, I. and Tan C.G., Metallurgical Society of CIM, Montreal, Canada, 321 335.
- Inami, T., Baba, K. and Ojima, Y. (1990) Clean and high productive operation at the Sumitomo Toyo smelter. Paper presented at the Sixth International Flash Smelting Congress, Brazil, October 14-19, 1990.
- Jensen-Holm H. (1986) The Vanadium catalyzed sulfur dioxide oxidation process. Haldor Topsoe A/S, Denmark.
- King, M.J. (1999) Control and Optimization of Metallurgical Sulfuric Acid Plants. Ph.D. Dissertation, University of Arizona.
- Kohn, H. and Sugawara, Y. (1981) SO₂ pollution control with lime-gypsum process at Onahama smelter. In *Sulfur Dioxide Control in Pyrometallurgy*, ed. Chatwin, T.D. and Kikumoto, N., TMS, Warrendale, PA, 103 119.
- Lide, D.R. (1990) *Handbook of Chemistry and Physics 71st Edition*, CRC, Boca Raton, 6-6 6-11.
- Livbjerg, H., Jensen, K. and Villadsen, J. (1978) Supported liquid-phase catalysts. *Catal. Rev.-Sci. Eng.*, 17(2), 203 272.

Mars, P. and Maessen, J. G. H. (1968) The mechanism and the kinetics of sulfur dioxide oxidation on catalysts containing vanadium and alkali oxides. *Journal of Catalysis*, **10**, 1 12.

Mars, P. and Maessen, J. G. H. (1964) The mechanism of the oxidation of sulphur dioxide on potassium-vanadium oxide catalysts. In *Proceedings of 3rd International Congress on Catalysis*, Amsterdam, Holland, **1**, 226.

Newman, C.J., Collins, D.N. and Weddick, A.J. (1999) Recent operation and environmental control in the Kennecott smelter. In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 29 45.

Newman, C.J., MacFarlane, G., and Molnar, K.E. (1993) Increased productivity from Kidd Creek Copper operations. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Vol. II: Copper and Nickel Smelter Operations*, ed. Landolt, C., TMS, Warrendale, PA, 1477 1496.

Oshima, E. and Igarashi, T. (1993) Recent operation and improvements at Onahama smelter. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Vol. II, Copper and Nickel Smelter Operations*, ed. Landolt, C.A., Pergamon Press, New York, NY, 1319 1333.

Oshima, E., Igarashi, T., Nishikawa, M. and Kawasaki, M. (1997) Recent operation of the acid plant at Naoshima. In *Proceedings of the Nickel-Cobalt 97 International Symposium, Vol. III Pyrometallurgical Operations, Environment, Vessel Integrity in High-Intensity Smelting and Converting Processes*, ed. Díaz, C., Holubec, I. and Tan, C.G., Metallurgical Society of CIM, Montreal, Canada.

Parker, K.R. (1997) *Applied Electrostatic Precipitation*, Chapman and Hall, London, England.

Peippo, R., Holopainen, H. and Nokclainen, J. (1999) Copper smelter waste heat boiler technology for the next millennium. In *Copper 99–Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 71 82.

Perry, R. H., Green, D. W. and Maloney, J. O. (1984) *Perry's Chemical Engineers' Handbook - 6th Edition*, McGraw-Hill, New York, NY, 3-65 3-66.

Puricelli, S.M., Grendel, R.W. and Fries, R.M. (1998) Pollution to power: a case study of the Kennecott sulfuric acid plant. In *Sulfide Smelting '98*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 451 462.

Ritschel, P.M., Fell, R.C., Fries, R.M. and Bhambri, N. (1998) Metallurgical sulfuric acid plants for the new millennium. In *Sulphur 98 Preprints – Volume 2*, British Sulphur, London, UK, 123 145.

Ross, K.G. (1991) Sulphuric acid market review. In *Smelter Off-gas Handling and Acid Plants*, notes from Canadian Institute of Mining and Metallurgy professional enhancement short course, ed. Ozberk, E. and Newman, C.J., Ottawa, Canada, August 1991.

Ryan, P., Smith, N., Corsi, C. and Whiteus, T. (1999) Agglomeration of ESP dusts for recycling to plant smelting furnaces. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 561-571.

Shibata, T. and Oda, Y. (1990) Environmental protection for SO₂ gas at Tamano smelter. Paper presented at the Sixth International Flash Smelting Congress, Brazil, October 14-19, 1990.

St. Eloi, R.J., Newman, C.J. and Bordin, D.A. (1989) SO₂ emission control from the Kidd Creek copper smelter. *CIM Bulletin*, **82**(932), 93 100.

Terayama, T., Hayashi, T. and Inami, T. (1981) Ten years experience on pollution prevention at Sumitomo's Toyo copper smelter. In *Sulfur Dioxide Control in Pyrometallurgy*, ed. Chatwin, T.D. and Kikumoto, N., TMS, Warrendale, PA, 121 142.

Tomita, M., Suenaga, C., Okura, T. and Yasuda, Y. (1990) 20 years of operation of flash furnaces at Saganoscki smelter and refinery. Paper presented at the Sixth International Flash Smelting Congress, Brazil, October 14-19, 1990.

Trickett, A.A. (1991) Acid plant design and operations 2. In *Smelter Off-gas Handling and Acid Plants*, notes from Canadian Institute of Mining and Metallurgy professional enhancement short course, ed. Ozberk, E. and Newman, C.J., Ottawa, Canada, August 1991.

Willbrandt, P. (1993) Operational results of Norddeutsche Affinerie copper smelter. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Vol. II, Copper and Nickel Smelter Operations*, ed. Landolt, C.A., Pergamon Press, New York, NY, 1361 1376.

CHAPTER 15

Fire Refining and Casting of Anodes: Sulfur and Oxygen Removal

Virtually all the copper produced by smelting/converting is subsequently electrorefined. It must, therefore, be suitable for casting into thin, strong, smooth anodes for interleaving with cathodes in electrorefining cells, Fig. 1.7. This requires that the copper be fire refined to remove most of its sulfur and oxygen.

The molten blister copper from Peirce-Smith converting contains ~0.01% S and ~0.5% O, Chapter 9. The copper from single-step smelting and continuous converting contains 0.2% to 0.4% O and up to 1% S, Chapters 10 and 12. At these levels, the dissolved sulfur and oxygen would combine during solidification to form bubbles ('blisters') of SO_2 in newly cast anodes – making them weak and bumpy. In stoichiometric terms, 0.01 mass% dissolved sulfur and 0.01 mass% dissolved oxygen would combine to produce about 2 cm³ of SO_2 (1083°C) per cm³ of copper.

Fire refining removes sulfur and oxygen from liquid blister copper by:

- (a) air-oxidation removal of sulfur as SO_2 to ~0.002% S

then:

- (b) hydrocarbon-reduction removal of oxygen as CO and $\text{H}_2\text{O(g)}$ to ~0.15% O.

Sulfur and oxygen contents at the various stages of fire refining are summarized in Table 15.1.

15.1 Industrial Methods of Fire Refining

Fire refining is carried out in rotary refining furnaces resembling Peirce-Smith

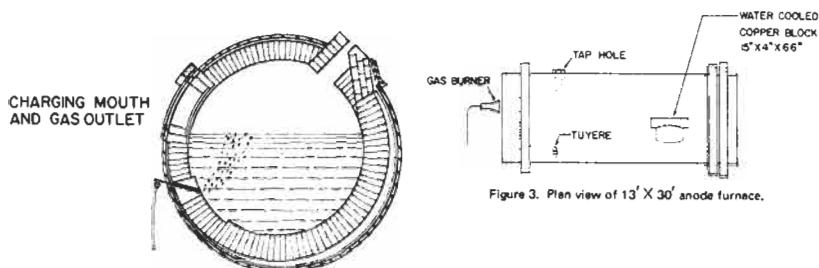


Figure 3. Plan view of 13' X 30' anode furnace.

Fig. 15.1a. Rotary refining (anode) furnace, end and front views (after McKerrow and Pannell, 1972). The furnaces are typically 3 to 5 m diameter and 9 to 14 m long, inside the steel shell.

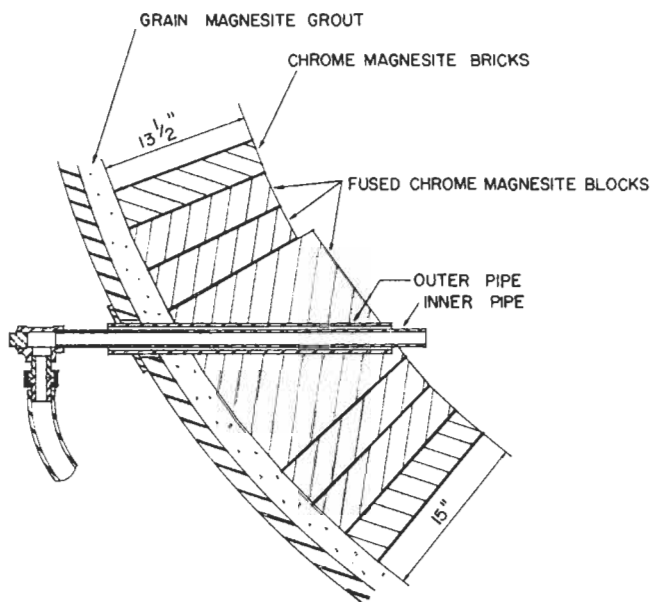


Fig. 15.1b. Detail of anode furnace tuyere (after McKerrow and Pannell, 1972). Note the two concentric pipes separated by castable refractory which permit easy replacement of the inside pipe as it wears back. The inside pipe protrudes into the molten copper to prevent seepage of gas back through the refractory wall of the furnace. Reprinted by permission of CIM, Montreal, Canada.

Table 15.1. Sulfur and oxygen contents at various stages of fire refining.

Stage of process	mass% S	mass% O
Blister copper*	0.01–0.03 (Lehner <i>et al.</i> , 1994)	0.1–0.8 (Lehner <i>et al.</i> , 1994)
After oxidation	0.002–0.005	0.6–1 (Reygadas <i>et al.</i> , 1987)
After reduction (‘poling’)	0.002–0.005	0.05–0.2 (Lehner <i>et al.</i> , 1994)
Cast anodes	0.002–0.005 (Davenport <i>et al.</i> , 1999)	0.1–0.2 (Davenport <i>et al.</i> , 1999)

*From Peirce-Smith and Hoboken converters. The copper from direct-to-copper smelting and continuous converting contains 0.2% to 0.4% O and up to 1% S.

converters (Fig. 15.1a) or, much less often, in hearth furnaces. It is carried out at about 1200°C which provides enough superheat for subsequent casting of anodes. The furnaces are heated by combusting hydrocarbon fuel throughout the process. About 2 to 3×10^6 kJ of fuel are consumed per tonne of copper.

15.1.1 Rotary furnace refining

Figure 15.1a shows a rotary refining furnace. Air and hydrocarbon flowrates into refining furnaces are slow, to provide precise control of copper composition. Only one or two tuyeres are used, Fig. 15.1b, Table 15.2. Gas flowrates are ~10 to 50 Nm³/minute per tuyere at 2 to 5 atmospheres pressure.

Refining a 250 tonne charge of blister copper (0.01% S) takes 2 or 3 hours: ~1 hour for air injection (S removal) and ~2 hours for hydrocarbon injection (O removal). High-sulfur copper from direct-to-copper smelting and continuous converting takes considerably longer (~5 hours) to desulfurize.

A typical sequence in rotary furnace refining is:

- molten copper is delivered by crane and ladle from converters to the anode furnace until 200 or 300 tonnes are accumulated
- the accumulated charge is then desulfurized by blowing air into the molten copper until its S-in-copper is lowered to ~0.002%
- the copper is deoxidized by blowing gas or liquid hydrocarbons into the molten copper bath.

Hydrocarbon blowing is terminated when the O-in-molten copper concentration has been lowered to ~0.15% O (as detected with disposable solid electrolyte probes [Electro-nite, 2002] or by examination of copper test blocks). Copper with this oxygen content ‘sets flat’ when it is cast into anodes.

Table 15.2. Details of seven rotary anode furnaces and five mold-on-wheel anode

Smelter	Caraiba Metais S/A, Dias d'Avila, Brazil	Norddeutsche Affinerie, Hamburg	PT Smelting Co. Gresik, Indonesia
Anode production tonnes/year			257 000
Number of anode furnaces			
total	2	2	3
active	2	2	3
Furnace dimensions, m			
diameter × length	4.19 × 9.92	4.25 × 10	3.12 × 12.5 (ID)
Tuyeres			
diameter, cm	4.8	0.8, 1, 1.2	
number per furnace	2	2	2
used during oxidation	2	2	2
used during reduction	2	2	2
reductant	natural gas	natural gas	diesel oil
Production details			
tap-to-tap duration, hours	9.91	9	11
anode production tonnes/cycle	150-200	270	400
oxidation duration, hours	1.28	0.5	5
air flowrate, Nm ³ /minute	18.33	6-7	50 air; 5 oxygen
reduction duration, hours	1.71	3	2
reducing gas flowrate Nm ³ /minute per tuyere	14 total	10	15 liters per minute
scrap addition, tonnes/cycle	0	0-10	0-30
Anode casting			
method	mold on wheel	mold on wheel	Contilanol
number of wheels, m		1	
diameter of wheels, m		12.8	
number of molds per wheel		24	
casting rate, tonnes/hour	60	75-80	100
Automatic weighing	yes	yes	yes
anode mass, kg	360	400	370
variation, kg	±4	±4	±7

casting plants, 2001. Hazelett continuous anode casting is described in Table 15.3.

Onahama Smelting & Refining, Japan	Sumitomo Mining Co. Toyo, Japan	Mexicana de Cobre, Nacozari, Mexico	Palabora Mining Company, South Africa
160 000			
3	2	3	3
3 or 2	2	3	3
two 3.96 × 9.15 one 4.40 × 10.0	4.2 × 14.2	4.6 × 10.7	3.96 × 9.14
5.5	4.4	5	1.9
2	2	2	4
2	2	2	1
2	2	2	1
recovered oil	LP gas	LP gas	80% ethanol/20% propanol mixture
10	11	9	24
300	400-500	380	240
1	~0.5	0.6	1 to 3
40	8	15	2.5 to 5
2	2	2.5	2.5 to 3.5
40	8	10.5 kg/min (total)	20 liters per minute for 90 minutes; 17 liters per minute for next 30 minutes; then 14 liters per minute
0-8	0-5	40-50	0
mold on wheel and Hazelett	mold on wheel	mold on wheel	mold on wheel
1	2	2	1
13	10	14.44/11.5	
24	18	28/20	22
50	100	55	35
yes	yes	yes	no
365	384	342	310
±5	±3	±2	±20

15.1.2 Hearth furnace refining

Although the rotary furnace dominates copper fire refining in primary smelters, secondary (scrap) smelters tend to use hearth-refining furnaces – they are better for melting solid scrap. Sulfur is removed by reaction of the scrap with an oxidizing flame above the bath and by injecting air through a manually moved steel pipe. Deoxidation is done by floating wooden poles on the molten copper. This reduction technique is slow and costly. It is an important reason why hearth furnace refining is used infrequently.

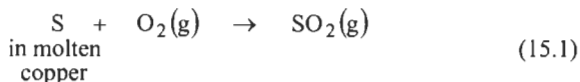
15.2 Chemistry of Fire Refining

Two chemical systems are involved in fire refining:

- (a) the Cu-O-S system (sulfur removal)
- (b) the Cu-C-H-O system (oxygen removal).

15.2.1 Sulfur removal: the Cu-O-S system

The main reaction for removing sulfur with air is:



while oxygen dissolves in the copper by the reaction:



The equilibrium relationship between gaseous oxygen entering the bath and S in the bath is, from Eqn. (15.1):

$$K = \frac{p\text{SO}_2}{[\text{mass}\% \text{S}] \times p\text{O}_2} \quad (15.3)$$

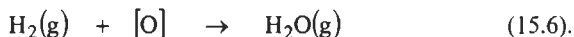
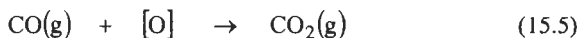
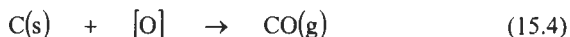
where K is about 10^6 at 1200°C (Engh, 1992).

The large value of this equilibrium constant indicates that even at the end of desulfurization (mass% S ~0.002; $p\text{O}_2$ ~0.21 atmospheres), SO_2 formation is strongly favored (i.e. $p\text{SO}_2 > 1$ atmosphere) and S is still being eliminated. Also, oxygen is still dissolving.

15.2.2 Oxygen removal: the Cu-C-H-O system

The oxygen concentration in the newly desulfurized molten copper is ~0.6 mass % O. Most of this dissolved O would precipitate as solid Cu_2O inclusions during casting (Brandes and Brook, 1998) – so it must be removed to a low level.

Copper oxide precipitation is minimized by removing most of the oxygen from the molten copper with gas or liquid hydrocarbons. Oxygen removal reactions are:



15.3 Choice of Hydrocarbon for Deoxidation

The universal choice for removing S from copper is air. Many different hydrocarbons are used for O removal, but natural gas, liquid petroleum gas and oil are favored, Table 15.2.

Gas and liquid hydrocarbons are injected into the copper through the same tuyeres used for air injection. Natural gas is blown in directly – liquid petroleum gas after vaporization. Oil is atomized and blown in with steam.

Wood poles (~0.3 m diameter and about the length of the refining furnace) are used in hearth refining furnaces. Wood 'poling' is clumsy, but it provides hydrocarbons and agitation along the entire length of the refining furnace.

Oxygen removal typically requires 5 to 7 kg of gas or liquid hydrocarbons per tonne of copper (Pannell, 1987). This is about twice the stoichiometric requirement, assuming that the products of the reaction are CO and H_2O . About 20 kg of wood poles are required for the same purpose.

15.4 Casting Anodes

The final product of fire refining is molten copper, ~0.002% S, 0.15% O, 1150–1200°C, ready for casting as anodes. Most copper anodes are cast in open anode-shaped impressions on the top of flat copper molds. Twenty to thirty such molds are placed on a large horizontally rotating wheel, Fig. 15.2, Table 15.2. The wheel is rotated to bring a mold under the copper stream from the anode furnace where it rests while the anode is being poured. When the anode

impression is full, the wheel is rotated to bring a new mold into casting position and so on. Spillage of copper between the molds during rotation is avoided by placing one or two tiltable ladles between the refining furnace and casting wheel. Most casting wheels operate automatically, but with human supervision.



Fig. 15.2. Segment of anode casting wheel. The mass of copper in the ladles is sensed by load cells. The sensors automatically control the mass of each copper pour without interrupting copper flow from the anode furnace. The anode molds are copper, usually cast at the smelter. Photograph courtesy of Miguel Palacios, Atlantic Copper, Huelva, Spain.

The newly poured anodes are cooled by spraying water on the tops and bottoms of the molds while the wheel rotates. They are stripped from their molds (usually by an automatic raising pin and lifting machine) after a half rotation. The empty molds are then sprayed with a barite-water wash to prevent sticking of the next anode.

Casting rates are 50 to 100 tonnes of anodes per hour. The limitation is the rate at which heat can be extracted from the solidifying/cooling anodes. The flow of copper from the refining furnace is adjusted to match the casting rate by rotating the taphole up or down (rotary furnace) or by blocking or opening a tapping-notch (hearth furnace). In a few smelters, anodes are cast in pairs to speed up the casting rate (Isaksson and Lehner, 2000).

Inco Limited has used molds with top and bottom anode impressions (Blechta and Roberti, 1991). The molds are flipped whenever the top impression warps due to thermal stress. This system reportedly doubles mold life (tonnes of copper cast per mold) and cuts costs. Riccardi and Park (1999) report that diffusing aluminum into the mold surface also extends mold life.

15.4.1 Anode uniformity

The most important aspect of anode casting, besides flat surfaces, is uniformity of thickness. This uniformity ensures that all the anodes in an electrorefining cell reach the end of their useful life at the same time. Automatic control of the mass of each pour of copper (i.e. the mass and thickness of each anode) is now used in most plants (Davenport *et al.*, 1999). The usual practice is to sense the mass of metal poured from a tiltable ladle, using load cells in the ladle supports as sensors.

Anode mass is normally 350–400 kg (Davenport *et al.*, 1999). Anode-to-anode mass variation in a smelter or refinery is ± 2 to 5 kg with automatic weight control, Table 15.2 and Geenen and Ramharter (1999).

Recent anode designs have incorporated (i) knife-edged lugs which make the anode hang vertically in the electrolytic cell and (ii) thin tops where the anode is not submerged (i.e. where it isn't dissolved during refining). The latter feature decreases the amount of un-dissolved 'anode scrap' which must be recycled at the end of an anode's life.

15.4.2 Anode preparation

Anode flatness and verticality are critical in obtaining good electrorefinery performance. Improvements in these two aspects at the Magma smelter/refinery were found, for example, to give improved cathode purity and a 3% increase in current efficiency.

For this reason, many refineries treat their anodes in an automated anode preparation machine to improve flatness and verticality (Garvey *et al.*, 1999; O'Rourke, 1999; Rada *et al.*, 1999, Virtanen, *et al.*, 1999). The machine:

- (a) weighs the anodes and directs underweight and overweight anodes to remelting
- (b) straightens the lugs and machines a knife edge on each lug
- (c) presses the anodes flat
- (d) loads the anodes in a spaced rack for dropping into an electrorefining cell.

Inclusion of these anode preparation steps has resulted in increased refining rates, improved cathode purities and decreased electrorefining energy consumption.

15.5 Continuous Anode Casting (Regan and Schwarze, 1999)

Continuous casting of anodes in a Hazelett twin-belt type caster (Fig. 15.3a) is being used by six smelters/refineries. The advantages of the Hazelett system over mold-on-wheel casting are uniformity of anode product and a high degree of mechanization/automation.

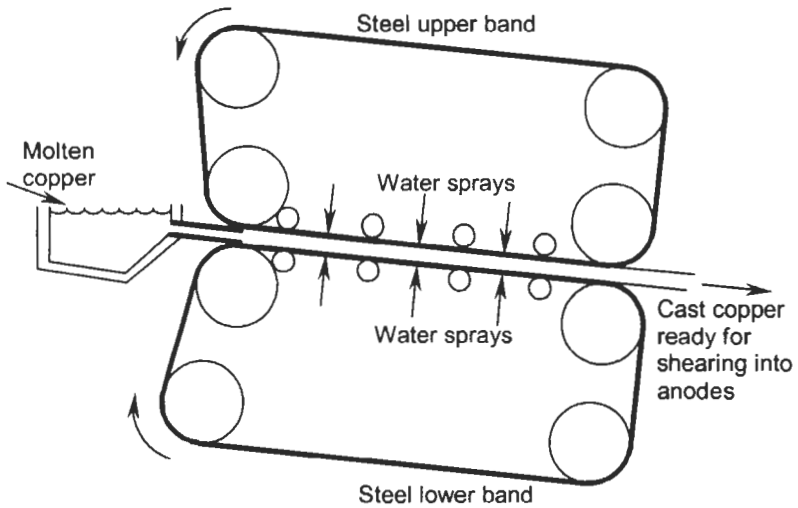
In Hazelett casting, the copper is poured at a controlled rate (30-100 tonnes per hour) from a ladle into the gap between two moving water-cooled low-carbon steel belts. The product is an anode-thickness continuous strip of copper (Fig. 15.3a, Table 15.3) moving at 4 to 6 m/minute.

The thickness of the strip is controlled by adjusting the gap between the belts. The width of the strip is determined by adjusting the distance between bronze or stainless steel edge blocks which move at the same speed as the steel belts, Fig. 15.3b.

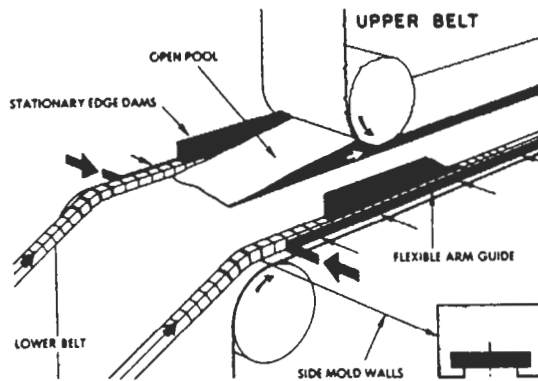
Recent Hazelett Contilnod casting machines have periodic machined edge blocks into which copper flows to form anode support lugs, Fig. 15.4. The lug shape is machined half-anode thickness in the top of these specialized blocks. The blocks are machined at a 5-degree angle to give a knife-edge support lug.

Identical positioning of the lug blocks on opposite sides of the strip is obtained by heating or cooling the dam blocks between the specialized 'lug blocks'.

The caster produces a copper strip with regularly spaced anode lugs. Individual anodes are produced from this strip by a 'traveling' hydraulic shear, Fig. 15.4. Details of the operation are given by Regan and Schwarze (1999) and Hazelett, (2002).



(a) Casting arrangement.



(b) Details of dam blocks

Fig. 15.3. Hazelett twin-belt casting machine for continuously casting copper anode strip (Regan and Schwarze, 1999). Reprinted by permission of TMS, Warrendale, PA. The anode strip is 2 to 4.5 cm thick and about 1 m wide. The most recent method of cutting the strip into anodes is shown in Fig. 15.4.

Table 15.3. Details of Hazlett continuous anode casting plants at Gresik, Indonesia and Onahama, Japan, 2001. The Gresik support lugs are ~half thickness.

Smelter	PT Smelting Co. Gresik Indonesia	Onahama Smelting & Refining Japan
Startup data	1998	1972
Anode production tonnes/year	257 000	160 000
Casting machine size, m		
length between molten copper entrance and solid copper exit	3.81	2.3
band width (total)	1.65	1.24
width of cast copper strip (between edge dams)	0.93	1.07
length of lug	0.18	0.175
thickness of cast strip	0.045	0.0158
thickness of lug	0.027	0.0158
Band details		
material	ASTM A607 Grade 45 steel	low carbon cold rolled steel
life, tonnes of cast copper lubrication	1200 silicone oil	600 silicone fluid
Edge block details		
material	hardened bronze	high chromium stainless steel
life, years	~3 years (~0.5 years for anode lug blocks)	~5 years
Method of controlling copper level at caster entrance	electromagnetic level indicator	manual
Temperatures, °C		
molten copper	1120-1150	1120
cast anode (leaving caster)	880-930	800
Casting details		
casting rate, tonnes/hour	100	50
caster use, hours/day	9	6
Method of cutting anodes from strip	hydraulic shear	blanking press
Anode details		
mass, kg	370	143
acceptable deviation	±7 kg	±3 kg
% acceptable anodes	97	97

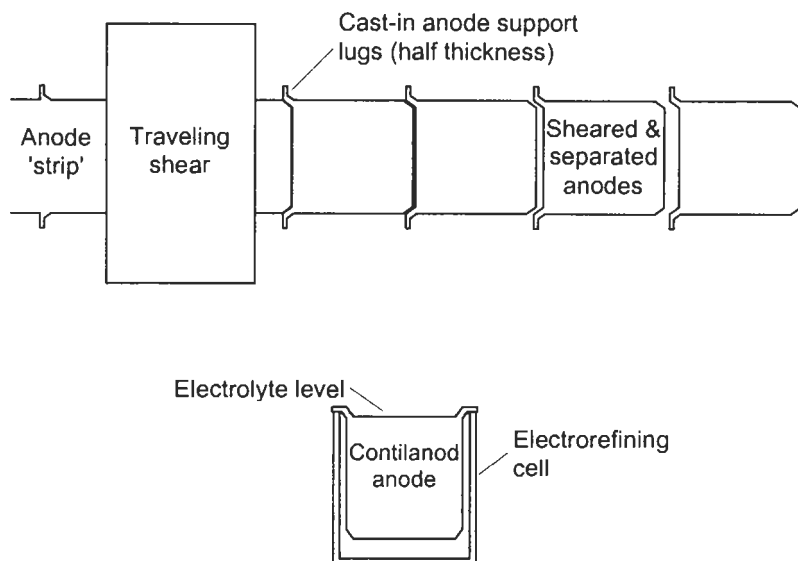


Fig. 15.4. Sketch of system for shearing anodes from Hazelett-cast copper strip (Regan and Schwarze, 1999, Hazelett, 2002). Suspension of an anode in an electrolytic cell is also shown.

15.5.1 Contilanol vs mold-on-wheel anode production

The casting part of continuous anode casting was successful from its beginning in 1966. The problem which slowed adoption of the process was cutting individual anodes from full anode thickness strip. This has been solved by the above-mentioned traveling shear.

The main advantage of Contilanol anodes is their uniformity of size, shape and surface. The resulting anodes do not require an anode preparation machine (Section 15.4.2) as do conventional mold-on-wheel anodes.

The operating and maintenance costs of Contilanol casting are higher than those of mold-on-wheel casting. However, inclusion of anode preparation machine costs with mold-on-wheel casting costs probably eliminates most of this difference.

It would seem that adoption of continuous anode casting will bring anode making up to the same high level of consistency as other aspects of copper refining.

15.6 New Anodes from Rejects and Anode Scrap

Smelters and refineries reject 2 or 3% of their new anodes because of physical defects or incorrect masses. They also produce 15 to 20% un-dissolved anode scrap after a completed electrorefining cycle (Davenport, *et al.*, 1999). These two materials are re-melted and cast into fresh anodes for feeding back to the electrorefinery. The post-refining scrap is thoroughly washed before re-melting.

The reject and scrap anodes are often melted in a smelter's Peirce-Smith converters. There is, however, an increasing tendency to melt them in Asarco-type shaft furnaces (Chapter 22) in the electrorefinery itself. The Asarco shaft furnace is fast and energy efficient for this purpose. Sulfur and oxygen concentrations in the product copper are kept at normal anode levels by using low sulfur fuel and by adjusting the O_2 /fuel ratio in the Asarco furnace burners.

15.7 Removal of Impurities During Fire Refining

Chapters 4, 9 10 and 12 indicate that significant fractions of the impurities entering a smelter end up in the smelter's metallic copper. The fire refining procedures described above do not remove these impurities to a significant extent. The impurities report mostly to the anodes.

As long as impurity levels in the anodes are not excessive, electrorefining and electrolyte purification keep the impurities in the cathode copper product at low levels. With excessively impure 'blister' copper, however, it can be advantageous to eliminate a portion of the impurities during fire refining (Jiao *et al.*, 1991; Newman *et al.*, 1992). The process entails adding appropriate fluxes during the oxidation stage of fire refining. The flux may be blown into the copper through the refining furnace tuyeres or it may be added prior to charging the copper into the furnace.

15.7.1 Antimony and arsenic removal

The Ventanas smelter (Chile) removes As and Sb from its molten blister copper by blowing basic flux (56% $CaCO_3$, 11% CaO , 33% Na_2CO_3) into the copper during the oxidation stage. About 7 kg of flux are blown in per tonne of copper.

About 90% of the As and 70% of the Sb in the original copper are removed to slag (Bassa *et al.*, 1987).

The Glogow I and Glogow II smelters use a similar technique (Czerniecki *et al.*, 1998).

15.7.2 Lead removal (Newman *et al.*, 1991)

The Timmins smelter removes lead from its molten Mitsubishi Process copper

by charging silica flux and solid electric furnace slag to its rotary anode furnace prior to adding the molten copper. The copper is then desulfurized with air and a Pb-bearing silicate slag is skimmed off. The desulfurized copper is conventionally deoxidized by hydrocarbon injection.

Lead in copper is lowered from about 0.6% to 0.15% with ~1 kg of silica flux and 1 kg of electric furnace slag per tonne of copper. The resulting slag is returned to the Mitsubishi smelting furnace for Cu recovery.

15.8 Summary

This chapter has shown that the final step in pyrometallurgical processing is casting of thin flat anodes for electrorefining. The anodes must be strong and smooth-surfaced for efficient electrorefining – bubbles or 'blisters' of SO₂ cannot be tolerated.

Blister formation is prevented by removing sulfur and oxygen from the smelter's molten copper by air oxidation then hydrocarbon reduction. The air and hydrocarbons are usually injected into the molten copper via one or two submerged tuyeres in a rotary 'anode' furnace.

Anodes are usually cast in open molds on a large rotating wheel. Uniformity of anode mass is critical for efficient electrorefining so most smelters automatically weigh the amount of copper poured into each anode mold.

The cast anodes are often straightened and flattened in automated anode preparation machines. Their lugs may also be machined to a knife-edge. Straight, flat, vertically hung anodes have been found to give pure cathodes and high current efficiencies in the electrorefinery.

Continuous casting of anodes in Hazelett twin belt casting machines has been adopted by six smelter/refineries. It makes anodes of uniform size, shape and surface quality, so has no need for an anode preparation machine.

Suggested Reading

Dutrizac, J.E., Ji, J. and Ramachandran, V. (1999) *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, TMS, Warrendale, PA.

Virtanen, H., Marttila, T. and Pariani, R. (1999) Outokumpu moves forward towards full control and automation of all aspects of copper refining. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 207-224.

References

- Bassa, R., del Campo, A. and Barria, C. (1987) Copper pyrorefining using flux injection through tuyeres in a rotary anode furnace. In *Copper 1987, Vol. IV, Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C. and Luraschi, A., AlfaBeta Impresores, Lira 140-Santiago, Chile, 149 166.
- Blechta, V.K. and Roberti, R.A. (1991) An update on Inco's use of the double cavity mold technology for warpage control. In *Copper 91-Cobre 91 Proceedings of the Second International Conference, Vol. III Hydrometallurgy and Electrometallurgy of Copper*, ed. Cooper, W.C., Kemp, D.J., Lagos, G.E. and Tan, K.G., Pergamon Press, New York, NY, 609 613
- Brandes, E.A. and Brook, G.B. (1998) *Smithells Metals Reference Book*, 7th edition, Butterworth-Heinemann, Oxford, 1215.
- Czernecki, J., Smieszek, Z., Gizicki, S., Dobrzanski, J. and Warmuz, M. (1998) Problems with elimination of the main impurities in the KGHM Polska Miedz S.A. copper concentrates from the copper production cycle (shaft furnace process, direct blister smelting in a flash furnace). In *Sulfide Smelting '98: Current and Future Practices*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 332.
- Davenport, W.G., Jenkins, J., Kennedy, B. and Robinson, T. (1999) Electrolytic copper refining – 1999 world tankhouse operating data. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 3 76.
- Electro-nite (2002) www.electro-nite.com (Products, Copper)
- Engh, T.A. (1992) *Principles of Metal Refining*. Oxford University Press, 52 and 422 www.oup.co.uk
- Garvey, J., Ledeboer, B.J. and Lommen, J.M. (1999) Design, start-up and operation of the Cyprus Miami copper refinery. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 107 126.
- Geenen, C. and Ramharter, J. (1999) Design and operating characteristics of the new Olen tank house. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 95 106.
- Hazelett (2002) The Contilnod process. www.hazelett.com (Casting machines, Copper anode casting machines, The Contilnod process.)
- Isaksson, O. and Lehner, T. (2000) The Ronnskar smelter project: production, expansion and start-up. JOM, **52**(8), 29.

Jiao, Q., Carissimi, E. and Poggi, D. (1991) Removal of antimony from copper by soda ash injection during anode refining. In *Copper 91-Cobre 91 Proceedings of the Second International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C., Luraschi, A. and Newman, C.J., Pergamon Press, New York, NY, 341 357.

Lehner, T., Ishikawa, O., Smith, T., Floyd, J., Mackey, P. and Landolt, C. (1994) The 1993 survey of worldwide copper and nickel converter practices. In *International Symposium on Converting, Fire-Refining and Casting*, TMS, Warrendale, PA.

McKerrow, G.C. and Pannell, D.G. (1972) Gaseous deoxidation of anode copper at the Noranda smelter. *Can. Metal. Quart.*, **11**(4), 629 633.

Newman, C.J., MacFarlane, G., Molnar, K. and Storey, A.G. (1991) The Kidd Creek copper smelter – an update on plant performance. In *Copper 91-Cobre 91 Proceedings of the Second International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C., Luraschi, A. and Newman, C.J., Pergamon Press, New York, NY, 65 80.

Newman, C.J., Storey, A.G., MacFarlane, G. and Molnar, K. (1992) The Kidd Creek copper smelter – an update on plant performance. *CIM Bulletin*, **85**(961), 122 129.

O'Rourke, B. (1999) Tankhouse expansion and modernization of Copper Refineries Ltd., Townsville, Australia. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 195 205.

Pannell, D.G. (1987) A survey of world copper smelters. In *World Survey of Nonferrous Smelters*, ed. Taylor, J.C. and Traulsen, H.R., TMS, Warrendale, PA, 3 118.

Rada, M. E. R., Garcia, J. M. and Ramirez, I. (1999) La Caridad, the newest copper refinery in the world. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 77 93.

Regan, P. and Schwarze, M. (1999) Update on the Contilnod process – continuous cast and sheared anodes. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 367 378.

Reygadas, P.A., Otero, A.F. and Luraschi, A.A. (1987) Modelling and automatic control strategies for blister copper fire refining. In *Copper 1987, Vol. IV, Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C. and Luraschi, A., Alfabeta Impresores, Lira 140-Santiago, Chile, 625 659.

Riccardi, J. and Park, A. (1999) Aluminum diffusion protection for copper anode molds. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 379 382.

Virtanen, H., Marttila, T. and Pariani, R. (1999) Outokumpu moves forward towards full control and automation of all aspects of copper refining. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 207 224.



Fig. 16.0 Copper-plated stainless steel blanks being lifted from a polymer concrete cell. The cathode copper will be stripped from the stainless steel blanks and sent to market. The anodes in the cell are now 'scrap'. They will be washed, melted and cast as new anodes. The cells in the background are covered with canvas to minimize heat loss. Photograph courtesy Miguel Palacios, Atlantic Copper, Huelva, Spain.

CHAPTER 16

Electrolytic Refining

(Written with Tim Robinson, CTI Ancor, Phoenix, AZ)

Almost all copper is treated electrolytically during its production from ore. It is electrorefined from impure copper anodes or electrowon from leach/solvent extraction solutions. Considerable copper scrap is also electrorefined.

This chapter describes electrorefining. Electrowinning is discussed in Chapter 19.

Electrorefining entails:

- (a) electrochemically dissolving copper from impure copper anodes into $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte
- (b) selectively electroplating pure copper from this electrolyte *without the anode impurities*.

It serves two purposes:

- (a) it produces copper essentially free of harmful impurities
- (b) it separates valuable impurities (e.g. gold and silver) from copper for recovery as byproducts.

Electrorefined copper, melted and cast, contains less than 20 parts per million impurities – plus oxygen which is controlled at 0.018 to 0.025%.

Table 16.1 presents industrial ranges of copper anode and cathode compositions. Figures 1.7, 16.1 and 16.2 show a flow sheet and industrial refining equipment.

16.1 Principles

Application of an electrical potential between a copper anode and a metal cathode in $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte causes the following.

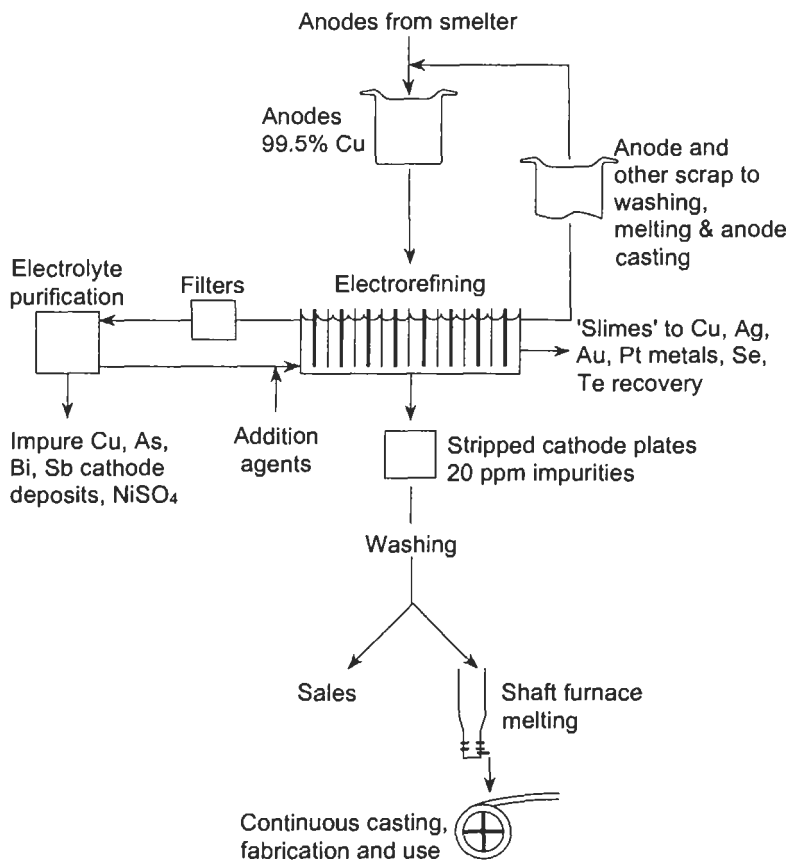


Fig. 16.1. Copper electrorefinery flow sheet. The process produces pure copper cathode 'plates' from impure copper anodes. $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte is used. The electrolyte purification circuit treats a small fraction of the electrolyte, Section 16.5.1. The remainder is re-circulated directly to refining (after reagent additions and heating).

- (a) Copper is electrochemically dissolved from the anode into the electrolyte – producing copper cations plus electrons:



- (b) The electrons produced by Reaction (16.1) are conducted towards the cathode through the external circuit and power supply.

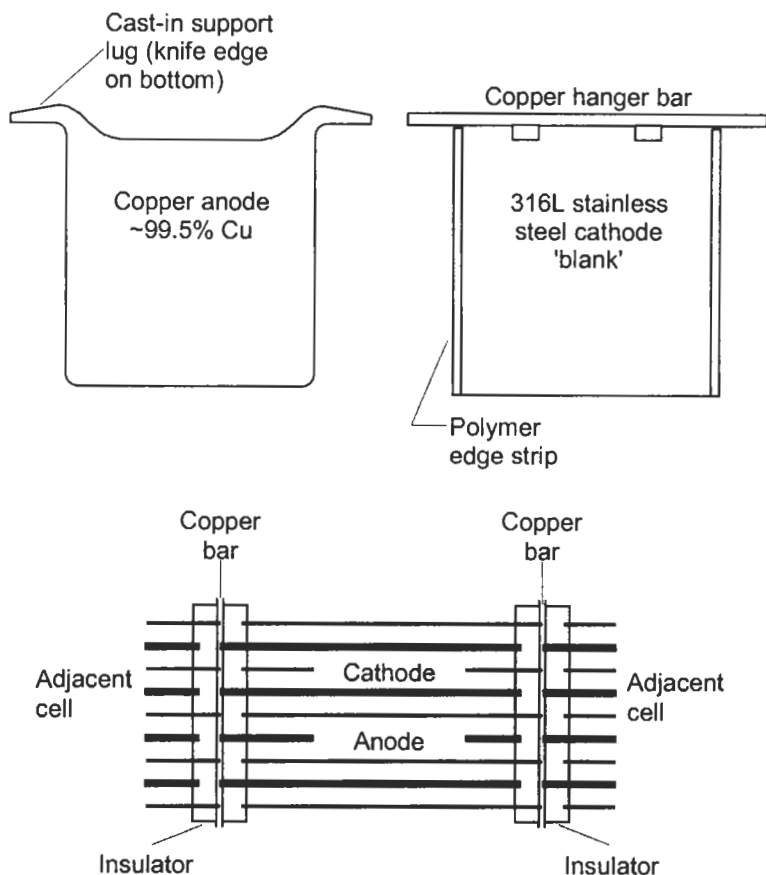


Fig. 16.2a. **Top:** copper anode and stainless steel cathode. The cathode is about a meter square. The anode is slightly smaller. **Bottom:** sketch of electrolytic circuitry. Current flow between anodes and cathodes is through the electrolyte.

- (c) The Cu^{++} cations in the electrolyte migrate to the cathode by convection and diffusion.
- (d) The electrons and Cu^{++} ions recombine at the cathode surface to form copper metal (without the anode impurities), i.e.:



Overall copper electrorefining is the sum of Reactions (16.1) and (16.2):



which has a theoretical potential of 0 volt.



Fig. 16.2b. Copper anodes and stainless steel cathodes in polymer concrete electrorefining cells. (Photograph courtesy Miguel Palacios, Atlantic Copper, Huelva, Spain)



Fig. 16.2c. Anode-cathode connections in industrial electrorefinery (photograph courtesy R. Douglas Stern, Phelps Dodge Mining Company). The cathode in the left foreground rests on a copper conductor bar, the anode behind it on an insulator. The cathode in the right foreground rests on the insulator, the anode behind it on the copper conductor bar. Electric current passes:

- (a) **left hand cell:** from the anode in the background through the electrolyte to the cathode in the foreground
- (b) **between cells:** from the left cell cathode through the conductor bar to the right cell anode
- (c) **right hand cell:** from the right cell anode through the electrolyte to the cathode in front of it.

In practice, resistance to current flow must be overcome by applying a potential between the anode and cathode. Small overvoltages must also be applied to plate copper on the cathode (~ 0.05 volt) and dissolve copper from the anode (~ 0.1 volt). Applied industrial anode-cathode potentials are ~ 0.3 volt (Table 16.4 and Davenport *et al.*, 1999).

16.2 Behavior of Anode Impurities During Electrorefining

The principal impurities in copper anodes are Ag, As, Au, Bi, Co, Fe, Ni, Pb, S, Sb, Se and Te, Table 16.1. They must be prevented from entering the cathode copper. Their behavior during electrorefining is summarized in Table 16.2 and the following paragraphs.

Au and platinum group metals

Gold and platinum group metals do not dissolve in sulfate electrolyte. They form solid 'slimes' which adhere to the anode surface or fall to the bottom of the electrolytic cell. These slimes are collected periodically and sent to a Cu and byproduct metals recovery plant, Appendix C.

Se and Te

Selenium and tellurium are present in anodes mainly as compounds with copper and silver. They also enter the slimes in these bound forms, e.g. Cu_2Se , Ag_2Se , Ag_2Te (Campin, 2000).

Pb and Sn

Lead forms solid PbSO_4 . Tin forms SnO_2 . Both join the slimes.

As, Bi, Co, Fe, Ni, S and Sb

These elements dissolve extensively in the electrolyte. Excessive buildup in the electrolyte and contamination of the cathodes is prevented by continuously removing them from an electrolyte bleed stream, Fig. 16.1.

16.2.1 Summary of impurity behavior

The above discussion indicates that Au, Pt metals, Se, Te, Pb and Sn do not dissolve in $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte – so they can't plate at the cathode. Their presence in cathode copper is due to accidental entrapment of slime particles in the depositing copper.

The discussion also indicates that As, Bi, Co, Fe, Ni, S and Sb dissolve in the electrolyte – so they could plate with Cu on the cathode. Fortunately, Cu plates at a lower applied potential than these elements (Table 16.3) – so they remain in the electrolyte while Cu is plating. Their presence in cathode copper is due to accidental entrapment of electrolyte.

Their concentration in cathode copper is minimized by:

- (a) electrodepositing smooth, dense copper 'plates' on the cathode
- (b) thoroughly washing the cathode product
- (c) controlling impurity levels in the electrolyte by bleeding electrolyte from the refinery and removing its impurities.

16.2.2 Silver

The above discussion indicates that the main cathode contamination mechanism is entrapment of slimes and electrolyte in the cathode deposit. An exception to this is *silver*. It:

- (a) dissolves to a small extent in the electrolyte
- (b) electroplates at a smaller applied potential than copper, Table 16.3.

Cathode copper typically contains 8 to 10 parts per million silver (Barrios *et al.*, 1999, Davenport *et al.*, 1999), most of it electroplated. Fortunately, silver is a rather benign impurity in copper.

Table 16.1. Industrial range of copper anode and cathode compositions (Davenport *et al.*, 1999).

Element	Anodes (range of %)	Cathodes (range of %)
Cu	98.4 – 99.8	99.99
O	0.1 – 0.25	not determined
Ag	0.01 – 0.60	0.0004 – 0.0016
S	0.001 – 0.008	0.0002 – 0.001
Sb	trace – 0.3	trace – 0.001
Pb	0.001 – 0.35	trace – 0.0005
Ni	0.003 – 0.6	trace – 0.0003
Fe	0.001 – 0.03	trace – 0.0003
As	trace – 0.25	trace – 0.0001
Se	0.001 – 0.12	trace – 0.0001
Te	0.001 – 0.05	trace – 0.0001
Bi	trace – 0.05	trace – 0.0001
Au	trace – 0.02	trace

Table 16.2. Fractions of anode elements entering 'slimes' and electrolyte. As, Bi and Sb are discussed by Larouche, 2001.

Element	% into 'slimes'	% into electrolyte
Cu	<0.2	>99.8
Au	100	0
Ag	>99	<1
Se	98	2
Te	98	2
Pb	98	2
Bi	60% with 0.1% Pb in anode	40
Sb	60% with 0.1% As, Bi, Pb and Sb (each) in anode	40
As	25% with 0.1% As in anode	75
S	1	99
Ni	1	99
Co	1	99
Fe	0	100
Zn	0	100

Table 16.3. Standard electrochemical potentials of elements in copper electrorefining (25°C, unit thermodynamic activity) (Lide, 2001). Plating of elements above Cu in the table (e.g. Ag) requires a smaller applied potential than that required to plate copper. Plating of elements below Cu (e.g. Fe) requires a larger applied potential than copper.

Electrochemical reaction	Standard reduction potential (25°C), volts
$\text{Au}^{3+} + 3\text{e}^{-} \rightarrow \text{Au}^{\circ}$	1.5
$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}^{\circ}$	0.80
$\text{Cu}^{2+} + 2\text{e}^{-} \rightarrow \text{Cu}^{\circ}$	0.34
$\text{BiO}^{+} + 2\text{H}^{+} + 3\text{e}^{-} \rightarrow \text{Bi}^{\circ} + \text{H}_2\text{O}$	0.32
$\text{HAsO}_2 + 3\text{H}^{+} + 3\text{e}^{-} \rightarrow \text{As}^{\circ} + 2\text{H}_2\text{O}$	0.25
$\text{SbO}^{+} + 2\text{H}^{+} + 3\text{e}^{-} \rightarrow \text{Sb}^{\circ} + \text{H}_2\text{O}$	0.21
$2\text{H}^{+} + 2\text{e}^{-} \rightarrow \text{H}_2$	0.0000
(pH = 0; $p_{\text{H}_2} = 1$ atmosphere)	
$\text{Pb}^{2+} + 2\text{e}^{-} \rightarrow \text{Pb}^{\circ}$	-0.13
$\text{Ni}^{2+} + 2\text{e}^{-} \rightarrow \text{Ni}^{\circ}$	-0.26
$\text{Co}^{2+} + 2\text{e}^{-} \rightarrow \text{Co}^{\circ}$	-0.28
$\text{Fe}^{2+} + 2\text{e}^{-} \rightarrow \text{Fe}^{\circ}$	-0.45

16.3 Industrial Electrorefining (Table 16.4)

Industrial electrorefining is done with large ($\sim 1 \text{ m} \times 1 \text{ m}$), thin (0.04–0.05 m) anodes and thin (0.001 to 0.003 m) cathodes interleaved about 0.05 m apart in a cell filled with electrolyte, Figs. 1.7 and 16.2. The anodes in the cell are all at one potential. The cathodes are all at another, lower potential. The anodes and cathodes are spaced evenly along the cell to equalize current among all anodes and cathodes. This ensures that all the anodes dissolve at the same rate and end their life at the same time. Equal anode masses are also important in this regard.

The process is continuous. Purified $\text{CuSO}_4\text{--H}_2\text{SO}_4\text{--H}_2\text{O}$ electrolyte continuously enters one end of each cell (near its bottom). It departs (slightly less pure) by continuously overflowing the other end of the cell into an electrolyte collection system. Anodes continuously dissolve and pure copper continuously plates on the cathodes.

The impure copper anodes are cast in a smelter and in the refinery itself as described in Chapter 15. They are typically 4 to 5 cm thick and weigh 300 to 400 kg. They slowly thin as their copper dissolves into the electrolyte. They are removed from the cell (and replaced with new anodes) before they are in danger of breaking and falling. They are washed then melted and recast as fresh anodes.

16.4 Cathodes

The starting cathodes in new refineries are stainless steel blanks – welded to copper support bars (Robinson *et al.*, 1995, Caid, 2002). Copper is electrodeposited onto these cathodes for 7 to 10 days. The copper-laden cathodes are then removed from the cell and replaced with fresh stainless steel blanks.

The copper-laden cathodes are washed in hot-water sprays and their copper ‘plates’ (50 to 80 kg, each side) are machine-stripped from the stainless steel. They go to market or to melting and casting. The empty stainless steel blanks are carefully washed and returned to refining.

Older refineries use thin copper ‘starter sheet’ cathodes, hung by starter sheet loops on copper support bars (Biswas and Davenport, 1980). Many refineries (especially in Europe and North America) have switched from this older technology to stainless steel blanks (Geenen and Ramharter 1999; Aubut *et al.*, 1999). Japanese refineries are also switching.

16.4.1 Stainless steel blank details

The stainless steel blanks are flat cold- and bright-rolled 316L stainless steel, ~3mm thick (Preimesberger, 2001). Electrodeposited copper attaches quite firmly to this surface so it doesn’t accidentally detach during refining.

The vertical edges of the blanks are covered with long, tight-fitting polymer edge strips. These strips prevent copper from depositing completely around the cathode. They are necessary to permit removal of the electrorefined copper plates from the stainless steel. Chemically stabilized modified polypropylene with heat-setting tape (Scheibler, 2002), chlorinated polyvinyl chloride (PVC) and acetonitrile butadiene styrene (ABS) strips (Marley, 2002) are used. The bottoms of the stainless steel blanks are given a sharp-edged Λ groove. This allows easy detachment of the plated copper from this region.

16.5 Electrolyte

Copper refining electrolytes contain 40 to 50 kg Cu/m³, 170 to 200 kg H₂SO₄/m³, 0.02 to 0.05 kg Cl/m³ and impurities (mainly Ni, As and Fe, Table 16.5). They also contain 1 to 10 parts per million organic leveling and grain refining addition agents. They are steam heated to 60-65°C, cooling several degrees during passage through the cell.

Electrolyte is circulated through each cell at ~0.02 m³/minute. This rate of flow replaces a cell’s electrolyte every few hours. Steady electrolyte circulation is essential to:

Table 16.4. Industrial copper electrorefining data.

Refinery	Caraiba Metais Brazil		Union Miniere Pirdop Bulgaria		Norddeutsche Affinerie	
Startup date	1982		1958		1992	
Cathode Cu, thousand tonnes/yr	220		35 (1998)		350-370	
Electrolytic cells						
number (total)	1150		492		1080	
construction material	1020 concrete 130 resin &PVC		changing to poly- mer concrete		concrete	
lining material	1020 Pb				antimonial Pb	
length × width × depth (inside), m	4.82×1.07×1.28		3 × 1 × 1.2		5.6 × 1.16 × 1.4	
anodes/cathodes per cell	42/43		25/26		57/56	
Anodes						
type	mold on wheel		mold on wheel		mold on wheel	
% Cu	99.94		99.4		98.5-99.6	
length × width × thickness, mm	925 × 890 × 50		930 × 830 × 45		905 × 950 × 53	
mass, kg	350		245		400	
center-line spacing, cm	11.0		10.8		9.5	
life, days	22		21		21	
% scrap after refining	19		21		11-12	
anode slimes kg/tonne anode	3.3		6		5 to 8	
Cathodes						
type	Cu starter sheet		Cu starter sheet		Isa stainless steel	
length × width × thickness mm	980 × 960 × 0.7		880 × 860 × 0.7		965 × 975 × (6-8)	
plating time, days	11		7		7	
mass Cu plated (total), kg	150		65		100-120	
ppm total impurities	25		<25		<20	
ppm Ag	8		7		10	
Electrolyte	Cu	H ₂ SO ₄	Cu	H ₂ SO ₄	Cu	H ₂ SO ₄
kg/m ³	43	185	45	180	42	170
inlet temperature, °C	65		63		63	
outlet temperature, °C	63		59		63	
inlet rate per cell, m ³ /minute	0.026		0.016			
addition agents, grams per tonne of cathode copper						
bone glue	128		60		27	
thiourea	77		45		54	
avitone	25		no			
Cl (as HCl or NaCl)	17		to 0.035 kg/m ³		HCl	
automatic control	yes		no		CollaMat for glue	
electrolyte filtering	partial				no	
Power and energy						
cathode current density, A/m ²	281		257		330-340	
cathode current efficiency, %	95		95		95-97	
cell voltage, V	0.35		0.21-0.35		0.33	
cell current, thousand amps	22.25		9.5		35-36	
kWh/tonne of Cu shipped (plating only)	307		388		300-320	

Davenport *et al.*, 1999 give additional information.

Gresik Indonesia	Sumitomo Toyo, Japan	Palabora Mining South Africa	Kennecott Utah Cu Magna Utah
1999		1968	1995
220	123	90	280
654	488	960	1400
polymer concrete	precast & polymer concrete	steel reinforced concrete	polymer concrete
none	FRP, PVC	6% Sb lead	none
6.3 × 1.2 × 1.4	5.6 × 1.25 × (1.4, 1.6)	3.8 × 1.07 × 1.14	4.81 × 1.19 × 1.52
59/58	51/50	32/33	47/46
Contilanolod	mold on wheel	mold on wheel	mold on wheel
99.3-99.7	99.4	99.5	99.1
974 × 934 × 45	1015 × 1015 × 39	922 × 920 × 43	1038 × 938 × 39
370	384	318	330
10.35	10.5	11.2	9.8
21	20	20	20
13.7	13.8	17	17
1 to 3	4	1.19	9.7
Isa stainless steel	Cu starter sheet	Cu starter sheet	Kidd stainless steel
1000 × 1000 × (6-12)	1050 × 1070 × 0.7	940 × 920 × 0.6	990 × 990 × 3
7 & 14	10	10	10
100 & 200	169	127	135
<17	<20	<20	<20
7-10	10	5-8	10
Cu H ₂ SO ₄	Cu H ₂ SO ₄	Cu H ₂ SO ₄	Cu H ₂ SO ₄
52 173	49 195	43-46 201-208	45 170
	61	71	65
63	62	65	63
0.035	0.025	0.018	0.020
52-53	100	76	80
72-76	70	41	100
0	20	25-30	0
40 (HCl)	30 (35% HCl)	21	NaCl to 40 ppm Cl
no	no	no	CollaMat for gluc
yes	no	yes, Scheibler	yes, 15% of circulation
295	267	277	282
97	98	91-95	95
0.3-0.4	0.31	0.29	0.28
34.2	30	16	25.5
285	302	390	320

- (a) bring warm, purified electrolyte into the cell
- (b) ensure uniform Cu^{++} and leveling/grain-refining agent concentrations across all cathode surfaces
- (c) remove dissolving impurities from the cell.

Table 16.5. Compositions of copper refining electrolytes (Davenport *et al.*, 1999). Impurity levels can be removed to lower levels than in this table, but at extra cost. Each refinery chooses its impurity levels to give high-purity, marketable cathode copper at minimum cost.

Component	Concentration, kg/m^3
Cu	40-50
H_2SO_4	150-200
Cl	0.02-0.05
protein colloids (gluc)	0.0001-0.001
thiourea	0.0001-0.0005
	Upper limits
Ni	25
As	20
Fe	2
Sb	0.7
Bi	0.6

16.5.1 Removal of impurities from the electrolyte

Soluble anode impurities dissolve continuously into the electrolyte. They are prevented from building by continuously removing them from a bleed stream. As, Bi, Co, Fe, Ni and Sb are the main impurities removed this way. About 0.1 to 0.2 m^3 of electrolyte is bled and purified per tonne of product copper.

Also, 1 or 2% more Cu dissolves from Cu_2O in the anode than plates on the cathodes. This extra Cu is also removed from the electrolyte bleed stream.

The impurities and Cu are removed in three main sequential steps (Bravo, 1995; Rada *et al.*, 1999):

- (a) electrowinning copper using Pb-Sn-Ca anodes and stainless steel or copper starter sheets, Chapter 19
- (b) electrowinning As, Bi and Sb from Cu-depleted electrolyte into an impure Cu-As-Bi-Sb cathode deposit
- (c) evaporation of water from the Cu-depleted electrolyte and precipitation of Ni sulfate crystals from the concentrated solution.

Step (a) may also be done by evaporation/crystallization of CuSO_4 (Bravo, 1995).

The remaining concentrated acid ($\sim 1000 \text{ kg H}_2\text{SO}_4/\text{m}^3$) is returned to electrolyte storage to maintain the refinery's acid balance. A small portion is neutralized or sold to prevent a gradual buildup of Ca, K, Mg and Na ions in the refinery.

As, Bi, Co and Sb may also be removed by solvent extraction (Rondas *et al.*, 1995), ion exchange (Dreisinger and Scholey, 1995, Roman *et al.*, 1999), chelating resins (Sasaki *et al.*, 1991) and activated carbon (Toyabe *et al.*, 1987).

16.5.2 Addition agents

Deposition of smooth, dense, pure copper is promoted by adding leveling and grain-refining agents to the electrolyte (De Maere and Winand, 1995). Without these, the cathode deposits would be dendritic and soft. They would entrap electrolyte and anode slimes.

The principal *leveling* agents are protein colloid 'bone glues'. All copper refineries use these glues, 0.05 to 0.12 kg per tonne of cathode copper (Davenport *et al.*, 1999). The glues consist of large protein molecules (MW 10 000 to 30 000) which form large cations in the electrolyte. Their leveling efficacy varies so they must be tested thoroughly before being adopted by a refinery.

The principal *grain-refining* agents are thiourea (0.03 to 0.15 kg per tonne of cathode copper) and chloride (0.02 to 0.05 kg/m^3 in electrolyte, added as HCl or NaCl). Avitone, a sulphonated petroleum liquid, is also used with thiourea as a grain refiner.

16.5.3 Leveling and grain-refining mechanisms

The leveling action of glue is caused by electrodeposition of large protein molecules at the tips of protruding, rapidly growing copper grains. This deposition creates an electrically resistant barrier at the tips of the protruding crystals, encouraging sideways crystal growth (Hu *et al.*, 1973; Saban *et al.*, 1992). The net result is encouragement of dense and level growth.

The grain-refining action of chlorine ions and thiourea has not been well explained. They may form Cu-Cl -thiourea cations which electrodeposit on the cathode surface where they form nucleation sites for new copper crystals (Knuutila *et al.*, 1987; Wang and O'Keefe, 1984).

16.5.4 Addition agent control

The addition agents are dissolved in water and added to electrolyte storage tanks

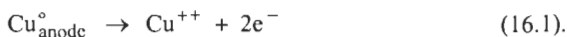
just before the electrolyte is sent to the refining cells. Several refineries automatically control their reagent addition rates based on measured glue and thiourea concentrations in the refining cell exit streams (CollaMat system for glue [Langner and Stantke, 1995; Stantke, 1999]; Reatrol system for thiourea [Ramachandran and Wildman, 1987; Conard *et al.*, 1990]).

The electrolyte in a cell's exit stream should contain enough addition agents (e.g. ~0.1 ppm glue, Stantke, 1999) to still give an excellent copper deposit. This ensures a high purity deposit on all the cell's cathodes.

16.5.5 Electrolyte temperature

Electrolyte is steam-heated to ~65°C (using titanium or teflon coils). This heating is expensive but it beneficially:

- (a) increases $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solubility, preventing it from precipitating on the anode, Section 16.13.1
- (b) lowers electrolyte density and viscosity (Price and Davenport, 1981), reducing slimes movement
- (c) speeds up all electrochemical reactions, e.g.:



Too high a temperature leads to excessive evaporation and energy consumption.

16.6 Cells and Electrical Connections

Industrial refining cells are 3 to 6 m long. They are wide and deep enough (~1.1 m × 1.3 m) to accommodate the refinery's anodes and cathodes with 0.1 to 0.2 m underneath. Each cell contains 30 to 60 anode/cathode pairs connected in parallel.

Modern cells are made of pre-cast polymer concrete (Davenport, *et al.*, 1999). Polymer concrete is a well-controlled mixture of river sand, two liquid self-setting polymer components and a (patented) reaction slowing inhibitor. These components are well mixed, then cast into a cell shaped mold.

Electrolyte penetration into this material is slow so the cells are expected to last 10+ years. Older cells are made of concrete, with a flexible polyvinyl chloride lining. These older cells are gradually being replaced with un-lined polymer concrete cells.

Polymer concrete cells are usually cast with built-in structural supports,

electrolyte distributors, drains etc. These are advantageous for fitting them into the tankhouse infrastructure.

The cells are connected electrically in series to form sections of 20 to 40 cells. Each section can be cut off electrically for inserting and removing anodes/cathodes and for cleaning and maintenance. The number of cells in each section is chosen to maximize the efficiency of these maneuvers.

The electrical connection between cells is made by connecting the cathodes of one cell to the anodes of the adjacent cell and so on. The connection is made by seating the cathodes of one cell and the anodes of the next cell on a common copper distributor bar (Fig. 16.2, Virtanen *et al.*, 1999).

Considerable attention is paid to making good contacts between the anodes, cathodes and distributor bar. Good contacts minimize energy loss and ensure uniform current distribution among all anodes and cathodes.

Electrorefining requires direct voltage and current. These are obtained by converting commercial alternating current to direct current at the refinery. Silicon controlled rectifiers are used.

16.7 Typical Refining Cycle

Production electrorefining begins by inserting a group of anodes and cathodes into the empty cells of a freshly cleaned section of the refinery. They are precisely spaced in a rack and brought to each cell by crane or wheeled carrier (sometimes completely automated, Hashiuchi *et al.*, 1999; Sutliff and Probert, 1995). The cells are then filled with electrolyte and quickly connected to the refinery's power supply. The anodes begin to dissolve and pure copper begins to plate on the cathodes. Electrolyte begins to flow continuously in and out of the cells. Copper-loaded cathodes are removed from the cells after 7-10 days of plating and a new crop of empty stainless steel blanks is inserted.

The copper-loaded cathodes are washed to remove electrolyte and slimes. Their copper 'plates' are then machine-stripped from the stainless steel blanks, sampled and stacked for shipping. Fully-grown copper starter sheet cathodes are handled similarly but are shipped whole (i.e. without stripping).

Two or three copper-plated cathodes are produced from each anode. Their copper typically weighs 100 to 150 kg. This multi-cathode process ensures that cathodes do not grow too close to slime-covered anodes.

The cells are inspected regularly during refining to locate short-circuited anode-cathode pairs. The inspection is done by infrared scanners (which locate 'hot' electrodes, Nakai *et al.*, 1999), gaussmeters and cell millivoltmeters.

Short circuits are caused by non-vertical electrodes, bent cathodes or nodular cathode growths between anodes and cathodes. They waste electrical current and lead to impure copper – due to settling of slimes on nodules and non-vertical cathode surfaces. They are eliminated by straightening the electrodes and removing the nodules.

Each anode is electrorefined until it is 80 to 85% dissolved, typically for 21 days, Table 16.4. Electrolyte is then drained from the cell (through an elevated standpipe), the anodes and cell walls are hosed-down with water and the slimes are drained from the bottom of the cell.

The cell's corroded anodes are removed, washed, then melted and cast into new anodes. The drained electrolyte is sent to filtration and storage. The slimes are sent to a Cu and byproduct metal recovery plant, Appendix C. The refining cycle begins again.

These procedures are carried out sequentially around the refinery (mostly during daylight hours) so that most of the refinery's cells are always in production – only a few are being emptied, cleaned and loaded.

16.8 Refining Objectives

The principal technical objective of the refinery is to produce high-purity cathode copper. Other important objectives are to produce this pure copper rapidly and with a minimum consumption of energy and manpower. The rest of the chapter discusses these goals and how they are attained.

16.9 Maximizing Cathode Copper Purity

The main factors influencing the purity of a refinery's cathode copper are:

- (a) the physical arrangement of the anodes and cathodes in the electrolytic cells
- (b) chemical conditions, particularly electrolyte composition, clarity, leveling and grain-refining agent concentrations, temperature and circulation rate
- (c) electrical conditions, particularly current density.

Thorough washing of cathodes after electrorefining is also essential.

16.10 Optimum Physical Arrangements

The highest purity cathode copper is produced when anodes and cathodes are

straight and vertical and when the depositing copper is smooth and fine-grained. This morphology minimizes entrapment of electrolyte and slime in the growing deposit.

These optimum physical conditions are obtained by:

- (a) avoiding bending of the stainless steel blanks during copper stripping and handling
- (b) casting flat, identical weight anodes
- (c) pressing the anodes flat
- (d) machining the anode support lugs so the anodes hang vertically
- (e) spacing the anodes and cathodes precisely in racks before loading them in the cells (Nakai *et al.*, 1999).

Activities (c) through (e) are often done by a dedicated anode preparation machine, Section 15.4.2.

Slime particles, with their high concentrations of impurities, are kept away from the cathodes by keeping electrolyte flow smooth enough so that slimes are not transported from the anodes and cell bottoms to the cathodes. This is aided by having an adequate height between the bottom of the electrodes and the cell floor. It is also helped by filtering electrolyte (especially that from cell cleaning) before it is recycled to electrorefining.

16.11 Optimum Chemical Arrangements

The *chemical* conditions which lead to highest-purity cathode copper are:

- (a) constant availability of high Cu^{++} electrolyte
- (b) constant availability of appropriate concentrations of leveling and grain-refining agents
- (c) uniform 65°C electrolyte temperature
- (d) absence of slime particles in the electrolyte at the cathode faces
- (e) controlled concentrations of dissolved impurities in the electrolyte.

Constant availability of Cu^{++} ions over the cathode faces is assured by having a high Cu^{++} concentration (40 to 50 kg/m³) in the electrolyte and by circulating electrolyte steadily through the cells.

Adequate concentrations of leveling and grain-refining agents over the cathode faces are assured by adding the agents to the electrolyte just before it is sent to the refining cells. Monitoring their concentrations at the cell exits is also helpful.

16.12 Optimum Electrical Arrangements

The main electrical factor affecting cathode purity is cathode current density, i.e. the rate at which electricity is passed through the cathodes, amperes/m². High current densities give rapid copper plating but also cause growth of protruding copper crystals. This causes entrapment of slimes on the cathodes and lowers cathode purity. Each refinery must balance these competing economic factors.

16.12.1 Upper limit of current density

High current densities give rapid copper plating. Excessive current densities may, however, cause anodes to passivate by producing Cu⁺⁺ ions at the anode surface faster than they can convect away. The net result is a high concentration of Cu⁺⁺ at the anode surface and precipitation of a coherent CuSO₄·5H₂O layer on the anode (Chen and Dutrizac, 1991; Dutrizac 2001).

The CuSO₄·5H₂O layer isolates the copper anode from the electrolyte and blocks further Cu⁺⁺ formation, i.e. it passivates the anode. The problem is exacerbated if the impurities in the anode also tend to form a coherent slimes layer.

Passivation can usually be avoided by operating with current densities below 300 A/m², depending on the impurities in the anode. Warm electrolyte (with its high CuSO₄·5H₂O solubility) also helps. Refineries in cold climates guard against cold regions in their tankhouse.

Passivation may also be avoided by periodically reversing the direction of the refining current (Kitamura *et al.*, 1976; Biswas and Davenport, 1994). However, this decreases refining efficiency. Periodic reversal of current has largely been discontinued, especially in stainless steel cathode refineries.

16.12.2 Maximizing current efficiency

Cathode current efficiencies in modern copper electrorefineries are ~ 93 to 98%. The unused current is wasted as:

anode to cathode short-circuits	3%
stray current to ground	1%
reoxidation of cathode copper by O ₂ and Fe ⁺⁺⁺	1%.

Short-circuiting is caused by cathodes touching anodes. It is avoided by precise, vertical electrode placement and controlled additions of leveling and grain-refining agents to the electrolyte. Its effect is minimized by locating and immediately breaking cathode-anode contacts whenever they occur.

Stray current loss is largely due to current flow to ground via spilled electrolyte.

It is minimized by good housekeeping around the refinery.

Reoxidation of cathode copper is avoided by minimizing oxygen absorption in the electrolyte. This is done by keeping electrolyte flow as smooth and quiet as possible.

16.13 Minimizing Energy Consumption

The electrical energy consumption of an electrolytic refinery, defined as:

$$\frac{\text{total electrical energy consumed in the refinery, kWh}}{\text{total mass of cathode copper produced, tonnes}}$$

is 300 to 400 kWh per tonne of copper. It is minimized by maximizing current efficiency and by maintaining good electrical connections throughout the refinery.

Hydrocarbon fuel is also used in the electrolytic refinery – mainly for heating electrolyte and melting anode scrap.

Electrolyte heating energy is minimized by insulating tanks and pipes and by covering the electrolytic cells with canvas sheets (Hoey *et al.*, 1987, Shibata, *et al.*, 1987).

Anode scrap melting energy is minimized by minimizing scrap production, i.e. by casting thick, equal mass anodes and by equalizing current between all anodes and cathodes. It is also minimized by melting the scrap in an energy efficient Asarco-type shaft furnace, Chapter 22.

16.14 Recent Developments in Copper Electrorefining

The main development in electrolytic refining over the last decade has been adoption of polymer concrete cells. There has also been considerable mechanization in the tankhouse.

The main advantages of polymer concrete cells (Sutliff and Probert, 1995) are:

- (a) they resist corrosion better than conventional concrete cells
- (b) they are thinner than conventional cells. This allows (i) more anodes and cathodes per cell and (ii) wider anodes and cathodes (with more plating area). The overall result is more cathode copper production per cell.
- (c) they eliminate liner maintenance and repair

- (d) they can be cast with built-in structural supports, electrolyte distribution equipment and piping.

They continue to be adopted.

16.15 Summary

This chapter has shown that electrolytic refining is the principal method of mass-producing high-purity copper. The other is electrowinning, Chapter 19. The copper from electrolytic refining, melted and cast, contains less than 20 parts per million impurities – plus oxygen which is controlled at 0.018 to 0.025%.

Electrorefining entails (i) electrochemically dissolving copper from impure copper anodes into $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte, and (ii) electrochemically plating pure copper from the electrolyte onto stainless steel or copper cathodes. The process is continuous.

Insoluble impurities in the anode adhere to the anode or fall to the bottom of the refining cell. They are removed and sent to a Cu and byproduct metal recovery plant. Soluble impurities depart the cell in continuously flowing electrolyte. They are removed from an electrolyte bleed stream.

The critical objective of electrolytic refining is to produce high purity cathode copper. It is attained with:

- (a) precisely spaced, flat, vertical anodes and cathodes
- (b) a constant, gently flowing supply of warm, high Cu^{++} , electrolyte across all cathode faces
- (c) provision of a constant, controlled supply of leveling and grain-refining agents.

Important recent developments have been adoption of pre-cast polymer concrete cells and continued adoption of stainless steel cathodes. These have resulted in purer copper, increased productivity and decreased energy consumption.

Suggested Reading

Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrorefining and Hydrometallurgy of Copper, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada.

Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA.

Hiskey, J.B. (1999) Principles and practical considerations of copper electrorefining and electrowinning. In *Copper Leaching, Solvent Extraction and Electrowinning Technology*, ed. Jergensen, G.V., SME, Littleton, CO, 169 186.

References

Aubut, J.Y., Belanger, C., Duhamel, R., Fiset, Y., Guilbert, M., Leclerc, N. and Pogacnik, O. (1999) Modernization of the CCR refinery. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 159 169.

Barrios, P., Alonso, A. and Meyer, U. (1999) Reduction of silver losses during the refining of copper cathodes. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 237 247.

Biswas, A.K. and Davenport, W.G. (1980) *Extractive Metallurgy of Copper*, 2nd Edition, Pergamon Press, New York, NY.

Biswas, A.K. and Davenport, W.G. (1994) *Extractive Metallurgy of Copper*, 3rd Edition, Elsevier Science Press, New York, NY.

Bravo, J.L.R. (1995) Studies for changes in the electrolyte purification plant at Caraiba Metais, Brazil. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Hydrometallurgy and Electrometallurgy of Copper*, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada, 315 324.

Caid (2002) T.A. Caid Industries Inc. www.tacaid.com (Cathodes)

Campin, S.C. (2000) Characterization, analysis and diagnostic dissolution studies of slimes produced during copper electrorefining. M.S. thesis, University of Arizona, Tucson, AZ.

Chen, T.T. and Dutrizac, J.E. (1991) A mineralogical study of anode passivation in copper electrorefining. In *Copper 91-Cobre 91 Proceedings of the Second International Conference, Vol. III Hydrometallurgy and Electrometallurgy*, ed. Cooper, W.C., Kemp, D.J., Lagos, G.E. and Tan, K.G., Pergamon Press, New York, NY, 369 389.

Conard, B.R., Rogers, B., Brisebois, R. and Smith, C. (1990) Inco copper refinery addition agent monitoring using cyclic voltammetry. In *Electrometallurgical Plant Practice*, ed. Claessens, P.L. and Harris, G.B., TMS, Warrendale, PA, 195 209.

Davenport, W.G., Jenkins, J., Kennedy, B. and Robinson, T. (1999) Electrolytic copper refining – 1999 world tankhouse operating data. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 3 76.

De Maere, C. and Winand, R. (1995) Study of the influence of additives in copper electrorefining, simulating industrial conditions. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrorefining and Hydrometallurgy of Copper*, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada, 267 286.

Dreisinger, D.B. and Scholey, B.J.Y. (1995) Ion exchange removal of antimony and bismuth from copper refinery electrolytes. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrorefining and Hydrometallurgy of Copper*, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada, 305 314.

Dutrizac, J.E. (2001) personal communication.

Garvey, J., Ledebor, B.J. and Lommen, J.M. (1999) Design, start-up and operation of the Cyprus Miami copper refinery. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, p. 123.

Geenen, C. and Ramharter, J. (1999) Design and operating characteristics of the new Olen tank house. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 95 106.

Hashiuchi, M., Noda, K., Furuta, M. and Haiki, K. (1999) Improvements in the tankhouse of the Tamano smelter. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 183 193.

Hoey, D.W., Leahy, G.J., Middlin, B. and O'Kane, J. (1987) Modern tank house design and practices at Copper Refineries Pty. Ltd. In *The Electrorefining and Winning of Copper*, ed. Hoffmann, J.E., Bautista, R.G., Ettel, V.A., Kudryk, V. and Wesely, R.J., TMS, Warrendale, PA, 271 293.

Hu, E.W., Roser, W.R. and Rizzo, F.E. (1973) The role of proteins in electrocrystallization during commercial electrorefining. In *International Symposium on Hydrometallurgy*, ed. Evans, D.J.I. and Shoemaker, R.S., AIME, New York, NY, 155 170.

Kitamura, T., Kawakita, T., Sakoh, Y. and Sasaki, K. (1976) Design, construction, and operation of periodic reverse current process at Tamano. In *Extractive Metallurgy of Copper. Volume I Pyrometallurgy and Electrolytic Refining*, ed. Yannopoulos, J.C. and Agarwal, J.C., TMS, Warrendale, PA, 525 538.

Knuutila, K., Forsen, O. and Pehkonen, A. (1987) The effect of organic additives on the electrocrystallization of copper. In *The Electrorefining and Winning of Copper*, ed. Hoffmann, J.E., Bautista, R.G., Ettel, V.A., Kudryk, V. and Wesely, R.J., TMS, Warrendale, PA, 129 143.

Langner, B.E. and Stantke, P. (1995) The use of the CollaMat system for measuring gluc activity in copper electrolyte in the laboratory and in the production plant. In *EPD Congress 1995*, ed. Warren, G.W., TMS, Warrendale, PA, 559 569.

Larouche, P. (2001) *Minor Elements in Copper Smelting and Refining*. M. Eng. Thesis, McGill University, Montreal, Canada.

Lide, D.R. (2001) *CRC Handbook of Chemistry and Physics*, CRC Press, Boca Raton, FL.

Marley (2002) Marley Plastics Pty Ltd. www.marley.com.au (Cathode Edge-Strip System)

Nakai, O., Sato, H., Kugiyama, K. and Baba, K. (1999) A new starting sheet plant at the Toyo copper refinery and productivity improvements. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 279 289.

Preimesberger, N., (2001) Personal communication www.tacaid.com

Price, D.C. and Davenport, W.G. (1981) Physico-chemical properties of copper electrorefining and electrowinning electrolytes. *Metallurgical Transactions B*, **12B**, 639 643.

Rada, M.E.R., Garcia, J.M. and Ramirez, G. (1999) La Caridad, the newest copper refinery in the world. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 77 93.

Ramachandran, V. and Wildman, V.L. (1987) Current operations at the Amarillo copper refinery. In *The Electrorefining and Winning of Copper*, ed. Hoffmann, J.E., Bautista, R.G., Ettel, V.A., Kudryk, V. and Wesely, R.J., TMS, Warrendale, PA, 387 396.

Robinson, T., O'Kane, J. and Armstrong, W. (1995) Copper electrowinning and the ISA process. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrorefining and Hydrometallurgy of Copper*, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada, 445 456.

Roman, E.A., Salas, J.C., Guzman, J.E. and Muto, S. (1999) Antimony removal by ion exchange in a Chilean tankhouse at the pilot plant scale. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrorefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 225 236.

Rondas, F., Scoyer, J. and Geenen, C. (1995) Solvent extraction of arsenic with TBP – the influence of high iron concentration on the extraction behaviour of arsenic. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrorefining and Hydrometallurgy of Copper*, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G. Metallurgical Society of CIM, Montreal, Canada, 325 335.

Saban, M.B., Scott, J.D. and Cassidy, R.M. (1992) Collagen proteins in electrorefining: rate constants for glue hydrolysis and effects of molar mass on glue activity. *Metallurgical Transactions*, **23B**(4), 125 133.

Sasaki, Y., Kawai, S., Takasawa, Y. and Furuya, S. (1991) Development of antimony removal process for copper electrolyte. In *Copper 91-Cobre 91 Proceedings of the Second International Conference, Vol. III Hydrometallurgy and Electrometallurgy*, ed. Cooper, W.C., Kemp, D.J., Lagos, G.E. and Tan, K.G., Pergamon Press, New York, NY, 245 254.

Scheibler (2002) Scheibler Filters Ltd. www.scheibler.com (Edgewise Products)

Shibata, T., Hashiuchi, M. and Kato, T. (1987) Tamano refinery's new process for removing impurities from electrolyte. In *The Electrowinning and Refining of Copper*, ed. Hoffmann, J.E., Bautista, R.G., Ettel, V.A., Kudryk, V. and Wesely, R.J., TMS, Warrendale, PA, 99 116.

Stantke, P. (1999) Guar concentration measurement with the CollaMat system. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrowinning and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 643 651.

Sutliff, K.E. and Probert, T.I. (1995) Kennecott Utah copper refinery modernization. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrowinning and Hydrometallurgy of Copper*, ed. Cooper, W.C., Dreisinger, D.B., Dutrizac, J.E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada, 27 39.

Toyabe, K., Segawa, C. and Sato, H. (1987) Impurity control of electrolyte at Sumitomo Niihama copper refinery. In *The Electrowinning and Refining of Copper*, ed. Hoffmann, J.E., Bautista, R.G., Ettel, V.A., Kudryk, V. and Wesely, R.J., TMS, Warrendale, PA, 117 128.

Virtanen, H., Marttila, T. and Pariani, R. (1999) Outokumpu moves forward towards full control and automation of all aspects of copper refining. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrowinning and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 207 224.

Wang, C-T. and O'Keefe, T.J. (1984) The influence of additives and their interactions on copper electrowinning. In *Proceedings of the International Symposium on Electrochemistry in Mineral and Metal Processing, Volume 84-10*, ed. Richardson, P.E., Srinivasan, S. and Woods, R., The Electrochemical Society, Pennington, NJ, 655 670.

CHAPTER 17

Hydrometallurgical Copper Extraction: Introduction and Leaching

(Written with Henry Salomon-de-Friedberg, Cominco, Trail, BC)

Previous chapters describe the concentration/pyrometallurgy/electrorefining processes that turn Cu-sulfide ores into high purity electrorefined copper. These processes account for ~80% of primary copper production.

The remaining 20% of primary copper production comes from hydrometallurgical processing of Cu-'oxide' and chalcocite ores, Table 17.1. This copper is recovered by leaching (this chapter), solvent extraction (Chapter 18) and electrowinning (Chapter 19). The final product is electrowon cathode copper equal in purity to electrorefined copper.

In 2002, about 2.5 million tonnes per year of metallic copper are being produced hydrometallurgically – almost all of it by *heap leaching*, Fig. 17.1. This production is increasing as more mines begin to leach all or some of their ore.

17.1 Heap Leaching

Copper leaching is dissolving Cu from minerals into an aqueous solution – almost always an $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solution. *Heap leaching* is trickling the $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solution through large 'heaps' of ore under normal atmospheric conditions, Fig. 17.1. It leaches the 'oxide' ores in Table 17.1 and chalcocite. Bornite, covellite and native copper are also slowly leached. Chalcopyrite is not leached under the mild conditions of heap leaching, Section 17.4.

17.1.1 Chemistry of heap leaching

Non-sulfide Cu minerals are leached directly by $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions according to reactions like:

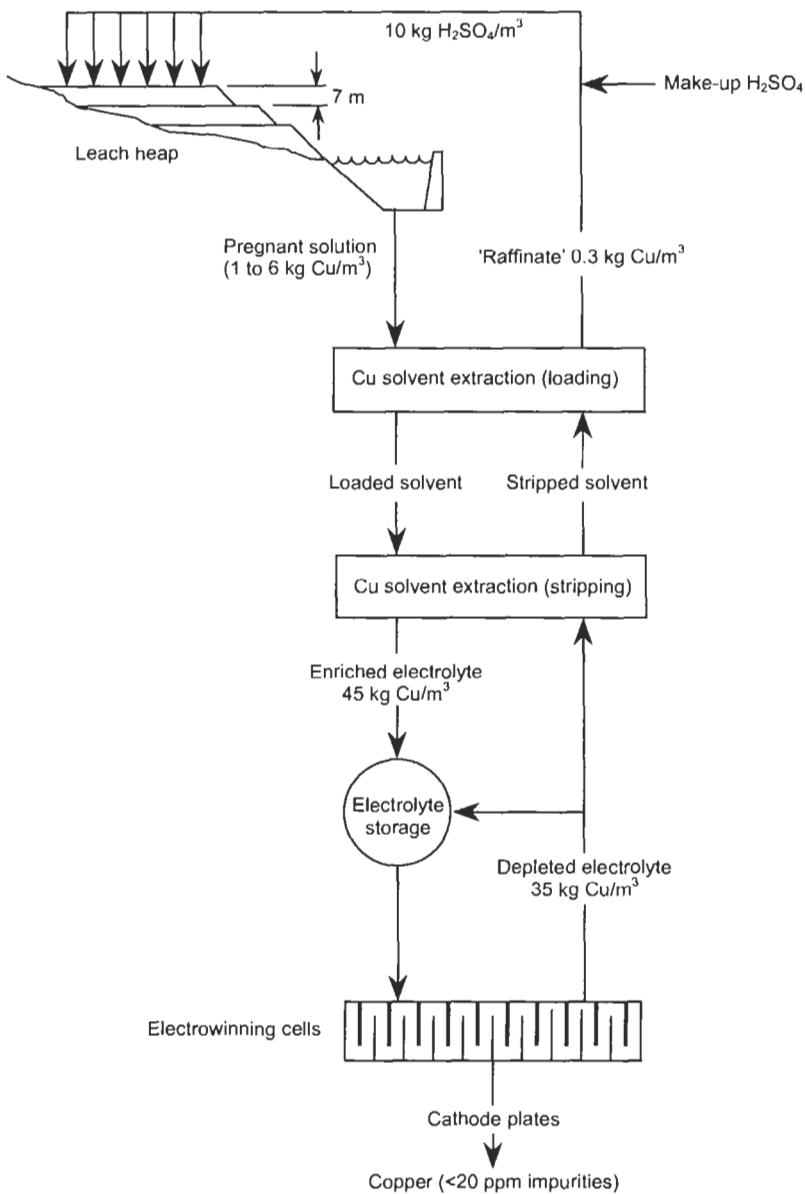
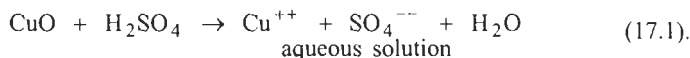


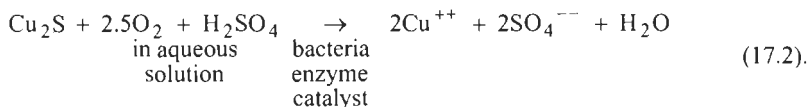
Fig. 17.1. Cu heap leach/solvent extraction/electrowinning flowsheet. Solvent extraction and electrowinning are described in Chapters 18 and 19.

Table 17.1. Copper minerals normally found in leach heaps. Carbonates, oxides, hydroxy-chlorides, hydroxy-silicates and sulfates are generally referred to as 'oxides'. They leach quickly. Chalcocite also leaches quickly, bornite and covellite slowly. Chalcopyrite is not leached.

Type	Common minerals	
<u>Secondary minerals</u>		
carbonates	azurite	$2\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
hydroxy-chlorides	atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$
hydroxy-silicates	chrysocolla	$\text{CuO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$
native copper	metal	Cu^0
oxides	cuprite	Cu_2O
	tenorite	CuO
sulfates	antlerite	$\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$
	brochantite	$\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$
supergene sulfides	chalcocite	Cu_2S
	covellite	CuS
<u>Primary sulfide minerals</u>		
(hypogene sulfides)	chalcopyrite	CuFeS_2
	bornite	Cu_5FeS_4
	pyrite, source of Fe^{++} , Fe^{+++} and H_2SO_4	FeS_2



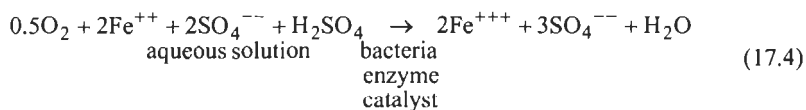
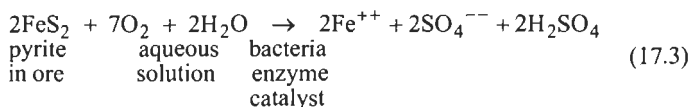
Leaching of sulfide minerals, on the other hand, requires an oxidant as well as H_2SO_4 . The oxidant is dissolved O_2 from air. A representative reaction is:



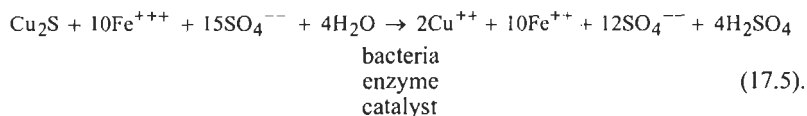
As shown, sulfide heap leaching is assisted by bacteria. They speed up leaching to economic rates, Section 17.1.3.

17.1.2 Oxidation by Fe^{+++}

Reaction (17.1) represents the overall sulfide leaching reaction. Industrial experiments show, however, that Fe is a requirement for rapid leaching. Equations representing its participation are:



and:



The Fe^{++} ions produced by Reaction (17.5) are then reoxidized by Reaction (17.4) and the process becomes cyclic. This would seem to be the most likely mechanism (Brierley and Brierley, 1999a), but direct oxidation (Eqn. 17.2) may also occur. Heap leach pregnant solutions typically contain 1-5 kg Fe per m^3 of solution (Jenkins, 1999).

17.1.3 Bacterial action

Reactions (17.2) through (17.5) can proceed without bacterial action but they are speeded up a million-fold by the enzyme catalysts produced by bacteria. The catalytic actions are most commonly attributed to **thiobacillus ferrooxidans**, **leptosprillum ferrooxidans** and **thiobacillus thiooxidans** (Weston *et al.*, 1995; Brierley and Brierley, 1999a,b). The bacteria are rod-shaped, $0.5 \times 2 \mu\text{m}$ long. Like all bacteria, they adapt readily to changes in their environment (Weston *et al.*, 1995). They are present in leach heaps in the order of 10^{12} bacteria per tonne of ore (Brierley and Brierley, 1999b).

The bacteria are indigenous to sulfide orebodies and their surrounding aqueous environment (Brierley and Brierley, 1999b). Mine water and moistening of the ore provides them to the leach solutions.

Optimum bacterial action takes place under the following conditions:

- (a) lixiviant pH between 1.5 and 6 (optimum ~2)
- (b) temperature between 5 and 45°C (optimum $\sim 30^\circ\text{C}$, often generated in leach heaps and dumps by exothermic sulfide oxidation reactions)

- (c) an adequate O_2 supply, often obtained by gently blowing air through perforated pipes beneath sulfide ore leach heaps (Salomon-de-Friedberg, 1998, 1999, 2000)
- (d) no organics in lixiviant or heap.

Brierley and Brierley (1999b) suggest that the bacteria might also need small amounts of minor nutrients such as NH_4^+ and PO_4^{3-} at the start of leaching. Once leaching has begun, however, these nutrients need not be added, i.e. they are provided by minerals in the ore (Salomon-de-Friedberg, 1999).

A useful instrument for monitoring bacterial activity is the 'Oxymax Respirometer' (Salomon-de-Friedberg, 2000, Columbus Instruments Corporation, 2002). It measures (for example) rates of O_2 uptake by leach solutions. It should be helpful for selecting optimum leach conditions.

17.1.4 Rates of sulfide leaching

Chalcocite leaches quickly under heap leach conditions. Bornite and covellite leach much more slowly. Commercial leaching is never based on bornite or covellite.

Chalcopyrite is hardly touched by heap leaching. It is believed that:

- (a) Fe is leached from $CuFeS_2$ before Cu – leaving behind a passive layer of metastable CuS_2
- (b) subsequent leaching of Cu from CuS_2 leaves a coherent layer of elemental sulfur (Hiskey, 1993).

Combined, these product layers inhibit further leaching, giving chalcopyrite's observed negligible leach rate.

17.2 Industrial Heap Leaching (Table 17.2)

Heap leaching is far and away the most important method of hydrometallurgical Cu extraction. It entails:

- (a) building flat-surface heaps of ore pieces, ~7 m high, 10^4 to 10^6 m² in top area
- (b) applying drops of H_2SO_4 - H_2O solution to the top surface of the heap via an equispaced network of polymer pipes and emitters or sprinklers
- (c) allowing the solution to trickle unimpeded through the heap, dissolving Cu minerals by Reactions (17.1) through (17.5)
- (d) collecting the Cu^{++} -rich pregnant solution on a sloped impermeable surface beneath the heap

- (e) directing gravity flow of pregnant solution to a pond or tank outside the heap
- (f) sending the collected solution to solvent extraction and electrowinning for metallic copper production
- (g) recycling Cu^{++} -depleted $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ 'raffinate' solution from solvent extraction to the heap for further leaching.

The following sections describe these steps.

17.2.1 Heap construction details

Leach heaps are either multi-'lift' (Fig. 17.1) or on/off. Multi-lift heaps consist of (i) an initial lift built on an impermeable surface and (ii) subsequent lifts built on top of the first lift (after it has been leached). On/off heaps consist of a single lift built on an impermeable surface, removed after leaching and replaced by a new lift. Multi-lift heaps are used around the world – on/off heaps are used in Chile.

Permanent and on/off heap advantages and disadvantages (Iasillo and Schlitt, 1999, Breitenbach, 1999)

Multi-lift heaps have the advantages that:

- (a) the ore need only be moved once – onto the heap
- (b) lixiviant flows through all the lifts until leaching is moved to another area – permitting recovery of Cu^{++} from slower-leaching minerals in the lower lifts.

They have the disadvantages that construction of a heap which may ultimately become 60 m high requires:

- (a) a strong impermeable base
- (b) versatile heap building equipment
- (c) a large initial base because the heaps are pyramidal, so the area at the top of a multi-lift heap is much smaller than its base.

On/off heaps have the advantages that:

- (a) they are simple to construct
- (b) their base need not be as strong as those needed for multi-lift heaps
- (c) the aeration and pregnant solution pipe-work can be maintained when ore is emptied from the pad.

Their main disadvantage is that their ore must be moved twice (on and off).

The simplicity and controllability of on/off pads is leading them to be used more widely, especially in Chile.

17.2.2 Impermeable base

Leach heaps are always built on an impermeable base. This permits complete collection of the leached Cu^{++} and prevents solution penetration into the underlying environment.

The base consists of 1 to 2 mm thick high density polyethylene sheet with (i) a rolled 0.1 m thick clay or earth layer beneath and (ii) a 0.5 m finely crushed rock (<2 cm diameter) layer above. Perforated pregnant solution collection pipes and aeration pipes are placed on top of this layer.

Considerable care is taken to avoid puncturing the polymer sheet during construction of the base. Care is also taken to cover the polymer layer as soon as it is laid down to avoid the destructive effects of sunlight.

The base is sloped to direct the Cu^{++} -rich pregnant solution to a collection basin. Breitenback (1999) recommends that the slope should be less than 5% (5 m drop in 100 m horizontal) to avoid slippage of the heap on the polymer liner.

17.2.3 Ore placement

Leach heaps are laid on their impermeable base by (i) dumping ore from trucks or by (ii) stacking the ore with a mobile conveyor. Trucks have the advantage of simplicity but they tend to compact the heap as they run over it to their dumping destination (Brierley and Brierley, 1999b). Mobile conveyors avoid most of this problem. They are used extensively in Chile. They are being adopted worldwide.

17.2.4 Aeration

A leach heap is a pile of ore pieces with the pieces surrounded by air. Lixiviant trickles through the heap down the ore surfaces and through cracks in the ore pieces. 'Oxide' leaching only requires lixiviant. Sulfide (i.e. Cu_2S) leaching also requires O_2 (from air) for Reactions (17.2), (17.3) and (17.4).

The air is provided by placing perforated polymer pipes on the heap base and by blowing air gently and uniformly upwards through the heap. Table 17.3 gives details.

It is important that the air pipes do not become filled with lixiviant. This is accomplished by:

- (a) placing the pipes ~1 m above the heap base
- (b) sloping them and blowing downwards in the direction of solution flow
- (c) providing a drainage manifold at their low end.

Table 17.2. Details of five heap leach operations. Details of the equivalent

Operation	Cerro Colorado	El Abra
Startup date	1994	1996
Cathode production, tonnes/year	130 000	194 000
H ₂ SO ₄ consumption, tonnes/tonne of cathode Cu	1.25	5.04
Ore information		
leached mineral	chalcocite, 0.8% chrysocolla, 0.36%	chrysocolla
%Cu in ore	1.2	0.63
leachable	1.16	0.55
non-leachable	0.04% in covellite	0.08
location of ore's leachable minerals	oxides on fracture surfaces, sulfides disseminated	disseminated
% of total Cu in ore recovered in solution	80% of leachable Cu	78
Heaps		
permanent or on/off	on/off	on/off
building machines	dump truck	conveyor stacking
usual total area under leach, thousand m ²	1600	710
usual number of 'cells' under leach	27	55
typical lift height, m	6-9	7 (0.3 m 'ripping')
maximum total heap height, m	6-9	7
aeration pipes beneath heap, yes/no		no
Heap base		
liner material & thickness, mm	HDPE 2 mm	HDPE 1.5 mm
Ore preparation		
crush, yes/no	yes	yes
agglomeration in rotation drum, yes/no	yes	yes
ore size on heap	90% <12 mm	80% <11.5-12.5 mm
Acid cure, yes/no		
on heap or during agglomeration	yes in rotating drum	yes in rotating drum, 45 to 55 seconds
kg/m ³ H ₂ SO ₄ in cure solution	concentrated	33 mass%
H ₂ SO ₄ , kg/tonne of ore		16-20
rest duration before leaching	20	3 to 4 days
Lixiviant		
	raffinate	H ₂ SO ₄ fortified raffinate
kg H ₂ SO ₄ /m ³ of solution	11	12-14
kg Cu ⁺⁺ /m ³ of solution	0.4	0.5-1.0
temperature, °C	17-22	15-20
application rate, m ³ /hour/m ² of heap surface	0.006	0.01
drop emitters or sprinklers (wobblers)	emitters	emitters
distance apart		
along header pipe, m	0.4	0.46
between header pipes, m	0.6	0.46
Leach cycle sequence		
	agglomerate in rotating drum with raffinate and H ₂ SO ₄ ; heap; rest for 20 days; leach for 480 days	acid cure in rotating drum, build cured ore into heap, rest 3 or 4 days, leach for 55 days
Pregnant solution		
kg Cu ⁺⁺ /m ³ of solution	4.8	5 to 6
kg H ₂ SO ₄ /m ³ of solution	5	6
temperature, °C	18-23	15-20
collection system	HDPE-lined ponds	ditches
total flow from leach system, m ³ /hour	4000	5000-7500

solvent extraction and electrowinning plants are given in Chapters 18 and 19.

Zaldivar (heap leach)	Hellenic Copper	Morenci (mine for leach)
1995	1996	1987
145 000	8000	366 000
14	5	1
chalcocite, bronchantite, chrysocolla	chalcocite	chalcocite, chrysocolla
1%	0.6 0.15	0.261 0.23% in covellite principally fracture filling
chalcocite disseminated, others on fracture surfaces		
75	78% of leachable	53% of leachable
on/off conveyor stacking	permanent excavator stacking	conveyor stacking
1200	250	2137
90	30	144
8	6	7-9
8	42	
yes	no	yes (10^{-3} m ³ air/minute/m ²)
HDPE	HDPE 1.5 mm	HDPE over clay
yes	yes	both
belt curing 80% <12 mm	50% <75 mm	<12 mm (crushed), 300 mm ROM
yes	no	yes, for about 30% of material, in rotating drum
concentrated 8		200 kg/m ³ H ₂ SO ₄ onto heap for 3 days
no		
H ₂ SO ₄ -fortified raffinate	H ₂ SO ₄ -fortified raffinate	raffinate
8	4	12 mine for leach, other 4-5
0.25	0.5	0.3
20.7	22	32
0.008	0.0075	0.006
emitters	emitters	both, principally emitters
0.5	0.6	0.9
0.5		
belt acid cure, leach with raffinate for 30 days, then leach with recycling pregnant solution for 270 days	18 months	mine for leach: crushed material fines are agglomerated with strong acid in a rotating drum, then stacked in 7 m lifts; leached for 90 days, rested for 30 days then leached again for 30 days
3.5	1.8	2.6
1.2	1	3
20.7	23	32
on-pad piping	ditches, pipes, ponds	(clay + HDPE)-lined ponds
4800	520	19 051

Table 17.3. Details of heap leach aeration system at Quebrada Blanca (Salomon-de-Friedberg, 1998, 1999, 2000). Salomon-de-Friedberg (1998) gives detailed numerical calculations. The air header pipe is placed on the uphill side of the heap base. Quebrada Blanca has ~20 of these heaps.

Item	Description
Individual heap (module)	85 m × 400 m horizontal dimensions (34 000 m ²). Consists of 7 m lifts, eventually piled to a total of 60 m high.
Air supply rate	170 m ³ /minute (0.005 m ³ /min/m ² of top surface). The design assumes 20% utilization of O ₂ entering heap
Air header (400 m long)	0.45 m diameter HDPE pipe, corrugated outside for strength, smooth inside
Air distribution lines (85m long)	5 cm HDPE pipes, 2 mm diameter hole every 1 m, rotated around the pipe. The pipes are spaced 2 m apart.
Fan	single stage axial fan, ~0.1 atmosphere gage delivery pressure

17.2.5 Pregnant solution collection

The product pregnant solution (1 to 6 kg Cu⁺⁺/m³) from heap leaching flows by gravity down ~10 cm polymer drain pipes on the sloping heap base to a collection trench. The solution gets into the pipes through 2 mm wide, 20 mm long slits in the polymer pipe. The pipes are spaced 2 to 4 m apart about 45° across the slope.

The solution then flows by pipeline from the collection trench to a pond or tank. It is sent from there by gravity or pumping to solvent extraction/ electrowinning for copper metal production.

High density polyethylene pipes are used for low pressure flows. 316L stainless steel pipe is used for high pressure pumped flows.

17.2.6 Ore preparation

Preparation of ore for heap leaching varies from simple placement of run-of-mine (ROM) ore on the leach heaps to:

- placement of run-of-mine ore on the heap followed by trickling strong H₂SO₄-H₂O solution through the heap ('acid curing')
- crushing of the ore followed by rotating-drum agglomeration with strong sulfuric acid then placement of the agglomerate on the leach heap.

Placement of run-of-mine ore is the cheapest method. However, it gives the slowest and least efficient Cu⁺⁺ recovery.

'Acid curing' quickly dissolves Cu^{++} from readily soluble 'oxide' minerals and it acidifies the heap, thereby preventing ferric sulfate precipitation during subsequent leaching. Typically, 10 or 20 kg of strong sulfuric acid per tonne of ore are supplied to the heap over a period of ~10 days (shorter for 'oxide' ores and longer for sulfide ores, Iasillo and Schlitt, 1999). Most heap leach operations find that a preliminary acid cure economically enhances Cu^{++} extraction rate and efficiency, Table 17.2.

17.2.7 Crushing, agglomeration and acid curing

Cu^{++} extraction rate and efficiency improve with decreasing ore piece size (Iasillo and Schlitt, 1999; Brierley and Brierley, 1999b). This has led many heap leach operators to crush their run-of-mine ore to 1 cm pieces. Crushing below 1 cm doesn't further improve Cu^{++} extraction (Salomon-de-Friedberg, 1999) while crushing below 0.5 cm adversely decreases heap permeability (Brierley and Brierley, 1999b).

The crushed ore is agglomerated with strong sulfuric acid in revolving 3 m diameter, 9 m long drums, sloped ~6°. This (i) agglomerates the fines created during crushing and (ii) acid cures the ore. The agglomerated material is then placed on the leach heaps.

Optimum agglomeration conditions are (Salomon-de-Friedberg, 2000):

- ~1 cm crush size
- 60 to 90 seconds agglomeration
- ~10 RPM drum rotation speed
- ~9% moisture in agglomerate
- ~5 kg (or less) H_2SO_4 per tonne of ore.

Close attention is also paid to avoiding too much clay in the agglomerate. More than 20% clay in agglomerate severely decreases heap permeability (Salomon-de-Friedberg, 2000).

The rapid and efficient extraction of Cu^{++} obtained by crush/agglomerate/acid cure leaching is leading to its wider use, in Chile (Dufresne, 2000) and elsewhere, Table 17.2.

17.3 Steady-State Leaching

The lixiviant for industrial leaching is the Cu^{++} -depleted solution ('raffinate') returning from solvent extraction, Fig. 17.1. Its composition is typically 0.4 kg Cu and ~5 kg $\text{H}_2\text{SO}_4/\text{m}^3$ of solution as it leaves the solvent extraction circuit. Sulfuric acid is often added (to ~10 kg $\text{H}_2\text{SO}_4/\text{m}^3$) before the raffinate is recycled

to the leach heap. Water may also be added to maintain design lixiviant flowrate.

The lixiviant is added via an equispaced network of polymer pipes and drop emitters or sprinklers on top of the heap. Its addition rate is about 10^{-2} m^3 of lixiviant per hour per m^2 of heap surface. This low rate prevents pooling of lixiviant on the heap surface (allowing free movement of air in the heap).

Sprinklers and drip emitters are used almost equally. Sprinklers (wobblers) have the advantage that they distribute solution evenly over large areas. Drip emitters require little maintenance and avoid excessive evaporation and cooling.

The lixiviant almost always enters the heap at ambient temperature. In cold areas it may be heated to enhance Cu^{++} extraction rate (Salomon-de-Friedberg, 2000).

17.3.1 Optimum leach conditions

Optimum leach conditions are:

- (a) uniform heaps of optimum agglomerate which maintain their permeability throughout their life
- (b) leach conditions which maximize bacterial activity ($\sim 30^\circ\text{C}$, pH ~ 2 , 5-10 kg $\text{H}_2\text{SO}_4/\text{m}^3$ of lixiviant, no organics)
- (c) uniform, lixiviant application ($\sim 10^{-2} \text{ m}^3/\text{hour}/\text{m}^2$) on the heap surface without pooling
- (d) well-designed impervious heap base sloping less than 5% with an efficient pregnant leach solution collection system
- (e) adequate heap temperature, provided in cold regions by heating raffinate, insulating pipes and covering heaps with polymer mesh or sheet (Salomon-de-Friedberg, 2000).

And for sulfide leaching:

- (f) a controlled, uniform air supply, $\sim 10^{-2} \text{ m}^3$ of air/min/ m^2 of heap surface, blown in from perforated pipes beneath the heap.

17.4 Leaching of Chalcopyrite Concentrates

Chalcopyrite is not leached under the mild oxidizing conditions of heap leaching. It can, however, be leached under stronger oxidizing conditions. This has led to extensive study into leaching of chalcopyrite *concentrates* as an alternative to smelting, Table 17.4. Industrial plants were built in the 1970's, 80's and 90's. None, however, remains in production.

The potential advantages of chalcopyrite concentrate leaching over smelting are:

- (a) avoidance of gaseous effluents, particularly SO_2 (Ferron, 1999)
- (b) construction of small leach plants at mine sites rather than shipping concentrate to large, distant smelters (King and Dreisinger, 1995)
- (c) treatment of high-impurity concentrates (Dreisinger and Saito, 1999)
- (d) lower costs.

The principal proposed processes have been:

- (a) ammonia-air leach
- (b) halide leach
- (c) high and moderate pressure oxygen leach.

Their status is given in Table 17.4.

17.5 Other Leaching Processes

Minor Cu leaching processes are *in situ*, tailings and agitation leaching of oxide concentrates and roaster calcines. They are discussed in Biswas and Davenport (1980, 1994).

17.6 Future Developments

The main future developments in Cu hydrometallurgy are:

- (a) continued growth of heap leaching for efficient recovery of Cu from 'oxide' and chalcocite ores
- (b) continued improvement in heap leaching through optimization of crushing, acid curing, agglomeration, heap construction, aeration, lixiviant composition, lixiviant application rate, bacterial activity and temperature
- (c) continued study of all aspects of chalcopyrite leaching.

17.7 Summary

Hydrometallurgical extraction accounts for about 2.5 million tonnes of metallic copper per year (about 20% of total primary copper production). Virtually all of this is produced by heap leaching.

Heap leaching consists of trickling $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ lixiviant uniformly through flat-surface heaps of crushed ore agglomerate or run-of-mine ore. 'Oxide' ores are leached quickly by H_2SO_4 without oxidation. Chalcocite (and to a much lesser extent bornite and covellite) are oxidized and leached by $\text{H}_2\text{SO}_4\text{-H}_2\text{O-O}_2\text{-Fe}^{+++}$ solutions.

Table 17.4. Description and status of chalcopyrite concentrate leach processes (McElroy and Young, 1999).

Name of process	Description	Status
Arbiter ammonia-O ₂ pressure leach (Arbiter & McNulty, 1999)	agitation pressure leach, solvent extraction, electrowinning	100 tonnes copper per day plant started in 1974 but closed in 1977 due to technical difficulties and high costs
Escondida ammonia-air leach (Duyvesteyn and Sabacky, 1993, 1995; Arbiter and McNulty, 1999)	Ammonia-air agitation leach of Cu ₂ S to CuS + Cu ⁺⁺ followed by solvent extraction electrowinning recovery of metallic copper	80 000 tonnes of copper per year plant started in 1994 but closed due to its slow rate of copper production
Halide leach (Cymet, CLEAR, Cuprex and Intec processes)	Halide leach, electrowinning (Biswas and Davenport, 1994; Moyes, 2002)	Industrial scale attained. Interest seems to have waned due to impure products, environmental problems and adverse economics
Oxygen sulfuric acid pressure leach	High (7 atmospheres) and moderate O ₂ pressure leach with sulfuric acid, raffinate, electrolyte and various additives (Anderson, 2000; Collins <i>et al.</i> , 2000; Fleming <i>et al.</i> , 2000)	development is continuing

Economic rapid leaching of sulfide ores is made possible by indigenous bacteria which speed up the leaching process a million-fold. Their activity is maximized by a pH of ~2, a temperature of ~30°C and an adequate O₂ supply.

The product of heap leaching is pregnant solution containing 1 to 6 kg Cu⁺⁺/m³. It is collected on a sloping impervious HDPE sheet base beneath the leach heaps. It is sent to solvent extraction/electrowinning for copper production, Chapters 18 and 19. The Cu⁺⁺-depleted 'raffinate' from solvent extraction is recycled to leaching, usually fortified with H₂SO₄.

Cu⁺⁺ leach rate and recovery are maximized by optimizing crush size, acid curing, agglomeration, heap permeability, lixiviant composition, aeration and bacterial activity.

Most Cu minerals are amenable to heap leaching. A critical exception is chalcopyrite (CuFeS₂), which doesn't dissolve under heap leach conditions. It can be leached under strongly oxidizing conditions, but not yet economically.

Suggested Reading

Jenkins, J., Davenport, W. G., Kennedy, B. and Robinson, T. (1999) Electrolytic copper – leach, solvent extraction and electrowinning world operating data. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV, Hydrometallurgy of Copper*, TMS, Warrendale, PA, 493 566.

Jergensen II, G.V. (1999) *Copper Leaching, Solvent Extraction and Electrowinning Technology*, SME, Littleton, CO.

Young, S.K. (1999) A look at leach SX-EW with 2020 vision. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV, Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 611 619.

References

Anderson, C.G. (2000) The treatment of chalcopyrite concentrates with nitrogen species catalyzed oxidative pressure leaching. In *EPD Congress 2000*, ed. Taylor, P.R., TMS, Warrendale, PA, 489 501.

Arbiter, N. and McNulty, T. (1999) Ammonia leaching of copper sulfide concentrates. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV, Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 197 212.

Biswas, A.K. and Davenport, W.G. (1980) *Extractive Metallurgy of Copper 2nd Edition*, Pergamon Press, New York, NY.

Biswas, A.K. and Davenport, W.G. (1994) *Extractive Metallurgy of Copper 3rd Edition*, Elsevier Science Press, New York, NY (Chapter 18).

Breitenbach, A.J. (1999) The good, the bad, and the ugly lessons learned in the design and construction of heap leach pads. In *Copper Leaching, Solvent Extraction and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 139 147.

Brierley, C.L. and Brierley, J.A. (1999a) Copper bioleaching: state-of-the-art. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV, Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 59 68.

Brierley, C.L. and Brierley, J.A. (1999b) Bioheap processes – operational requirements and techniques. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 17 27.

Collins, M.J., Stikma, J., Buban, K.R. and Masters, I.M. (2000) Pressure acid leaching of zinc and copper concentrate by Dynatec. In *EPD Congress 2000*, ed. Taylor, P.R., TMS, Warrendale, PA, 597 605.

Columbus Instruments (2002) Oxymax-F measures $O_2/CO_2/CH_4$ consumption and production www.colinst.com (Environmental Instruments, Respirometer for Fermentation)

Dreisinger, D.B. and Saito, B.R. (1999) The total pressure oxidation of El Indio ore and concentrate. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV, Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 181 195.

Dufresne, M.W. (2000) The Collahuasi copper project, Chile. *Canadian Institute of Mining, Metallurgy and Petroleum Bulletin*, **93** (1039), 25 30.

Duyvesteyn, W.P.C. and Sabacky, B.J. (1993) The Escondida process for copper concentrates. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Vol. I: Fundamental Aspects*, ed. Reddy, R.G. and Weizenbach, R.N., TMS, Warrendale, PA, 881 910.

Duyvesteyn, W.P.C. and Sabacky, B.J. (1995) Ammonia leach process for Escondida concentrates. *Transactions of the Institution of Mining and Metallurgy*, **104**, C125 C140.

Ferron, C.J. (1999) New atmospheric leach process for copper sulphide ores and concentrates. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV, Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 151 165.

Fleming, C.A., Ferron, C.J., Dreisinger, D.B. and O'Kane, P.T. (2000) A process for the simultaneous leaching and recovery of gold, platinum group metals and base metals from ores and concentrates. In *EPD Congress 2000*, ed. Taylor, P.R., TMS, Warrendale, PA, 419 431.

Hiskey, J.B. (1993) Chalcopyrite semiconductor electrochemistry and dissolution. In *Extractive Metallurgy of Copper, Nickel and Cobalt (the Paul E. Queneau International Symposium), Vol. I: Fundamental Aspects*, ed. Reddy, R.G. and Weizenbach, R.N., TMS, Warrendale, PA, 949 969.

Iasillo, E. and Schlitt, W.J. (1999) Practical aspects associated with evaluation of a copper heap leach project. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jorgensen II, G.V., SME, Littleton, CO, 123 138.

Jenkins, J., Davenport, W. G., Kennedy, B. and Robinson, T. (1999) Electrolytic copper – leach, solvent extraction and electrowinning world operating data. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV, Hydrometallurgy of Copper*, TMS, Warrendale, PA, 493 566.

King, J.A. and Dreisinger, D.B. (1995) Autoclaving of copper concentrates. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III, Electrowinning and Electrowinning of Copper*, ed. Dutrizac, J.E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada, 511 533.

McElroy, R. and Young, W. (1999) Pressure oxidation of complex copper ores and concentrates. In *Copper Leaching, Solvent Extraction and Electrowinning Technology*, ed. Jorgensen II, G.V., SME, Littleton, CO, 29 40.

Moyes, J.A. (2002) The Intec copper process (superior and sustainable copper production). www.intec.com.au (Intec copper process)

Salomon-de-Friedberg, H. (1998) Design aspects of aeration in heap leaching. Paper presented at the Randol Cu Hydrometallurgical Roundtable '98, November 1998, Vancouver, BC, Canada.

Salomon-de-Friedberg, H. (1999) Recent changes to operating practices at Minera Quebrada Blanca. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV, Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 3-12.

Salomon-de-Friedberg, H. (2000) Quebrada Blanca: lessons learned in high altitude leaching. Paper presented to Instituto de Ingenieros de Minas de Chile, Expomin 2000, Santiago, Chile, May 2000.

Weston, J.M., Dreisinger, D.B., Hackl, R.P. and King, J.A. (1995) Continuous biological leaching of copper from a chalcocite ore and concentrate in a saline environment. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III, Electrowinning and Electrowinning of Copper*, ed. Dutrizac, J.E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada, 377-392.

CHAPTER 18

Solvent Extraction Transfer of Cu from Leach Solution to Electrolyte

(Written with Jackson Jenkins, Phelps Dodge, Morenci, AZ)

The pregnant leach solutions produced by most leaching operations are:

- (a) too dilute in Cu (1-6 kg Cu/m³)

and:

- (b) too impure (1-10 kg Fe/m³)

for direct electrodeposition of high purity cathode copper. Electrowinning from these solutions would give soft, impure copper deposits.

Industrial electrowinning requires pure, Cu-rich electrolytes with >35 kg Cu/m³. This high concentration of Cu:

- (a) ensures that Cu⁺⁺ ions are always available for plating at the cathode surface
- (b) gives smooth, dense, high purity, readily marketable cathode copper.

Solvent extraction provides the means for producing pure, high Cu⁺⁺ electrolytes from dilute, impure pregnant leach solutions. It is a crucial step in the production of ~2.5 million tonnes of metallic copper per year. It continues to grow in importance as more and more Cu ore is leached.

18.1 The Solvent Extraction Process

Copper solvent extraction (Fig. 18.1) entails:

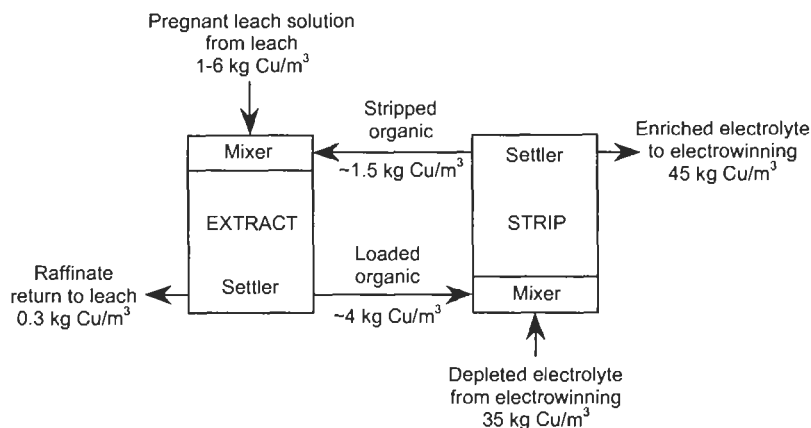


Fig. 18.1. Schematic plan view of copper solvent extraction circuit. The inputs are pregnant leach solution and Cu-depleted electrolyte. The products are Cu-enriched electrolyte and low-Cu raffinate. Fig. 18.3 shows an industrial mixer-settler. Fig. 18.4 shows the most common industrial circuit.

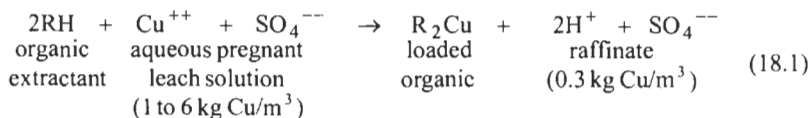
- contacting pregnant aqueous leach solution ($1\text{--}6\text{ kg Cu}^{++}/\text{m}^3$, 0.5 to $5\text{ kg H}_2\text{SO}_4/\text{m}^3$) with a Cu-specific liquid organic extractant – *causing extraction of Cu^{++} from the aqueous solution into the organic extractant*
- separating by gravity the now-Cu-depleted aqueous leach solution (raffinate) from the now-Cu-loaded organic extractant
- sending the low-Cu raffinate back to leach
- sending the Cu-loaded organic extractant to contact with strong- H_2SO_4 electrowinning electrolyte ($170\text{--}200\text{ kg H}_2\text{SO}_4/\text{m}^3$) – *causing Cu to be stripped from the organic into the electrolyte*
- separating by gravity the now-Cu-stripped organic extractant from the now-Cu $^{++}$ -enriched aqueous electrolyte
- returning the stripped organic extractant to renewed contact with pregnant leach solution
- sending the Cu $^{++}$ -enriched electrolyte to electrowinning where its Cu $^{++}$ is electrodeposited as pure metallic copper.

The process is continuous. It typically takes place in ‘trains’ of 2 extraction mixer-settlers for steps (a) and (b) and 1 strip mixer-settler for steps (e) and (f). An extraction system typically consists of 1 to 4 ‘trains’ (Jenkins *et al.*, 1999).

The organic extractants are aldoximes and ketoximes (Kordosky et al., 1999). They are dissolved 5 to 20 volume% in purified kerosene.

18.2 Chemistry

The organic extractant removes Cu^{++} from pregnant leach solution by the reaction:

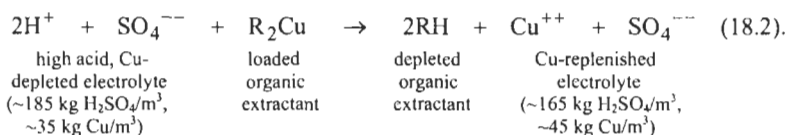


where RH is the aldoxime or ketoxime extractant.

Loading of organic extractant with Cu is seen to be favored by a low concentration of sulfuric acid (H^+) in the aqueous phase. So contact of dilute H_2SO_4 aqueous pregnant leach solution with organic gives extraction of Cu from the aqueous phase into the organic phase.

After this organic loading step, the organic and aqueous phases are separated. The Cu^{++} -depleted raffinate is sent back to leach to pick up more Cu^{++} . The Cu-loaded organic phase is sent forward to a 'strip' mixer-settler where its Cu is stripped into Cu^{++} -depleted aqueous electrolyte.

The strip reaction is the reverse of Reaction 18.1, i.e.:



It is pushed to the right by the high sulfuric acid concentration of the aqueous electrolyte. It strips Cu from the organic extractant and enriches the electrolyte to its desired high- Cu^{++} concentration.

In summary, the organic extractant phase is:

- loaded with Cu from weak H_2SO_4 pregnant leach solution
- separated from the pregnant leach solution
- contacted with strong H_2SO_4 electrolyte and stripped of its Cu.

It is the different H_2SO_4 strengths of pregnant leach solution and electrolyte which make the process work.

18.3 Extractants

The organic extractants used for Cu are oximes, Fig. 18.2. Two classes are used: aldoximes and ketoximes, Table 18.1. They are dissolved in petroleum distillate to produce an organic phase, 8 to 20 volume% extractant. This organic is (i) immiscible with $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ solutions and (ii) fluid enough (viscosity = 0.01 to 0.02 kg/m·s) for continuous mixing, gravity separation and pumping around the solvent extraction circuit.

A successful Cu-extractant for any leach project must (Kordosky, 1992; Kordosky *et al.*, 1999):

- efficiently extract Cu from the project's pregnant leach solution
- efficiently strip Cu into the project's electrowinning electrolyte
- have economically rapid extraction and strip kinetics
- disengage quickly and completely from leach solution and electrolyte, i.e. not form a stable emulsion

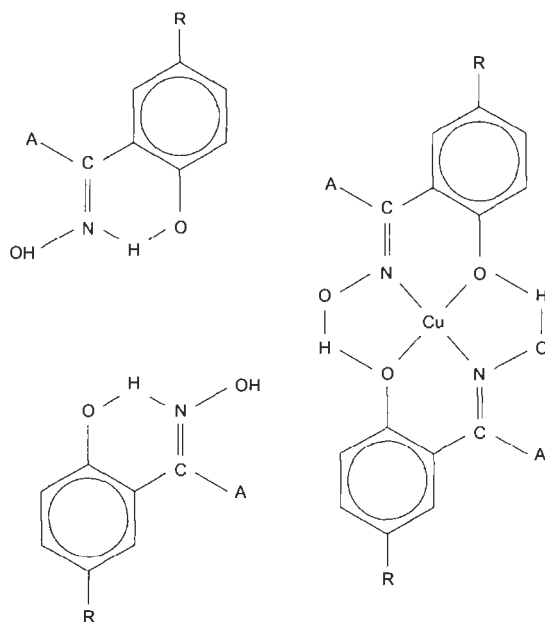


Fig. 18.2. Oxime molecules and copper complex. The copper complex is formed from two oxime molecules, Eqn. 18.1. Aldoximes: $\text{R} = \text{C}_9\text{H}_{19}$ or $\text{C}_{12}\text{H}_{25}$, $\text{A} = \text{H}$. Ketoxime: $\text{R} = \text{C}_9\text{H}_{19}$, $\text{A} = \text{CH}_3$ (Dalton *et al.*, 1986; Kordosky *et al.*, 1999).

- (e) be insoluble in the project's aqueous solutions
- (f) be stable under extraction and strip conditions so that it can be recycled many times
- (g) not absorb sulfuric acid
- (h) extract Cu preferentially over other metals in the pregnant leach solution, particularly Fe and Mn
- (i) not transfer deleterious species from pregnant leach solution to electrolyte, particularly Cl
- (j) be soluble in an inexpensive petroleum distillate diluent
- (k) be nonflammable, nontoxic and non-carcinogenic.

Ketoxime and aldoxime extractants satisfy these requirements.

18.3.1 Ketoximes vs aldoximes

Ketoximes have a methyl (CH_3) group for A in Fig. 18.2. Aldoximes have hydrogen.

Ketoximes are relatively weak extractants with excellent physical properties, Table 18.1.

Table 18.1. Properties of Cu solvent extraction extractants (Kordosky *et al.*, 1999). Aldoxime-ketoxime extractants are customized by adjusting their relative quantities.

Property	Ketoxime	Aldoxime with modifier	Aldoxime-ketoxime mixtures, no modifiers
Extractive strength	moderate	strong	customized
Stripping ability	very good	good	customized
Cu/Fe selectivity	excellent	excellent	excellent
Cu extraction and stripping speed	fast	very fast	fast
Phase separation speed	very fast	very fast	very fast
Stability	very good	very good*	very good
Crud generation**	low	variable	low
Examples	LIX 84-I	LIX 622 (tridecanol modified) Acorga M5640 (ester modified)	LIX 984N

* Depends on modifier. **Depends on pregnant leach solution and modifier.

Aldoximes are strong extractants. However, their Cu can only be stripped by contact with 225+ kg H₂SO₄/m³ electrolyte. This level of acid is too corrosive for industrial electrowinning. It also tends to degrade the extractant. For these reasons, aldoximes are only used when mixed with ketoximes or modifiers, e.g. highly branched alcohols or esters.

The most common extractants in 2002 are ketoxime-aldoxime and ester-modified aldoxime solutions.

18.3.2 Diluents

Undiluted ketoxime and aldoxime extractants are thick, viscous liquids. They are totally unsuitable for pumping, mixing and phase separations. They are, for this reason, dissolved 8 to 20 mass% in moderately refined high flash point petroleum distillate (purified kerosene), hydrogenated to avoid reactive double bonds (Bishop *et al.*, 1999).

Commercial diluents typically contain ~20 volume% alkyl aromatics, ~40% naphthenes and ~40% paraffins (Chevron Phillips, 2002).

18.3.3 Rejection of Fe and other impurities

An efficient extractant must carry Cu forward from pregnant leach solution to electrolyte while *not* forwarding impurities, particularly Fe, Mn and Cl. This is a critical aspect of efficient electrowinning of high purity copper. Fortunately, ketoxime and aldoxime extractants have small solubilities for these impurities. Ester-modified aldoximes are especially good in this respect (Cupertino *et al.*, 1999, Kordosky *et al.*, 1999).

Impurities may, however, be carried forward to electrolyte in droplets of pregnant leach solution in the Cu-loaded organic. This carryover can be minimized by (i) coalescing the pregnant solution droplets on polymer scrap; (ii) filtering and (iii) washing the loaded organic (Jenkins *et al.*, 1999).

18.4 Industrial Solvent Extraction Plants

Solvent extraction plants are designed to match the rate at which Cu is leached in the preceding leach operation. They vary in capacity from 20 to 600 tonnes of Cu per day. Table 18.2 gives operational details of five solvent extraction plants. Additional details are given in Jenkins *et al.*, 1999.

The key piece of equipment in a solvent extraction plant is the mixer-settler, Fig. 18.3 (Lightnin, 2002). Mixer-settler operation consists of:

- (a) pumping aqueous and organic phases into a mixer at predetermined rates

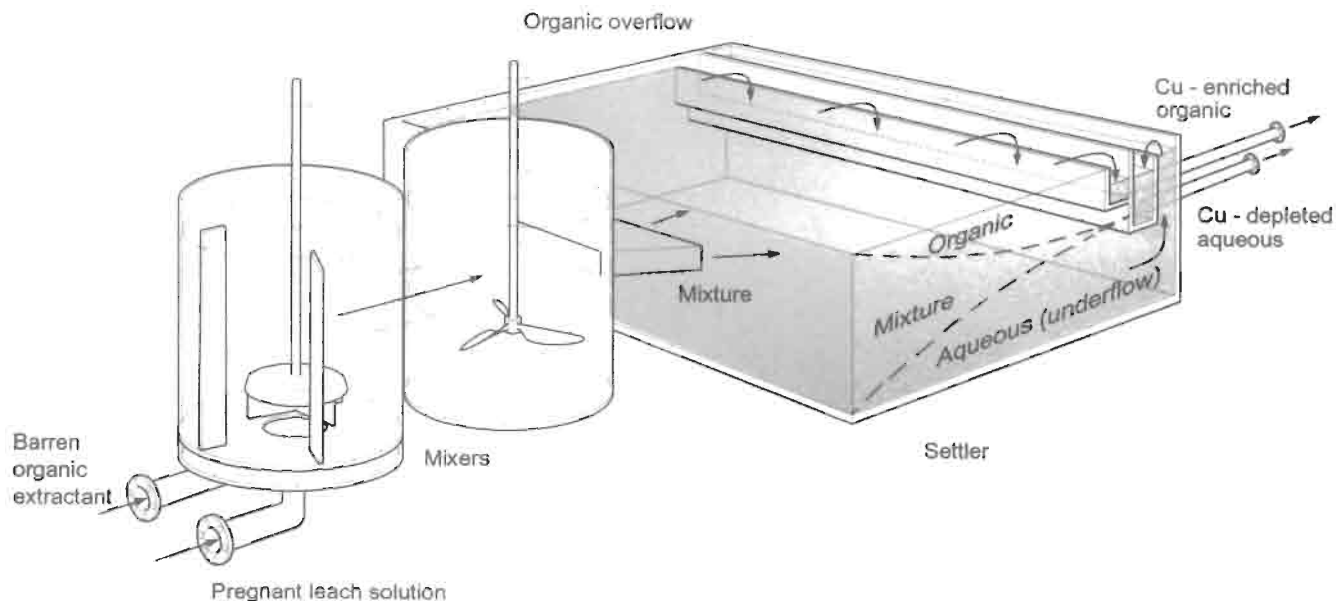


Fig. 18.3. Copper solvent extraction mixer-settler. The two mixing compartments, the large settler and the organic overflow/aqueous underflow system are notable. Flow is distributed evenly in the settler by picket fences (not shown), Table 18.2.

Table 18.2. Details of five Cu solvent extraction plants, 2001. Details of the

Operation	Cerro Colorado		El Abra	
Startup date	1994		1996	
Cathode production, tonnes/year	130 000		218 000	
Total pregnant solution input rate, m ³ /hour	4000		5000-7500	
SX plant details				
plant type	series		2 series	
			2 series-parallel	
number of SX 'trains'	5		4	
extraction mixer-settlers per train	2		series 2; series-parallel 3	
strip mixer-settlers per train	1		series 2; series-parallel 1	
Mixer-settler details				
Mixers				
round or square	square		square	
number of mixing compartments	3		3	
compartment size: depth × width × length, m			3.1 × 3.7 × 12.7	
mixer system	Lightnin pump mixer		suction mixer	
	77030			
construction materials	316 stainless steel		polymer concrete	
liquids residence time, minutes	3		2.4	
Settler				
length × width × depth, m	22 × 22 × 0.9		28 × 29 × 1.1	
flow distributor system	2 picket fences		2 picket fences	
construction materials	HDPE-lined concrete		HDPE-lined concrete	
organic depth, m	0.28-0.3		0.27	
aqueous depth, m	0.45		0.63	
estimated residence time, minutes	4			
estimated phase separation time, minutes	3		3	
Organic details				
extractant	LIX 860-NIC/LIX 84-IC		PT5050-LIX 984NC	
volume% in organic diluent	13		21.4%L1, 15.8% L2	
diluent	Orform SX-12		Conosol 170ES	
organic washing?	no wash		water wash to pH 1.1	
aqueous removal from organic	none		Wemco coalescers	
crud removal system	pneumatic pump		pneumatic pump	
crud treatment system	Chuquicamata mechanical		centrifuge and pressure	
	breakage		filter	
organic cleaning system	clay treatment with		zeolite treatment	
	Sparkle filter			
organic removal from raffinate	skimmer		Wemco coalescers	
Flowrates per train, m ³ /hour				
pregnant solution input rate	750		1400 series	
			2400 series-parallel	
organic flowrate, extraction to strip	1040		1500-1650	
depleted electrolyte input rate	180		450-500	
% of electrolyte flow sent to SX	18		25	
Solution details, kg/m ³	Cu	H ₂ SO ₄	Cu	H ₂ SO ₄
pregnant solution	4.8	5	4.94	6.44
raffinate	0.4	11	0.70	12.10
barren organic	3		3.33	
loaded organic	5.6		7.40	
depleted electrolyte	37	180	36.33	171.41
enriched electrolyte	52	159	40.29	170.9
organic removal from electrolyte	none		Wemco pacesetter	
			coalescence	
electrolyte treatment before tankhouse	garnet/anthracite filtration		sand/garnet/anthracite	
			filtration	

equivalent leach and electrowinning plants are given in Chapters 17 and 19.

Zaldivar		Hellenic Copper		Morenci (Stargo)	
1995		1996		1998	
145 000		8000		156 000	
4800		520		4320	
series		series-parallel		series-parallel	
4		1		1	
2		2		3	
1		1		1	
round		square		round	
2		2		3	
Outokumpu VSF mixers		Davy impeller		5 diameter, 3.2 high Outokumpu Spirok and Dop pump mixers	
Ti & 316L stainless steel		316L stainless steel		stainless steel	
		2		3	
23.5 × 25 × 0.9		22 × 9 × 1		24 × 26 × 1.25	
1 distributor, 1 picket fence		1 picket fence		3 picket fences	
HDPE-lined concrete		316L stainless steel		316L stainless steel	
0.25-0.3		0.3		0.425	
		0.7		0.375	
15		15		12	
		0.5		70 seconds	
LIX 984 NC		Acorga M5640		LIX 984	
14.3		8		21	
Orform SX 12		Escaid 110		Conosol 170	
one wash mixer-settler		no wash		1 wash stage mixer-settler	
8 Dissep garnet/antracite filters		aqueous entrainment pumps in loaded organic tank		drain loaded organic tank	
diaphragm pump		2.5 cm diaphragm pump		interface pumping and settler dumping	
centrifuge		bentonite mixing-recovery		clay mixing and filter press	
clay treatment + centrifuge + clay filter		filter press		clay mixing and filter press	
floating absorption system		pumping from pond		skimmed from organic recovery tanks	
1200		520		4320	
1100				2160	
350				1250	
21		20		65	
Cu	H ₂ SO ₄	Cu	H ₂ SO ₄	Cu	H ₂ SO ₄
3.8	0.55	1.8	1	3.00	3.50
0.28	6	0.2	4	0.30	7.00
3		1.3		3.80	
7.2		3.8		9.80	
41.5	165	30	180	38.0	200.0
55	151	38	160	50.0	185.0
				organic is floated from rich booster tank	
Cominco column flotation		sand/antracite filters and heat exchanging		6 antracite garnet filters	
Dissep sand/antracite filters					

- (b) mixing the aqueous and organic with impellers
- (c) overflowing the mixture from the mixer through flow distributors into a flat settler where the aqueous and organic phases separate by gravity (organic and aqueous specific gravities, 0.85 and 1.1 respectively [Spence and Soderstrom, 1999])
- (d) overflowing the organic phase and underflowing the aqueous phase at the far end of the settler.

Typical mixer-settler aqueous and organic flowrates are 500-4000 m³ per hour (each).

The *mixer* is designed to create a well-mixed aqueous-organic dispersion. Modern mixers consist of two or three mixing chambers. They create the desired dispersion and smooth forward (plug) flow into the settler. Mixer aqueous/organic contact times are 2 to 3 minutes – which brings the liquids close to equilibrium. Entrainment of very fine droplets is avoided by using low tip-speed (<400 m/minute) impellers (Spence and Soderstrom, 1999).

The *settler* is designed to separate the dispersion into separate aqueous and organic layers. It:

- (a) passes the dispersion through one or two flow distributors (picket fences or screens) to give smooth, uniform forward flow
- (b) allows separate layers to form as the dispersion flows smoothly across the large settler area.

The vertical position of the aqueous-organic interface is controlled by an adjustable weir at the far end of the settler. It avoids accidentally overflowing aqueous or underflowing organic.

Modern settlers are square in plan. This shape is the best for smooth flow and an adequate residence time. Liquid residence times in the settlers are 10 to 20 minutes, Table 18.2. This time is sufficient to guarantee complete phase separation (laboratory separations occur in 0.5 to 2 minutes [Spence and Soderstrom, 1999]). The aqueous phase is ~0.5 m deep. The organic phase is ~0.3 m deep. Advance velocities are typically 1 to 5 m per minute.

18.4.1 'Trains'

2002 solvent extraction plants consist of one to four identical solvent extraction circuits ('trains') – each capable of treating 500 to 4000 m³ of pregnant solution per minute. Each train transfers 20-250 tonnes of Cu from pregnant solution to electrolyte per day, depending on the Cu content and flowrate of the pregnant solution.

18.4.2 Circuit design

Most copper solvent extraction is done in series circuits, Fig. 18.4. The two extraction mixer-settlers typically transfer ~90% of Cu-in-pregnant-leach-solution to the extractant (Jenkins *et al.*, 1999). The remaining Cu is not lost. It merely circulates around the leach circuit.

The single strip mixer-settler strips 50% to 65% of the Cu-in-loaded-organic into electrolyte. The remainder circulates around the solvent extraction circuit, Fig. 18.4. These transfer efficiencies can be increased by adding extraction and strip mixer-settlers to the circuit. However, the 2 extraction, 1 strip mixer-settler configuration predominates.

18.5 Quantitative Design of Series Circuit

This section describes the preliminary design of a series solvent extraction circuit. It is based on the data in Table 18.3 and Fig. 18.4.

Table 18.3. Preliminary specifications for design of solvent extraction circuit. They are also given in Fig. 18.4.

Circuit type	series: 2 extraction mixer-settlers 1 strip mixer-settler expected extraction from pregnant solution into organic: 90%
Extractant	LIX 984N in Orfom SX 12 diluent Loads ~0.25 kg Cu/m ³ per volume% LIX 984N in organic (Cognis, 1997)
Specified organic/aqueous ratio in extraction mixer-settlers (A/O)	1/1 (m ³ organic per hour/m ³ aqueous per hour)*
Expected pregnant leach solution composition and input rate	3 kg Cu/m ³ , 1000 m ³ /hour
Specified composition of Cu depleted electrolyte from tankhouse	35 kg Cu/m ³ (sufficient to give high-purity cathode copper at electrowinning cell exits)
Specified composition of Cu-enriched electrolyte returning to tankhouse	45 kg Cu/m ³
Stripping data from laboratory tests (Cognis, 1997)	45 kg Cu/m ³ in enriched electrolyte is at equilibrium with ~1.5 kg Cu/m ³ in stripped organic

*O/A ratios of ~1 permit easy switching between aqueous-continuous and organic-continuous operation. Industrial O/A ratios are discussed in Biswas and Davenport (1994).

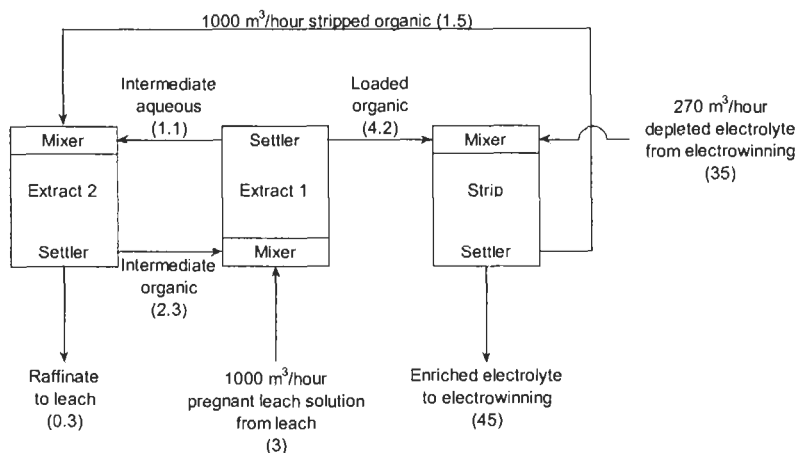


Fig. 18.4. Plan view of series solvent extraction circuit. The bracketed numbers are Cu concentrations in kg Cu/m³. Industrial mixer-settlers are tight against each other to minimize plant area and flow distances. Note the two extraction mixer-settlers (Extract 1 and Extract 2) and one strip mixer-settler. This is the most common arrangement (Jenkins *et al.*, 1999). Flowrates and Cu concentrations are those in Table 18.3.

18.5.1 Percent extractant in organic

LIX 984N extracts up to:

0.25 kg Cu per m³ of organic phase per volume% LIX 984N in the organic

(Cognis, 1997). The LIX 984N strength which will extract a specified amount of Cu is calculated by the mass balance:

$$\begin{aligned}
 & \frac{0.25 \text{ kg of Cu extracted}}{\text{per m}^3 \text{ of organic per volume\% LIX 984 in the organic}} \times \frac{\text{volume\% LIX 984}}{\text{in the organic}} \times \frac{\text{volumetric flowrate}}{\text{of organic, m}^3/\text{hour}} \\
 &= \frac{\text{required Cu extraction from}}{\text{pregnant leach solution into organic,}} \times \frac{\text{volumetric flowrate of}}{\text{pregnant leach solution, m}^3/\text{hour}} \quad (18.3) \\
 & \quad \text{kg Cu/m}^3 \text{ of pregnant leach solution}
 \end{aligned}$$

or:

$$\text{volume\% LIX 984N in organic} = \frac{\text{required Cu extraction from pregnant leach solution}}{0.25} \times \text{A/O.}$$

(where A/O is the aqueous/organic volumetric ratio entering the extraction mixer-settler).

Extraction of Cu from a 3 kg Cu/m³ pregnant leach solution with the Table 18.3-prescribed A/O volume ratio of 1/1 requires, therefore:

$$\text{volume\% LIX 984N in organic} = \frac{3}{0.25} \times 1 = 12\%$$

So each train of the solvent extraction plant requires pumping of 1000 m³/hour of 12 volume% LIX 984N in Orfom SX 12 diluent.

This calculation is the first step in choosing the organic phase for a proposed solvent extraction circuit. The chosen organic must then be tested with actual leach and electrowinning solutions to ensure suitability for the proposed operation.

18.5.2 Extraction efficiency

Under the dynamic conditions of two industrial mixer-settlers in series, Cu extraction from pregnant leach solution is about 90% (Jenkins *et al.*, 1999). In the case of a 3 kg Cu/m³ pregnant solution, the raffinate leaving the series of two extraction mixer-settlers will contain ~ 0.3 kg Cu/m³ of raffinate, Fig. 18.4.

18.5.3 Rate of Cu extraction into organic

The overall rate at which Cu is extracted into the solvent extraction organic phase is given by the equation:

$$\text{Cu extraction rate} = \frac{\text{leach solution flow rate, m}^3/\text{hour}}{\text{m}^3/\text{hour}} \times \left[\text{Cu in pregnant solution} - \text{Cu in raffinate} \right] \quad (18.4).$$

In this case it is:

$$\begin{aligned} \text{Cu extraction rate} &= \frac{1000 \text{ m}^3/\text{hour}}{\text{leach solution}} \times \left[\begin{array}{l} 3 \text{ kg Cu/m}^3 \\ \text{of pregnant} \\ \text{leach solution} \end{array} - \begin{array}{l} 0.3 \text{ kg Cu/m}^3 \\ \text{of raffinate} \end{array} \right] \\ &= 2700 \text{ kg Cu/hour.} \end{aligned}$$

This is also the overall rate at which metallic copper will have to be plated in the electrowinning plant. It allows the electrowinning designer to calculate the cathode area and current density for the proposed electrowinning plant.

18.5.4 Equilibrium strip Cu concentrations

The sulfuric acid concentration in depleted electrolyte is very high ($\sim 185 \text{ kg H}_2\text{SO}_4/\text{m}^3$ of electrolyte). This causes copper to strip from the solvent extraction organic into the electrolyte. Table 18.3 indicates that:

the 45 kg Cu/m³ electrolyte specified for return to the electrowinning tankhouse will be at equilibrium with:

$\sim 1.5 \text{ kg Cu/m}^3$ organic (12% LIX 984N in Orfom 12).

These concentrations are shown in Fig. 18.4. The precise equilibrium values would need to be determined with the project's actual electrolyte.

18.5.5 Electrolyte flowrate into the strip mixer-settler

Section 18.5.3 indicates that the electrowinning plant must plate 2700 kg metallic copper per hour. From the strip mixer-settler point of view, it means that 2700 kg of Cu per hour must be transferred to electrolyte.

This, and the Table 18.3-specified depleted and enriched electrolyte compositions (35 and 45 kg Cu/m³), permit calculation of the rate at which electrolyte must flow into and out of the strip mixer-settler, i.e.:

$$\begin{aligned} \text{electrowinning} \\ \text{rate} \\ \text{kg Cu/hour} &= \\ &\text{electrolyte flowrate} \times \left[\begin{array}{l} \text{Cu in electrolyte} \\ \text{to and from solvent} \\ \text{extraction, m}^3/\text{hour} \end{array} \times \begin{array}{l} \text{leaving solvent} \\ \text{extraction, kg Cu/m}^3 \end{array} - \begin{array}{l} \text{Cu in electrolyte} \\ \text{entering solvent} \\ \text{extraction, kg Cu/m}^3 \end{array} \right] \end{aligned}$$

from which the electrolyte flowrate in and out of the strip mixer-settler is:

$$\text{electrolyte flowrate} = \frac{2700 \text{ kg Cu/hour}}{(45 - 35) \text{ kg Cu/m}^3 \text{ of electrolyte}} = \frac{270 \text{ m}^3 \text{ of electrolyte}}{\text{per hour}}$$

Figure 18.4 summarizes flows and Cu concentrations in the newly designed plant.

18.6 Stability of Operation

Industrial solvent extraction circuits are easily controlled and forgiving.

Consider, for example, how the Section 18.5 circuit responds to an increase in Cu concentration in pregnant leach solution (which would happen if easily-leached ore is encountered in the mine). Suppose that the pregnant solution improves from the 3 kg Cu/m^3 in Fig. 18.4 to 3.3 kg Cu/m^3 .

Copper extraction from the extra 0.3 kg Cu/m^3 will probably be about 65% instead of 90% so that:

- (a) the raffinate will contain 0.4 kg Cu/m^3 rather than 0.3 kg Cu/m^3
- (b) 2900 kg of Cu will be transferred to organic in the extraction mixer-settlers, Eqn. (18.4).

The resulting flows and Cu concentrations are shown in Fig. 18.5.

Of course, the rate at which copper is being plated will also have to be increased to $2900 \text{ kg copper per hour}$. This can be done by increasing current density and by bringing unused cells into operation.

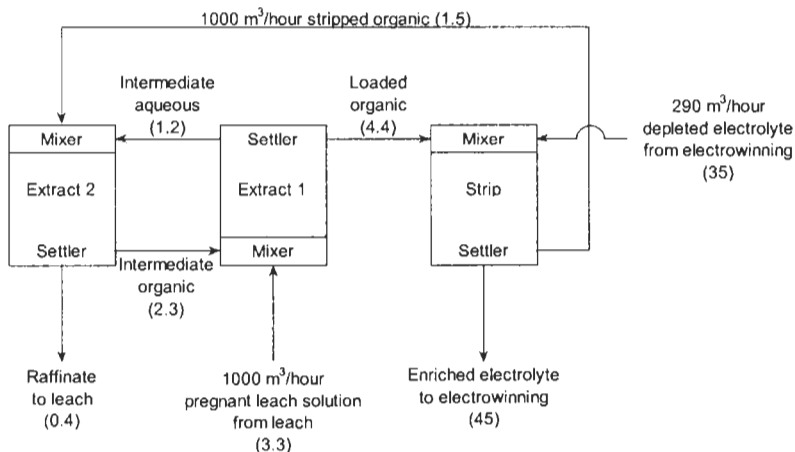


Fig. 18.5. Solvent extraction circuit that has been perturbed by receiving 3.3 kg Cu/m^3 pregnant leach solution instead of 3 kg Cu/m^3 pregnant leach solution, Fig. 18.4. It is assumed that Cu electrowinning rate has been increased (by increasing current density) to match the rate at which Cu is being transferred from pregnant leach solution to electrolyte. Note that the only operating variable that has to be changed is electrolyte recycle rate.

If electrowinning is already at its maximum plating rate, the rate that lixiviant is being applied to the ore heaps will have to be slowed from 1000 m³ per hour to 930 m³ per hour and the organic flowrate will have to be decreased to match. This will bring net leaching rate, organic extraction rate, electrolyte stripping rate back to 2700 kg Cu/hour, matching the electrowinning plant's maximum plating rate.

18.6.1 Series-parallel circuit

A recently adopted solvent extraction circuit is the series-parallel circuit shown in Appendix D. This circuit doubles the rate at which pregnant leach solution enters the solvent extraction system. Overall, it increases the rate at which Cu is transferred from pregnant leach solution to electrolyte.

Its disadvantage is that its efficiency of extracting Cu from pregnant leach solution into organic is lower than that of a series circuit. This is because:

- (a) the parallel portion of the pregnant leach solution goes through only one extraction mixer-settler before returning to leach
- (b) the series portion of the pregnant leach solution mixes with partially Cu-loaded organic solution (from the parallel mixer-settler, Appendix D) rather than low-Cu stripped organic, Fig. 18.4.

The series/parallel circuit is a low cost way of increasing the productivity of an existing series plant. It is probably not the best option for a new plant.

18.7 'Crud'

An occasional problem in solvent extraction is 'crud'. Crud is a semi-solid formed from pregnant leach solution solids, colloidal silica, vegetation, mold, organic degradation precipitates and minor organic constituents (Spence and Soderstrom, 1999; Virnig *et al.*, 1999).

It usually forms a layer at the settler aqueous/organic interface – preventing efficient aqueous/organic disengagement.

Crud is removed from the settler by vacuum pumping or by emptying the settler and pumping the crud from the settler floor (Jenkins *et al.*, 1999).

It is separated from its host organic (Jenkins *et al.*, 1999) by:

- (a) centrifuging or filtering (with or without breaking up the solids)
- (b) washing out the liquid with diluent, organic or water

- (c) mixing the crud with clay, then centrifuging or filtering.

The crud solids are sent to the leach heaps.

The host organic is rejuvenated by mixing it with bentonite clay or zeolite then filtering. The organic is then returned to the solvent extraction circuit.

Crud formation is minimized by minimizing the amount of solids in the pregnant leach solution. This is done by allowing the pregnant solution to settle in ponds and by directing rain runoff away from pregnant solution collection areas.

It is also minimized by (i) avoiding crud-forming electrowinning addition agents and by (ii) using crud-inhibiting extractants, Table 18.3.

18.8 Summary

Solvent extraction transfers dissolved Cu from low-Cu⁺⁺, impure pregnant leach solutions to high-Cu⁺⁺, pure electrowinning electrolytes. It is a crucial step in producing high purity electrowon copper from leached ores.

As applied to copper, the process consists of:

- (a) extracting Cu from aqueous pregnant leach solution into an organic extractant
- (b) separating the aqueous and organic phases by gravity
- (c) stripping Cu from the organic extractant into high-H₂SO₄ electrowinning electrolyte.

The process is done continuously in large mixer-settlers.

Loading of Cu into the organic extractant is favored by the low acid concentration (0.5 to 5 kg/m³ H₂SO₄) of the pregnant leach solution. Stripping of Cu from the organic extractant is favored by the high acid concentration (170-200 kg/m³ H₂SO₄) of the electrolyte.

The organic extractants used throughout the copper industry are aldoximes and ketoximes, 8 to 20 volume% in petroleum distillate. The two are often mixed to give optimum extraction, strip and phase separation properties. Ester modified aldoximes are also used extensively.

About 2.5 million tonnes of Cu per year pass through solvent extraction in preparation for electrowinning. This production continues to grow as more and more ore is being leached.

Suggested Reading

Cupertino, D.C., Charlton, M.H., Buttar, D., Swart, R.M. and Maes, C.J. (1999) A study of copper/iron separation in modern solvent extraction plants. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 263 276.

Jenkins, J., Davenport, W.G., Kennedy, B. and Robinson, T. (1999) Electrolytic copper – leach, solvent extraction and electrowinning world operating data. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 493 566.

Jergensen, G.V. (1999) *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, SME, Littleton, CO.

Kordosky, G.A., Sudderth, R.B. and Virnig, M.J. (1999) Evolutionary development of solvent extraction reagents: real life experiences. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 259 271.

Spence, J.R. and Soderstrom, M.D. (1999) Practical aspects of copper solvent extraction from acidic leach liquors. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 239 257.

Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G. (1999) *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV Hydrometallurgy of Copper*, TMS, Warrendale, PA.

References

Bishop, M.D., Gray, L.A., Greene, M.G., Bauer, K., Young, T.L., May, J., Evans, K.E. and Amerson-Treat, I. (1999) Investigation of evaporative losses in solvent extraction circuits. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 277 289.

Biswas, A.K. and Davenport, W.G. (1994) *Extractive Metallurgy of Copper, 3rd Edition*, Elsevier Science Press, New York, NY, 394 395.

Chevron Phillips (2002) Orfom SX 12 Solvent Extraction Diluent www.cpchem.co (Mining chemicals, Orfom SX 12)

Cognis (1997) *The Chemistry of Metals Recovery Using LIX Reagents (MID Redbook)*, Cognis Corporation, Tucson, AZ www.cognis.com

Cupertino, D.C., Charlton, M.H., Buttar, D., Swart, R.M. and Maes, C.J. (1999) A study of copper/iron separation in modern solvent extraction plants. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 263 276.

Dalton, R.F., Severs, K.J. and Stephans, G. (1986) Advances in solvent extraction for copper by optimized use of modifiers. Paper presented at Mining Latin America, Chile, November 1986.

Jenkins, J., Davenport, W.G., Kennedy, B. and Robinson, T. (1999) Electrolytic copper – leach, solvent extraction and electrowinning world operating data. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference. Vol. IV Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 493 566.

Kordosky, G.A. (1992) Copper solvent extraction: the state of the art. *Journal of Metals*, **44**(5), 40 45.

Kordosky, G.A., Sudderth, R.B. and Virnig, M.J. (1999) Evolutionary development of solvent extraction reagents: real life experiences. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 259 271.

Lightnin (2002) Solvent extraction. www.lightnin-mixers.com (Your industry, Mining and minerals, Solvent extraction)

Spence, J.R. and Soderstrom, M.D. (1999) Practical aspects of copper solvent extraction from acidic leach liquors. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 239 257.

Virnig, M.J., Olafson, S.M., Kordosky, G.A. and Wolfe, G.A. (1999) Crud formation: field studies and fundamental studies. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 291 304.

CHAPTER 19

Electrowinning

(Written with Tim Robinson, CTI Ancor, Phoenix, AZ)

Chapters 17 and 18 show how leaching and solvent extraction produce $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte with $\sim 45 \text{ kg/m}^3 \text{ Cu}^{++}$. This chapter shows how the Cu^{++} in this electrolyte is electrowon as pure metallic copper.

Electrowinning entails:

- (a) immersing metal cathodes and inert (but conductive) anodes in $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte
- (b) applying an electrical potential between the anodes and cathodes
- (c) plating pure metallic copper from the electrolyte onto the cathodes.

Industrially, the anodes are rolled Pb-alloy sheets. They are nearly inert, but corrode slowly.

The cathodes are stainless steel blanks. In older plants the cathodes may be thin copper 'starter sheets'.

Copper is electroplated on the cathodes for about one week, after which:

- (a) the plated copper is machine-stripped from the stainless steel cathode blanks, washed and sent to market

or:

- (b) the entire copper 'starter sheet' cathode is washed and sent to market.

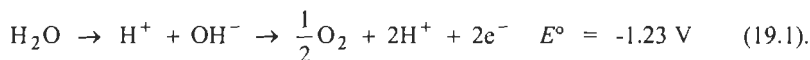
About 2.5 million tonnes of copper are electrowon per year. Production continues to increase due to the growth of ore leaching.

19.1 Electrowinning Reactions

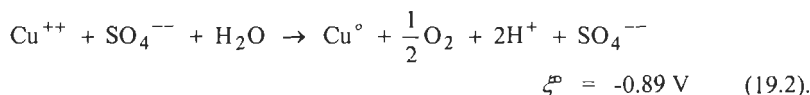
The electrowinning cathode reaction is the same as in electrorefining, i.e.:



The anode reaction is, however, completely different. It is formation of oxygen gas at the inert anode:



The overall electrowinning reaction is the sum of Reactions (16.2) and (19.1) plus sulfate ions:



The electrowinning products are:

- (a) pure copper metal at the cathode
- (b) oxygen gas at the anode
- (c) regenerated sulfuric acid in the solution.

The copper is stripped, washed and sent to market. The oxygen enters the atmosphere. The acid is recirculated to solvent extraction in Cu-depleted electrolyte where its H^{+} exchanges with fresh Cu^{++} , Eqn. (18.2).

The electrical potential needed for electrowinning is ~2 volts as compared to ~0.3 volt for electrorefining. It is made up of:

theoretical voltage for Reaction (19.2)	~0.9 V
oxygen deposition overvoltage	~0.5 V
copper deposition overvoltage	~0.05 V
electrical resistance @ 300 A/m ² cathode current density	~0.5 V.

The energy requirement for electrowinning, ~2000 kWh/tonne of copper, is also considerably greater than that for electrorefining, 300-400 kWh/tonne of copper. This difference is due to electrowinning's large voltage requirement.

19.2 Electrowinning Tankhouse Practice (Fig. 19.1, Table 19.1)

Electrowinning differs from electrorefining mainly in:

- (a) its use of inert Pb-alloy anodes instead of soluble copper anodes
- (b) its higher applied voltage.

Its use of inert anodes means that (i) the anodes remain in the cells for 5+ years, (ii) there is little anode scrap and (iii) no precious metal slimes.

The electrolytic cells, anodes and cathodes are approximately the same size as their electrorefining counterparts, i.e.:

cells:	polymer concrete, 6.5 m long $\times$ 1.2 m wide $\times$ 1.5 m deep
anodes:	rolled Pb-Sn-Ca alloy, 1.1 m long $\times$ 0.9 m wide $\times$ 0.006 m thick
cathodes:	stainless steel, 1.2 m long $\times$ 1.0 m wide $\times$ 0.003 m thick.

Modern cells are polymer concrete. Older cells are concrete with polyvinyl chloride linings.

The anodes and cathodes are interleaved as in electrorefining, Fig. 19.1. The anodes in a cell are all at one potential. The cathodes are all at another, lower potential. Anodes and cathodes are usually separated by several polymer spacer knobs. This minimizes lead corrosion product carryover from anodes to electrodepositing copper.

Hollow polyethylene balls (~2 cm diameter) are usually floated, 5 to 10 cm deep, on the electrolyte along with fluorocarbon surfactant. They suppress sulfuric acid mist that is generated by oxygen bubbles forming on the anode and bursting at the electrolyte surface. Polypropylene BB's, 0.3 cm diameter, 0.15 cm long, are also used.

Mechanical mist suppressant systems, such as polymer brushes around the anode tops are also occasionally used to minimize sulfuric acid mist generation (Pfalzgraff, 1999). In some plants the mist is cleared from the workplace by large blowers.

Electrolyte flows continuously from an active storage tank into each cell through a manifold around the bottom of the cell, Fig. 19.1. It overflows the cell into a collection system and eventual recycle to solvent extraction for Cu^{++} replenishment. It is added at ~0.2 m³/minute into each cell, Table 19.1. This gives constant availability of warm, high Cu^{++} electrolyte over the surfaces of all the cathodes.

The plating period is ~7 days. The grown cathodes in a cell are then removed and replaced by washed empty stainless steel blanks. About 30% are removed and replaced at a time without cutting off electrical power. This procedure maintains an adherent corrosion product layer on the lead alloy anodes, minimizing lead contamination of the electrodepositing copper. It also maximizes productivity.

19.2.1 Current density

Cathode current density is 280 to 340 amperes/m², Table 19.1 and Jenkins, *et al.*, 1999. This gives a plating rate of 0.5 to 0.25 kg of copper per hour on each cathode.

Copper plating rate increases with increasing current density. However, excessive current density gives rough, nodular cathode deposits and decreased copper purity. Each plant chooses its current density as a balance between these opposing factors.

19.2.2 Anodes

Electrowinning anodes are almost always cold rolled Pb-Sn-Ca alloy containing about:

98.4% Pb (oxygen scavenged prior to alloying)
1.5% Sn
0.1% Ca.

Sn provides corrosion resistance and corrosion layer conductivity. Ca and cold rolling add strength (Prengaman and Siegmund, 1999).

The Pb-Sn-Ca blades are soldered onto slotted copper hanger bars for support in the electrolytic cells. Lead is then electrodeposited around the joints to protect them from corrosion.

The Pb-Sn-Ca alloy forms an adherent corrosion layer. This minimizes Pb contamination of the cathode copper and extends anode life.

19.2.3 Cathodes

Most electrowinning tankhouses employ re-usable 316L stainless steel blank cathodes. They are virtually identical to electrorefining cathodes, Section 16.4.

A few older tankhouses use copper starter sheet cathodes, Section 16.4. The starter sheets are obtained from an electrorefinery or are made in the electrowinning itself. As with refining, these older plants are switching to stainless steel (Addison *et al.*, 1999).

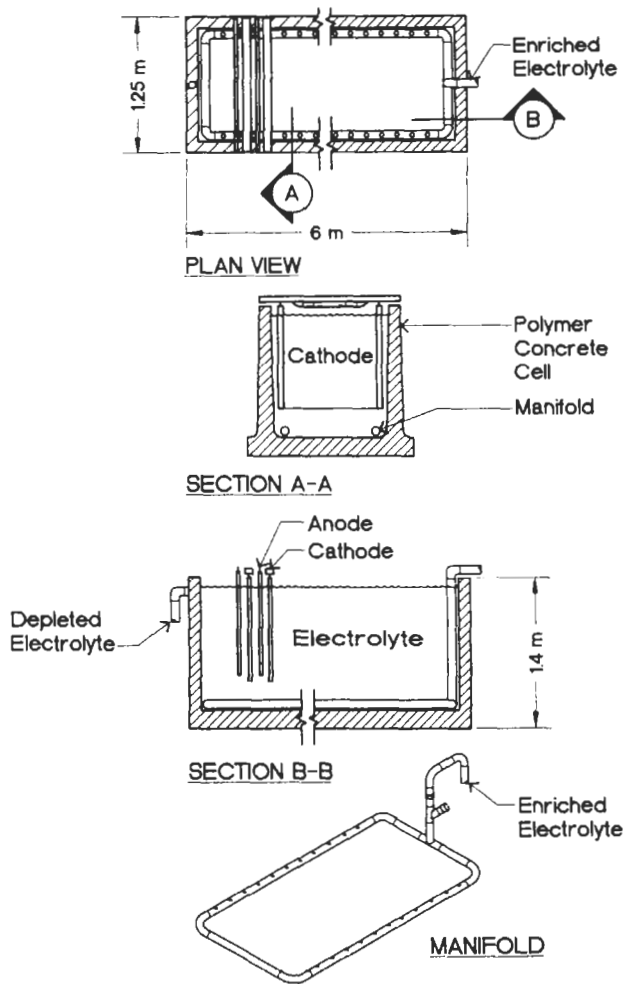


Fig. 19.1. Top, end and side views of electrowinning cell (after Jenkins and Eamon, 1990). An electrolyte input manifold for uniformly distributing electrolyte over all the cathode faces is also shown. Single, multi-holed horizontal pipes on the cell floor are also used.

Table 19.1. Details of five Cu electrowinning plants, 2001.

Operation	Cerro Colorado	El Abra
Startup date	1994	1996
Cathode production, tonnes/year	130 000	218 000
Electrolytic cells		
total number	420	680
construction material	polymer concrete	polymer concrete
lining material	none	none
length × width × depth (inside), m	6.39 × 1.27 × 1.42	6.57 × 1.2 × 1.4
anodes, cathodes per cell	63, 62	67, 66
spacers between anodes & cathodes		'yo-yo' type
cell inspection system	OSI CP 1000	gaussmeter (once a day)
time between cell cleanouts, days	45	120
mist suppression system	BB's and ventilation	balls, FC 1100
electrolyte input arrangement	5.1 cm diameter bottom manifold with 120 six mm holes angled 45° up	PVC cell distributor with 7 mm holes 45° upward
Anodes		
material, %	98.4% Pb, 1.5% Sn, 0.08% Ca, 0.02% Al	98.585% Pb 1.35% Sn 0.065% Ca
cast or rolled	rolled	rolled
length × width × thickness	1.077 × 0.94 × 0.006	1.1 × 0.94 × 0.006
center-to-center spacing in cell	9.5	9.5
life, years	5	4-6
Cathodes		
type	ISA 316L stainless steel	Kidd 316L stainless steel
length × width × thickness	1 × 1 × ?	1.05 × 1.3 × 0.004
side edge strip material	PVC	polypropylene
bottom strip material	wax	none
plating time, days	7	6
mass Cu plated on each side of blank, kg	38-42	50
stripping method	Wenmec machine	Epcm/Aisco machine
impurities, ppm	Pb<3, S<5, Fe 1.8, Mn<4, Co<1, Ni<0.8, Sn<0.2	Pb<3, S<8
Power and energy		
cathode current density, A/m ²	280	300-340
cathode current efficiency, %	93	86
cell voltage, V	1.98-2	1.7-2.0
cell current, kiloamperes	33	35-45
kWh/tonne of Cu shipped	1890	1975
Electrolyte		
circulation rate into each cell, m ³ /minute	0.2	0.22
Into cells		
Cu, kg/m ³	41	44
H ₂ SO ₄ , kg/m ³	175	170
temperature, °C	50	43
out of cells		
Cu, kg/m ³	38	36
H ₂ SO ₄ , kg/m ³	180	183
temperature, °C	51	45
other electrolyte components		
Fe ²⁺ , kg/m ³	0.4	0.21
Fe ³⁺ , kg/m ³	1.5	1.5
Co ²⁺ , ppm	150	150
Cl ⁻ , ppm	20	35
Mn ²⁺ , ppm		38
addition rates, g per tonne of cathode		
guar gum	270	300-350
other	430	Co ²⁺ to 150 ppm
electrolyte treatments before entering tankhouse	gamet/anthracite filtration, heat exchange	
electrolyte bleed rate, m ³ /day	60	240
to control	Pb in cathodes	Cl ⁻ and Fe ³⁺
destination	raffinate pond	SX wash stage & other

Additional details are given in Jenkins *et al.*, 1999.

Zaldivar	Hellenic Copper	Morenci, Stargo
1995	1996	2000
145 000	5200	146 000
368	50	324
polymer concrete	precast monolithic concrete	CTI polymer concrete
none	paraliner	none
$6.7 \times 1.2 \times 1.5$	$3.48 \times 1.25 \times 1.5$	$6.98 \times 1.18 \times 1.37$
64/63	31/30	66/65
two 'butterflies' on bottom corners	polymer cones on bottom corners	vinyl-ester cap blocks
IR camera, twice daily	gaussmeter	IR camera, hand held
60	365	90
19 mm balls, FC 1100, ventilation manifold with 120 six mm holes	plastic balls	balls and FC 1100
	2 bottom distribution pipes with 30 six mm diameter holes, 30° from vertical	cell bottom manifold
98.6 Pb, 1.3 Sn, 0.08 Ca	98.4 Pb, 1.5 Sn, 0.1 Ca	98.5 Pb, 1 Sn, 0.5 Ca
rolled	rolled	rolled
$1.04 \times 0.93 \times 0.009$	$1.092 \times 0.92 \times 0.006$	$1.04 \times 0.914 \times 0.015$
10.1	10	10.2
5	5	7
ISA 316L stainless steel	ISA 316L stainless steel	ISA 316L stainless steel
$1.23 \times 1.03 \times 0.003$	$1.079 \times 1.036 \times 0.003$	$1.245 \times 0.99 \times 0.003$
polypropylene	CPVC	single durometer CPCV
wax	CPVC	none
5	7-10	7
40	50-60	43.2
Wenmcc/ISA machine	semi-automatic machine	Wenmcc machine
Pb<2, S<4, Fe<2	Pb<0.1, S 0.9, Fe 1.2, Mn<0.1, Co<0.1, Ni 0.2	Pb<3, S<4
317-326	150-275	290
91	88-92	93
1.9	1.8	2.1
42	10-18	45
1840	2000	1900
0.36	0.11	0.19
44	44	44
148	150	196
50	42	47.2
43	37	38
165	165	199
50	42	48.2
0.17	0.5	0.28
1.5	1.5	1.25
140	100	130
<5	30	30
	Mn 2	Mn 35, Pb 0.05
250	50	250
Co ⁺⁺ 800	Co ⁺⁺ to 100 ppm	Co ⁺⁺
Cominco column flotation, Dissep sand anthracite filters	dual media filter	anthracite/garnet filters, heat exchangers
300	30	25
	Cl, Fe	Fe and Mn
raffinate pond	pregnant leach solution	pregnant leach solution

19.2.4 Electrolyte

Electrowinning electrolyte typically contains 44 kg Cu⁺⁺ and 170 kg H₂SO₄ per m³ as it enters an electrowinning cell. It contains ~5 kg Cu⁺⁺ less per m³ as it leaves the cell.

Depleted electrolyte is replenished with Cu⁺⁺ by sending it back to solvent extraction where it strips Cu⁺⁺ from loaded organic extractant, Chapter 18. One quarter to one half of the circulating electrolyte is sent to solvent extraction. The remainder is sent to an active storage tank where it is mixed with enriched electrolyte returning from solvent extraction.

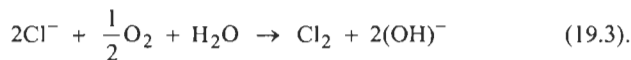
The enriched electrolyte from solvent extraction is filtered and treated in column or Jameson flotation cells before it re-enters the electrowinning tankhouse. It is also heated to 45 or 50°C by heat exchange with outgoing electrolyte.

19.2.5 Additives

All electrowinning plants dissolve guar gum in their electrolytes (~250 grams per tonne of cathode copper). Guar promotes dense, level copper deposits with minimum impurity entrainment. It behaves much as glue in electrorefining – but it is compatible with solvent extraction organics. Its concentration in the electrolyte may be measured like glue in electrorefining electrolytes (Stantke, 1999).

Cobalt sulfate solution is also added to provide ~150 ppm Co⁺⁺ in electrowinning electrolyte. Co⁺⁺ promotes O₂ evolution at the anode (Reaction 19.1) rather than Pb oxidation. This minimizes Pb contamination of the depositing copper and extends anode life (Prengaman and Siegmund, 1999).

Chloride ions are either naturally present in electrowinning electrolyte or are added as HCl. They promote dense, fine grain, low impurity copper deposits on the cathode. With stainless steel cathodes, chloride ion concentration must be kept below ~30 ppm. More than this causes chlorine gas evolution:



This Cl₂ ‘pit’ corrodes the top of the stainless blade, causing the depositing copper to stick and resist detachment. Leach operations with high concentrations of Cl⁻ in their pregnant leach solution wash their loaded solvent extraction organic to prevent excessive Cl⁻ transfer to electrolyte.

19.3 Maximizing Copper Purity

The three main impurities in electrowon cathode copper are:

- (a) Pb (1 or 2 ppm) from anode corrosion product entrapment
- (b) S (4 or 5 ppm) from PbSO_4 anode corrosion product and electrolyte entrapment
- (c) Fe (1 or 2 ppm) from electrolyte entrapment.

Cathode purity is maximized (Maki, 1999) by:

- (a) straight, vertical, equispaced cathodes and anodes with no anode-cathode contact
- (b) immediate thorough washing of cathode copper with 70 to 80°C water
- (c) rolled Pb-Sn-Ca anodes with adherent corrosion products
- (d) frequent removal of anode corrosion products from the bottom of the electrowinning cells
- (e) avoidance of excessive turbulence
- (f) addition of Co^{++} to the electrolyte to minimize Pb corrosion
- (g) Mn^{++} in electrolyte below ~20 ppm to avoid rapid Pb corrosion and flaky corrosion products (Miller, 1995)
- (h) steady electrical current at all times to maintain an adherent anode corrosion layer
- (i) electrolyte free of solids and solvent extraction organics
- (j) steady uniform flow of warm, pure, high Cu^{++} electrolyte across all cathode faces
- (k) 45 to 50°C electrolyte to give pure fine-grained copper deposits
- (l) use of guar and HCl addition agents to give dense, smooth copper deposits (but with Cl^- below 30 ppm in electrolyte)
- (m) Fe in electrolyte below ~2 kg/m³ to minimize Fe in cathode copper.

19.4 Maximizing Current Efficiency

Current efficiencies in modern electrowinning plants are 90 to 95%. The unused current is wasted by:

- (a) anode/cathode short circuits
- (b) stray current to ground
- (c) reduction of Fe^{+++} to Fe^{++} at the cathode and re-oxidation of Fe^{+++} to Fe^{++} at the anode.

High current efficiency is important because it maximizes copper plating rate

and minimizes electrical energy consumption.

Anode/cathode short circuits are detected by frequent infrared and gaussmeter inspections. They are avoided by evenly spaced straight, vertical electrodes. Bending of stainless steel blanks during copper stripping is avoided.

Stray current losses are prevented by avoiding electrolyte spills and by good housekeeping around the tankhouse.

$\text{Fe}^{+++} \rightarrow \text{Fe}^{++}$ current wastage is minimized by minimizing Fe concentration in electrolyte. This is done by preventing leach solution carryover to electrolyte during solvent extraction. It is also kept under control by bleeding a small portion of (Fe-bearing) electrolyte from the tankhouse.

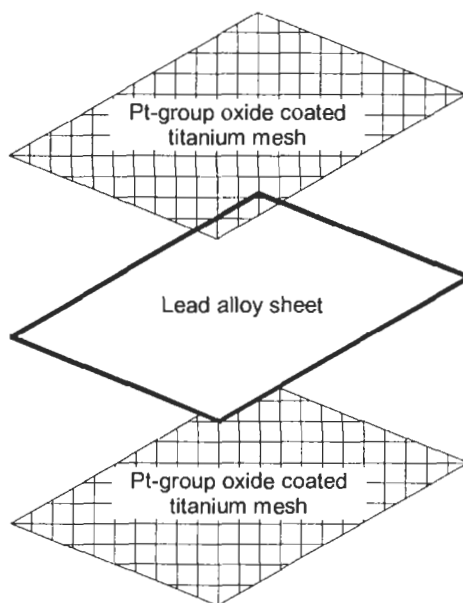


Fig. 19.2. Sketch of lead-titanium mesh sandwich anode. The titanium mesh is coated with a 'standard platinum group metal oxide coating' (Hardee and Brown, 1999). The coated titanium mesh is reported to decrease (i) Pb concentration in cathode copper and (ii) electrical energy consumption. The anode support lugs are not shown.

19.5 Future Developments

Copper electrowinning's most important need is a truly inert anode (Dattilo and Lutz, 1999, Delpancke *et al.*, 1999). Today's lead alloy anode is satisfactory but it corrodes slowly and slightly contaminates the electrowon copper.

In 2002, the leading candidate for an inert anode is the iridium/titanium/lead sandwich, Fig. 19.2.

The IrO_2 and titanium layers provide inertness. The Pb-alloy center provides toughness.

The potential advantages of this anode (Hardee and Brown, 1999; Hiskey, 1999) are:

- (a) minimization of Pb contamination
- (b) reduced need for cell cleaning
- (c) a 0.3 to 0.4 volt decrease in oxygen overpotential.

Advantage (c) lowers electrowinning energy consumption and decreases the need for Co^{++} additions to electrolyte.

The disadvantages of the new anode are its cost and its need for gentle handling (to avoid penetrating the IrO_2/Ti surface layer).

Full-size anodes have been given 6-month trials in industrial copper electrowinning cells (Hardee and Brown, 1999). Full-scale industrial tests are expected.

19.6 Summary

Electrowinning produces pure metallic copper from leach/solvent extraction electrolytes. About 2.5 million tonnes of pure copper are electrowon per year.

Electrowinning entails applying an electrical potential between inert Pb-alloy anodes and stainless steel (occasionally copper) cathodes in $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte. Pure copper electroplates on the cathodes. O_2 is generated at the anodes.

The copper is stripped from the cathode and sold. The O_2 joins the atmosphere. The Cu^{++} depleted electrolyte is returned to solvent extraction for Cu^{++} replenishment.

Electrowon copper is as pure or purer than electrorefined copper. Its only significant impurities are sulfur (4 or 5 ppm) and lead and iron (1 or 2 ppm each). Careful control and attention to detail can decrease these impurity concentrations to the low end of these ranges.

Suggested Reading

Dutrizac, J.E., Ji, J. and V. Ramachandran (1999) *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrowinning and Electrowinning of Copper*, TMS, Warrendale, PA.

Jergensen II, G.V. (1999) *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, SME, Littleton, CO.

Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G. (1999) *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV Hydrometallurgy of Copper*, TMS, Warrendale, PA.

References

Addison, J.R., Savage, B.J., Robertson, J.M., Kramer, E.P. and Stauffer, J.C. (1999) Implementing technology: conversion of Phelps Dodge Morenci, Inc. Central EW tankhouse from copper starter sheets to stainless steel technology. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrowinning and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 609 618.

Dattilo, M. and Lutz, L.J. (1999) Merrill composite anodes for copper electrowinning. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrowinning and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 597 601.

Delplancke, J.L., Winand, R., Gueneau de Mussy, J.P. and Pagliero, A. (1999) New anode compositions for copper electrowinning and copper electrodeposition at high current density. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrowinning and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 603 608.

Hardee, K. L. and Brown, C. W. (1999) Electrocatalytic titanium mesh surfaces combined with standard lead substrates for process improvements and power saving in copper electrowinning. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrowinning and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 575 584.

Hiskey, J. B. (1999) Principles and practical considerations of copper electrowinning and electrowinning. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 169 186.

Jenkins, J. and Eamon, M.A. (1990) Plant practices and innovations at Magma Copper Company's San Manuel SX-EW plant. In *Electrometallurgical Plant Practice*, ed. Claessens, P.L. and Harris, G.B., Pergamon Press, New York, NY, 41 56.

Jenkins, J., Davenport, W.G., Kennedy, B. and Robinson, T. (1999) Electrolytic copper – leach, solvent extraction and electrowinning world operating data. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. IV Hydrometallurgy of Copper*, ed. Young, S.K., Dreisinger, D.B., Hackl, R.P. and Dixon, D.G., TMS, Warrendale, PA, 493 566.

Maki, T. (1999) Evolution of cathode quality at Phelps Dodge Mining Company. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 223 225.

Miller, G. M. (1995) The problem of manganese and its effects on copper SX-EW operations. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. III Electrefining and Electrowinning of Copper*, ed. Dutrizac, J. E., Hein, H. and Ugarte, G., Metallurgical Society of CIM, Montreal, Canada, 649 663.

Pfalzgraff, C.L. (1999) Do's and don't's of tankhouse design and operation. In *Copper Leaching, Solvent Extraction, and Electrowinning Technology*, ed. Jergensen II, G.V., SME, Littleton, CO, 217 221.

Prengaman, R.D. and Siegmund, A. (1999) Improved copper electrowinning operations using wrought Pb-Ca-Sn anodes. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 561 573.

Stantke, P. (1999) Guar concentration measurement with the CollaMat system. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Electrefining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 643 651.

CHAPTER 20

Collection and Processing of Recycled Copper

Previous chapters describe production of primary copper – i.e. extraction of copper from ore. This chapter and the next describe production of secondary copper – i.e. recovery of copper from scrap. About half the copper reaching the marketplace has been scrap at least once, so scrap recycle is of the utmost importance.

This chapter describes:

- (a) scrap recycling in general (Henstock, 1996; Neff and Schmidt, 1990)
- (b) major sources and types of scrap
- (c) physical beneficiation techniques for isolating copper from its coatings and other contaminants.

Chapter 21 describes the chemical aspects of secondary copper production and refining.

20.1 The Materials Cycle

Figure 20.1 shows the 'materials cycle' flowsheet. It is valid for any material not consumed during use. Its key components are:

- (a) raw materials – ores from which primary copper is produced
- (b) primary production – processes described in previous chapters of this book
- (c) engineering materials – the final products of smelting/refining, mainly cast copper and pre-draw copper rod, ready for manufacturing
- (d) manufacturing – production of goods to be sold to consumers
- (e) obsolete products – products that have been discarded or otherwise taken out of use

- (f) discard – sending of obsolete products to a discard site, usually a landfill.

Obsolete copper products are increasingly being recycled rather than sent to landfills. This is encouraged by the value of their copper and the increasing cost and decreasing availability of landfill sites.

20.1.1 Home scrap

The arrow marked (1) in Figure 20.1 shows the first category of recycled copper, known as *home* or *run-around* scrap. This is copper that primary producers cannot further process or sell. Off-specification anodes, cathodes, bar and rod are examples of this type of scrap. Anode scrap is another example.

The arrow shows that this material is reprocessed directly by the primary producer, usually by running it through a previous step in the process. Off-specification copper is usually put back into a converter or anode furnace then electrorefined. Physically defective rod and bar is re-melted and re-cast.

The annual amount of home scrap production is not known because it is not reported. However, industrial producers try to minimize its production to avoid recycle expense.

20.1.2 New scrap

The arrows marked (2), (2a) and (2') in Figure 20.1 denote *new, prompt industrial* or *internal arising* scrap. This is scrap that is generated during manufacturing. The primary difference between this and home scrap is that it may have been adulterated during processing by alloying or by applying coatings and coverings. Examples of *new* scrap are as numerous as the products made with copper, since no manufacturing process is 100% efficient.

The pathway taken by *new* scrap depends on its chemical composition and the degree to which it has become entwined with other materials. The simplest approach is to recycle it internally (2a). This is common practice with gatings and risers from castings. They are simply re-melted and cast again. Direct recycling has the advantages of:

- (a) retaining the value of added alloying elements such as zinc or tin which would be lost if the alloy were sent to a smelter
- (b) eliminating the cost of removing the alloying elements, which would be required if the metal were reprocessed at a smelter.

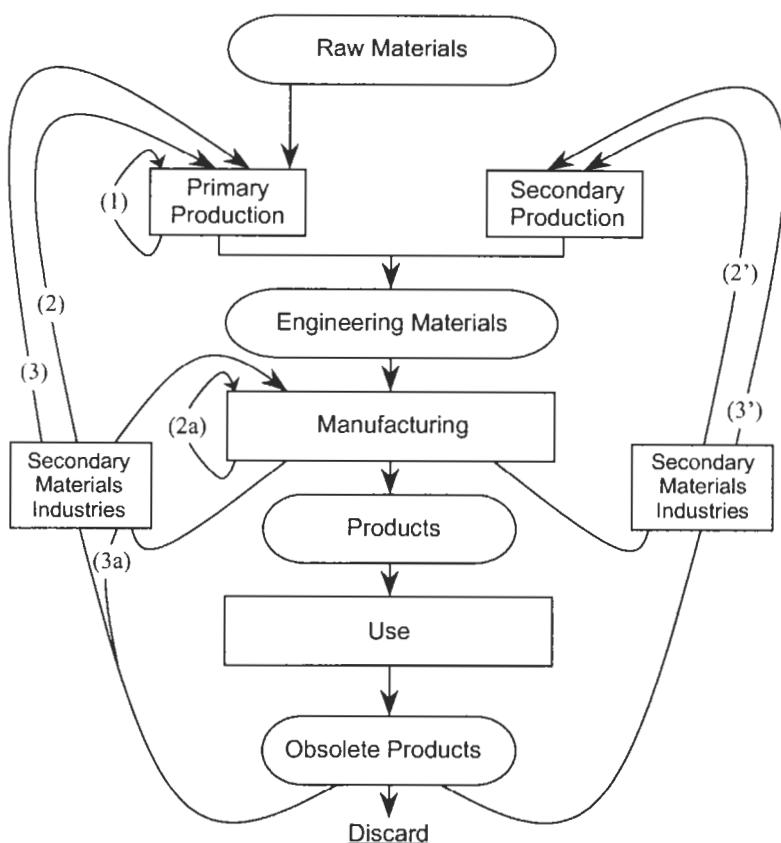


Fig. 20.1. Flowsheet of 'materials cycle'. This is valid for any material not consumed during use. The arrow marked (1) shows *home* or *run-around* scrap. The arrows marked (2), (2a) and (2') denote *new, prompt industrial* or *internal arising* scrap. The paths marked (3), (3a) and (3') show *old, obsolete, post-consumer*, or *external arising* scrap.

Similar reprocessing is done for scrap copper tube and uncoated copper wire.

In fact, path (2a) is the most common recycling route for *new* scrap. As much as 90% of *new* U.S. copper scrap is recycled along this path (Edelstein, 1999).

If the *new* scrap has coatings or attachments that cannot easily be removed, or if the manufacturing facility cannot directly reuse its *new* scrap (e.g., a wire-drawing plant without its own melting facilities), then paths (2) and (2') are followed.

The secondary materials industries described in Figure 20.1 fill the role that mining and ore beneficiation facilities fill for primary copper production. In many cases they simply remove the coatings or attachments from the scrap to make it suitable for reuse by the manufacturing facility. If purification or refining is needed, the cleaned-up scrap is sent to a primary or secondary smelter/refinery. Since these facilities produce cathode grade copper, alloying elements present in the scrap are lost.

Specific activities of secondary materials industries are described later in this chapter.

20.1.3 *Old scrap*

The final category of copper scrap (paths (3), (3a) and (3')) is termed *old, obsolete, post-consumer, or external arising* scrap. It is obtained from products that have ended their useful life. *Old* scrap is a huge potential source of recyclable copper. It is also difficult to process. The challenges for processing *old* scrap include:

- (a) low Cu 'grades' – *old* copper scrap is often mixed with other materials and must be separated from this waste
- (b) unpredictability – deliveries of materials and objects vary from day to day, making processing difficult
- (c) location – *old* scrap is scattered about the landscape rather than being concentrated in a specific location like primary ore or *new* scrap.

As a result, *old* scrap is often landfilled rather than recycled.

However, the incentive to recover copper (and other metals) from discarded items is growing, due mainly to the increased cost and decreased availability of space for landfills (Sasaki, *et al.*, 1999).

Table 20.1 categorizes and quantifies generation and disposal of *old* copper scrap in Japan (Sasaki, *et al.*, 1999). It shows that the most plentiful and most efficiently recovered type of *old* copper scrap is wire and cable scrap.

It also shows that the most underutilized types of *old* copper scrap are electric appliance and automobile scrap. As a result, much of the current research into scrap processing is focused on copper recovery from these sources (Ikeda, *et al.*, 1995; Ochi, *et al.*, 1999; Suzuki, *et al.*, 1995).

20.2 Secondary Copper Grades and Definitions

The Institute of Scrap Recycling Industries (ISRI, 1990) currently recognizes 45

grades of copper-base scrap. However, most of these are for alloy scrap, which is much less available than 'pure' copper scrap. Alloy scrap is also more likely to be directly recycled than copper scrap. As a result, most of the ISRI designations are of little importance to copper recyclers.

Table 20.1. Old copper scrap generation and disposition in Japan, 1997 (1000 tonnes) (Sasaki, *et al.*, 1999).

Source of Scrap	Disposed	Collected	Landfilled	Percent Recycled
Power, Telecommunications, Railway Cables	197	197	0	100
Electric Appliances, Machinery	142	29	113	20
Automotive	79	38	41	48
Industrial machines, ships, rail cars	62	51	11	82
Buildings	118	81	37	69
Total	598	396	202	66

The most important categories of copper scrap are:

- (a) *Number 1 scrap.* This scrap has a minimum copper content of 99% and a minimum diameter or thickness of 1.6 mm. Number 1 scrap includes wire, 'heavy' scrap (clippings, punchings, bus bars) and wire nodules
- (b) *Number 2 scrap.* This scrap has a minimum copper content of 96% and is in the form of wire, heavy scrap, or nodules. Several additional restrictions are included (ISRI, 1990).
- (c) *Light copper.* This category has a minimum copper content of 92% and consists primarily of pure copper which has either been adulterated by painting or coating (gutters, downspouts) or has been heavily oxidized (boilers, kettles). It generally contains little alloyed copper.
- (d) *Refinery brass.* This category includes mixed-alloy scrap of all compositions and has few restrictions other than a minimum copper content of 61.3%.
- (e) *Copper-bearing scrap.* This is a catch-all category for low-grade material such as skimmings, sludges, slags, reverts, grindings and other residues.

In addition, copper recycling often includes the treatment of *wastes*. The definition of this word is a matter of debate in industrialized countries, because the sale and transportation of materials designated as *waste* is more heavily regulated than that of materials designated as scrap. In fact, material graded as copper-bearing scrap is defined in many countries as *waste*, despite the fact that it can be recycled profitably. *Wastes* generally have:

- (a) a low copper content;

- (b) a low economic value; and
- (c) a high processing cost per kg of contained copper.

As a result, recyclers sometimes charge a per-tonne fee for processing these materials (Lehner, 1998).

20.3 Scrap Processing and Beneficiation

20.3.1 Wire and cable processing

Wire and cable are by far the most common forms of *old* scrap. It is these forms for which the most advanced reprocessing technology exists. Nijkerk and Dalmijn (1998) divide scrap wire and cable into three types:

- (a) *Above-ground*, mostly high-tension power cable. These cables are high-grade (mainly copper, little insulation) and fairly consistent in construction. They are easy to recycle.
- (b) *On-the-ground*, with a variety of coverings and sizes. These are usually thin wires, so the cost of processing per kg of recovered copper is higher than that for cable. Wire is also more likely to be mixed with other waste, requiring additional separation. Automotive harnesses and appliance wire are examples.
- (c) *Below-ground/underwater*, which feature complex construction and many coverings. These cables often contain lead sheathing, bitumen, grease and mastic. This means that fairly complex processing schemes are required to recover their copper without creating safety and environmental hazards.

Copper recovery from scrap cable by shredding (also known as chopping or granulating) has its origins in World War II when it was developed to recover rubber coatings (Sullivan, 1985). Shredding has since become the dominant technology for scrap wire and cable processing (Nijkerk and Dalmijn, 1998).

Figure 20.2 shows a typical cable-chopping flowsheet. Before going to the first 'granulator', the scrap cable is sheared into lengths of 36 inches or less (Marcher, 1984; Sullivan, 1985). This is especially important for larger cables. The first granulator, or 'rasper', is typically a rotary knife shear with one rotating shaft. The knives on this shaft cut against a second set of stationary knives.

Rotation speed is about 120 rpm, and a screen is provided to return oversize product to the feed stream. Its primary task is size reduction rather than separation of the wire from its insulation. Depending on the type of material fed to the rasper, the length of the product pieces is 10 to 100 mm.

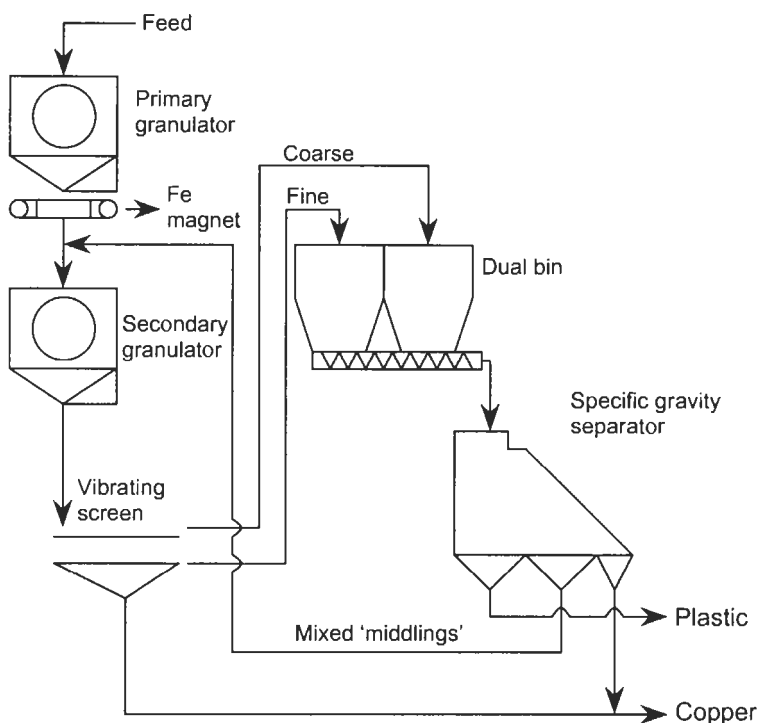


Fig. 20.2. Recycle cable 'chopping' flowsheet for separating copper from insulation and Fe. The specific gravity separator is an air table which blows insulation upwards while allowing copper to 'sink'.

Another function of the primary granulator is to 'liberate' any pieces of steel that are attached to the scrap cable. These are removed from the product by a magnetic separator.

The partially chopped cable is then fed to a second granulator (Marcher, 1984; Sullivan, 1985; Borsecnik, 1995). The second granulator is similar in operation to the first, but operates at much higher speeds (400 rpm) and has more knives (five sets) and smaller blade clearances (as small as 0.05 mm). It chops the cable to lengths of 6 mm or smaller, mostly liberating the copper from its insulation. Again, a screen is used to return oversize material.

The final unit process in scrap cable and wire processing is separation of copper from insulation. This is normally accomplished using the difference between the specific gravity of the copper (8.96) and that of the insulating plastic and rubber (1.3-1.4). Figure 20.2 shows a 'specific gravity separator', which typically

produces three fractions:

- (a) a 'pure' plastic fraction
- (b) copper 'chops' meeting Number 1 or Number 2 scrap purity specifications, Section 20.2
- (c) a middlings fraction which is returned to the second granulator for re-processing.

The separator is most commonly an air table (Marcher, 1984; Sullivan, 1985; Borsecnik, 1995) which ultimately recovers 80-90% of the input copper. The use of heavy media separation as a 'cleaner' step for recovering more copper from the plastic fraction has recently been suggested (Mankosa and Carver, 1995).

A significant difference between copper chops and plastic is particle shape – the copper chops are longer than the plastic. Efforts have been made to develop separation processes based on this characteristic (Huang, *et al.*, 1995; Koyanaka, *et al.*, 1997).

Underground cable processing is complicated by the complexity of its construction, the flammability of its coverings and the presence of aluminum or lead in the shredding product. Nijkerk and Dalmijn (1998) describe the use of cable *stripping* for larger cables. This follows shearing and involves slicing open the cable and removing the copper wire by hand. Smaller underground cables can be successfully chopped. Attempts have been made to introduce cryogenic shredding to reduce the flammability hazard. Eddy-current separators can be used following shredding to separate lead and aluminum from copper.

20.3.2 Automotive copper recovery

Figure 20.3 shows a flowsheet for recovering materials from junked automobiles (Suzuki, *et al.*, 1995). There are three potential sources of recyclable copper in this flowsheet.

The first is the radiator, which is manually removed from the car before shredding. Radiator assemblies have traditionally been constructed using a tin-lead solder (Anon., 1996). This requires that the radiator assembly be smelted and refined to produce pure copper. However, new assembly techniques using different solders or brazes might allow direct recycling of radiator/heater assemblies without the need for refining. The recycling rate for radiators is nearly 100%.

The second source of copper in Figure 20.3 is the 'nonferrous metal scrap' stream remaining after (i) the car has been shredded and (ii) its iron and steel have been magnetically removed.

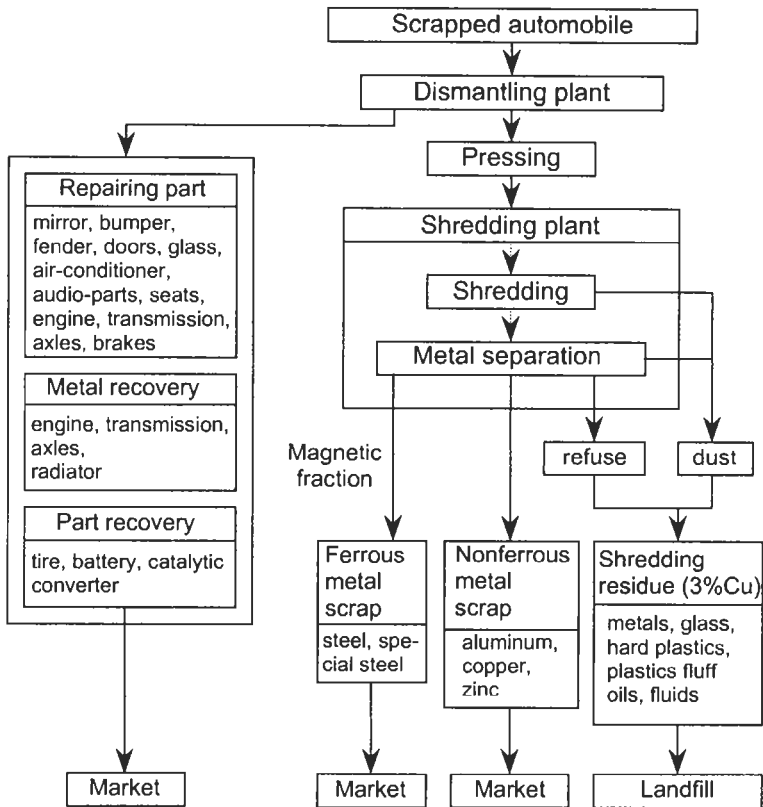


Fig. 20.3. Flowsheet for recovering metals from scrap automobiles. Procedures for recovering copper are detailed in Section 20.3.2.

Three metals dominate this stream: aluminum, copper and zinc. The copper consists mostly of wire from the car's electrical circuits.

Several methods are used to separate the copper from the other metals, e.g. hand-picking, air tabling and heavy-media separation. Because aluminum and zinc are more easily oxidized than copper, Cu-Al-Zn mixtures can be sold to copper smelters without complete separation. However, this eliminates the value of the aluminum and zinc and increases the cost of smelting (per kg of copper).

The final potential source of copper in Figure 20.3 is the 'shredding residue' which remains after the metals have been removed. This residue consists primarily of dust and organic matter – plastic from the dashboard and steering wheel, fluff from

the seat cushions, and pieces of carpet and fabric. However, shredding residue also contains up to 3% copper and has some fuel value.

This shredding residue is oxygen smelted in a reverberatory furnace in Onahama, Japan (Kikumoto *et al.*, 2000). Physical beneficiation has also been suggested (Izumikawa, 1999; Ochi *et al.*, 1999). However, most 'shredding residue' is landfilled (and its copper lost) due to its high transportation and treatment costs.

20.3.3 Electronic scrap treatment

Electronic scrap is a rapidly growing segment of the secondary copper supply (Allred and Busselle, 1997). Significant efforts have been made to develop copper-recovery techniques for this material.

Electronic scrap is defined as 'waste generated by the manufacture of electronic hardware and the discarding of used electronic products' (Sum, 1991). As such, it includes both *old* and *new* scrap.

Although it consists of a variety of items, the overall composition of electronic scrap can be divided into three categories: (i) plastic (~30% in 1991); (ii) refractory oxides (~30%) and (iii) metals (~40%). About half its metal content is copper. It also contains significant amounts of gold and silver.

Copper smelting/refining is already set up to recover gold and silver. It is, therefore, a logical destination for treating electronic scrap.

A potential problem with smelting electronic scrap is incomplete combustion of its plastic fraction and consequent evolution of organic compounds. However, high temperature oxygen smelting completely avoids this problem.

A more serious problem is the declining metal content of electronic scrap. The producers of circuit boards and other assemblies have learned over time to reduce the amount of metal needed in their products. As a result, the 0.1% gold content of electronic scrap mentioned by Sum in 1991 declined to 0.01% in 2000 (Maeda, *et al.*, 2000). This makes the scrap increasingly difficult to profitably recycle (Zhang and Forssberg, 1999).

The result has been development of 'minerals processing' strategies for isolating the metals of the electronic scrap. The approach is similar to that used for automobiles, i.e.:

- (a) disassembly to recover large items
- (b) shredding to reduce the size of the remaining material

- (c) liberation of metals from plastics and ceramics (Bernardes *et al.*, 1997).

Several techniques are then used to recover copper from the shredded scrap, specifically density, eddy current and electrostatic separation (Zhang and Forssberg, 1999). However, the use of minerals processing for treating electronic scrap is still in its infancy.

20.4 Summary

About half the copper reaching the market today has been scrap at least once. Scrap is generated at all stages in the life span of a copper product, including production (*home scrap*), manufacturing (*new scrap*) and post-consumer disposal (*old scrap*).

The purest copper scrap is simply re-melted and re-cast in preparation for manufacture and use. Less pure copper scrap is re-smelted and re-refined. Alloy scrap is usually recycled directly to make new alloy.

Considerable scrap must be physically treated to isolate its copper from its other components. An important example of this is recovery of copper from wire and cable. It is done by:

- (a) 'chopping' the wire and cable into small pieces to liberate its copper
- (b) physically isolating its copper by means of a specific gravity separation (air table).

Copper recovery from used automobiles and electronic devices follows a similar pattern, i.e.:

- (a) liberation by size reduction ('shredding')
- (b) isolation of copper by magnetic, specific gravity and eddy current separation.

The copper from these processes is then re-smelted and re-refined.

Old (obsolete) scrap is often discarded in landfills. There is, however, an increasing tendency to recycle this material due mainly to the increased cost and decreased availability of landfill sites.

Suggested Reading

Marcher, J. (1984) Separation and recycling of wire and cable scrap in the cable industry. *Wire J. Int.*, 17 (5), 106-114.

Sasaki, K., Ichiyama, K., Katagiri, N., Simada, M. and Maeda, S. (1999) Circulation of non-ferrous metals in Japan. In *REWAS '99, Vol. II*, ed. Gaballah, I., Hager, J. and Solobazal, R., TMS, Warrendale, PA, 1117 1126.

Sullivan, J.F. (1985) Recycling scrap wire and cable: the state of the art. *Wire J. Int.*, **18** (11), 36 50.

Sum, E.Y.L. (1991) The recovery of metals from electronic scrap. *JOM*, **43** (4), 53 61.

Suzuki, M., Nakajima, A. and Taya, S. (1995) Recycling scheme for scrapped automobiles in Japan. In *Third Int. Symp. Recycling of Metals and Eng. Mater.*, ed. Quencau, P.B. and Peterson, R.D., TMS, Warrendale, PA, 729 737.

References

Allred, R.E. and Busselle, R.D. (1997) Economical tertiary recycling process for mixtures of electronic scrap. In *1997 IEEE Int. Symp. on Electronics and the Environment*, IEEE, Piscataway, NJ, 115 120.

Anon. (1996) Recycling of copper/brass radiators. *Automotive Eng.*, **4**, 41 43.

Bernardes, A., Bohlinger, I., Rodrigues, D., Milbrandt, H. and Wuth, W. (1997) Recycling of printed circuit boards by melting with oxidising/reducing top blowing process. In *EPD Congress 1997*, ed. Mishra, B., TMS, 363-375.

Borsecnik, J. (1995) Triple/S Dynamics and the world of wire chopping. *Scrap Proc. Recyc.*, **52** (2), 203 211.

Edelstein, D.L. (1999) Copper. In *Recycling – Metals*, U.S. Geol. Survey, Washington, DC; <http://minerals.usgs.gov/minerals/pubs/commodity/recycle/870499.pdf>.

Henstock, M.E. (1996) *The Recycling of Non-Ferrous Metals*, ICME, Ottawa, Canada, 111 133.

Huang, P., Meloy, T.P., Marabini, A. and Allese, V. (1995) Recycling of power cables using particle shape. In *Waste Processing and Recycling in Mineral and Metallurgical Industries II*, ed. Rao, S.R., Amaratunga, L.M., Richards, G.G. and Kondos, P.D., The Metallurgical Society of CIM, Montreal, Canada, 235 244.

Ikedo, Y., Gamoh, K., Takahashi, K., Katagiri, T. and Yamguchi, S. (1995) An approach to recycling electric appliances. In *Third Int. Symp. Recycling of Metals and Eng. Mater.*, ed. Quencau, P.B. and Peterson, R.D., TMS, Warrendale, PA, 777 782.

Institute of Scrap Recycling Industries (1990) *Scrap Specifications Circular 1990: Guidelines for Nonferrous Scrap: NF-90*, ISRI, Washington, DC.

Izumikawa, C. (1999) Metal recovery from ash of automobile shredder residue—especially focusing on particle shape. In *REWAS '99, Vol. II*, ed. Gaballah, I., Hager, J. and Solobazal, R., TMS, Warrendale, PA, 1777 1786.

- Kikumoto, N., Abe, K., Nishiwaki, M. and Sato, T. (2000) Treatment of industrial waste material in reverberatory furnace at Onahama Smelter. In *EPD Congress 2000*, ed Taylor, P.R., TMS, Warrendale, PA, 19 27.
- Koyanaka, S., Ohya, H., Endoh, S., Iwata, H. and Ditzl, P. (1997) Recovering copper from electric cable wastes using a particle shape separation technique. *Adv. Powder Technol.*, **8**, 103 111.
- Lehner, T. (1998) Integrated recycling of non-ferrous metals at Boliden Ltd. Rönnskär Smelter. In *1998 IEEE Int. Symp. on Electronics and the Environment*, IEEE, Piscataway, NJ, 42 47.
- Maeda, Y., Inoue, H., Kawamura, S. and Ohike, S. (2000) Metal recycling at Kosaka Smelter. In *Fourth Int. Symp. Recycling of Metals and Eng. Mater.*, ed. Stewart, D.L., Stephens, R. and Daley, J.C., TMS, Warrendale, PA, 691 699.
- Mankosa, M.J. and Carver, R.M. (1995) Processing of chopped wire waste material using the Floatex Density Separator. In *Third Int. Symp. Recycling of Metals and Eng. Mater.*, ed. Queneau, P.B. and Peterson, R.D., TMS, Warrendale, PA, 111 120.
- Marcher, J. (1984) Separation and recycling of wire and cable scrap in the cable industry. *Wire J. Int.*, **17** (5), 106 114.
- Neff, D.V. and Schmidt, R.F. (1990) Recycling of copper. In *Metals Handbook (10th ed.)*, Vol. 2, *Properties and Selection: Nonferrous Alloys and Special-Purpose Materials*, ASM International, Materials Park, OH, 1213 1216.
- Nijkerk, A.A. and Dalmijn, W.L. (1998) *Handbook of Recycling Techniques*, Nijkerk Consultancy, The Hague, Holland, 123 127.
- Ochi, S., Yaoita, K. and Nakao, S. (1999) Recycling of shredder dust. In *REWAS '99, Vol. II*, ed. Gaballah, I., Hager, J. and Solobazal, R., TMS, Warrendale, PA, 1807 1816.
- Sasaki, K., Ichiyama, K., Katagiri, N., Simada, M. and Maeda, S. (1999) Circulation of non-ferrous metals in Japan. In *REWAS '99, Vol. II*, ed. Gaballah, I., Hager, J. and Solobazal, R., TMS, Warrendale, PA, 1117 1126.
- Sullivan, J.F. (1985) Recycling scrap wire and cable: the state of the art. *Wire J. Int.*, **18** (11), 36 50.
- Sum, E.Y.L. (1991) The recovery of metals from electronic scrap. *JOM*, **43** (4), 53 61.
- Suzuki, M., Nakajima, A. and Taya, S. (1995) Recycling scheme for scrapped automobiles in Japan. In *Third Int. Symp. Recycling of Metals and Eng. Mater.*, ed. Queneau, P.B. and Peterson, R.D., TMS, Warrendale, PA, 729 737.
- Zhang, S. and Forsberg, E. (1999) Intelligent liberation and classification of electronic scrap. *Powder Technology*, **105**, 295 301.

CHAPTER 21

Chemical Metallurgy of Copper Recycling

Most scrap copper is re-melted and re-cast without chemical treatment. The remainder, however, requires refining in order to be used again.

This scrap may be:

- (a) mixed with other metals in *obsolete* scrap
- (b) covered with metallic or organic coatings
- (c) heavily oxidized from years of outdoor use
- (d) in the form of mixed alloy scrap which is unsuitable for use as a specific alloy.

Regardless, it is necessary to remove impurities and cast this metal into an appropriate form before it is used again. The two main strategies for treating this scrap are:

- (a) smelting it in a specialized secondary copper smelter/refinery
- (b) smelting it as part of the feed to a primary (concentrate) smelter.

This chapter examines industrial practice for these strategies, focusing on the advantages and disadvantages of each.

21.1 The Secondary Copper Smelter

21.1.1 Smelting to black copper

Fig. 21.1 is a flowsheet for pyrometallurgical processing of low grade scrap in a secondary copper smelter. The blast furnace at the top accepts the 'copper bearing scrap' described in Section 20.2. This scrap includes:

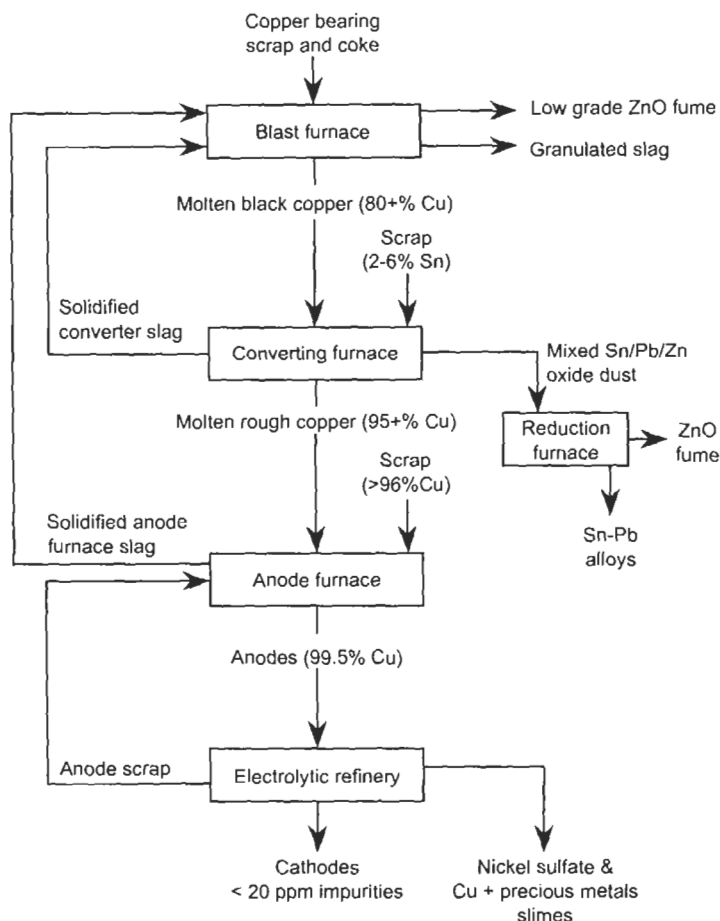


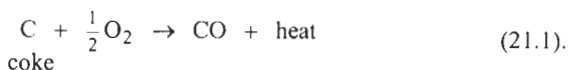
Fig. 21.1. Flowsheet for secondary scrap smelting/refining.

- (a) automobile shredder product from which the copper and iron cannot be separated, along with motors, switches and relays ('irony copper')
- (b) dross from decopperizing lead bullion
- (c) dusts from copper melting and alloying facilities
- (d) sludges from copper electroplating operations.

The feed to blast furnaces is low grade and highly oxidized. It requires reduction to metallic copper. Major metallic impurities are lead and tin (from bronze scrap, solder and decopperizing dross), zinc (from scrap brass), iron

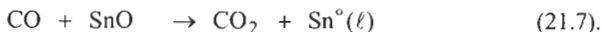
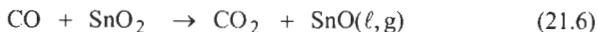
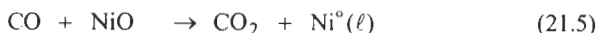
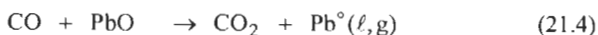
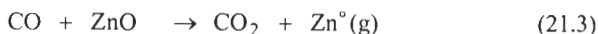
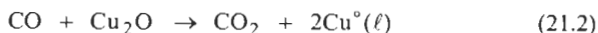
(from automotive scrap) and nickel (from scrap monel and other alloys). These elements are often present as mixtures of metal and oxide.

Heat and CO 'reductant' are supplied to secondary copper blast furnaces by combusting metallurgical coke included in the scrap charge, i.e.:

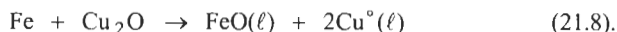


O₂ for the combustion is provided by blowing air 'blast' (sometimes enriched with oxygen) through tuyeres near the bottom of the furnace.

The carbon monoxide in turn reduces the oxides of the feed to metal or a lower oxide, i.e.:



Metallic iron in the scrap also performs some reduction, especially of easily reduced oxides like Cu₂O:



As a result of these reactions, blast furnaces generate three products. They are:

- (a) molten 'black copper', 74-80% Cu, 6-8% Sn, 5-6% Pb, 1-3% Zn, 1-3% Ni and 5-8% Fe (Custovic, *et al.*, 1987; Nelmes, 1987)
- (b) molten slag containing FeO, CaO, Al₂O₃, SiO₂ along with 0.6-1.0% Cu (as Cu₂O), 0.5-0.8% Sn (as SnO), 3.5-4.5% Zn (as ZnO) and small amounts of PbO and NiO
- (c) offgas containing CO, CO₂ and N₂ plus metal and metal oxide vapors.

Cooling and filtering of offgas (c) gives oxide dust containing 1-2% Cu, 1-3% Sn, 20-30% Pb and 30-45% Zn. The dust also contains chlorine from chlorinated

plastics in the feed. It is always reprocessed to recover its metal content (Hanusch and Bussmann, 1995).

Two innovations in scrap blast furnace operation have been:

- (a) oxygen enrichment of the blast to 23 or 24 volume% O₂
- (b) inclusion of scrap iron in the charge.

Oxygen enrichment:

- (a) increases smelting rate by decreasing the amount of N₂ that must be blown up the furnace shaft
- (b) decreases the coke requirement (per tonne of copper) by decreasing the amount of N₂ that must be heated

Scrap iron replaces some CO in Reactions (21.2) to (21.7). It thereby decreases the coke requirement.

In spite of these improvements, the need for coke as a fuel and the inefficiency of small blast furnaces makes this furnace increasingly uneconomic to operate. Several have closed over the past decade.

Blast furnaces are currently operated by Hüttenwerke Kayser in Germany and Brixlegg in Austria (Nolte, 1997; Nolte and Kreymann, 1999). Several are also operating in China (Jiang, 1997).

An alternative to the blast furnace for treating low-grade materials is the top-blown rotary converter (TBRC). The TBRC's inputs and products are similar to those of the blast furnace (Nelmes, 1987; Hedlund, 1995). The TBRC has the advantages of:

- (a) being fired with an industrial oxygen-fuel burner, eliminating the need for coke
- (b) vessel rotation which provides rapid reaction kinetics, improving productivity.

O'Brien (1992) indicates that the TBRC requires 70% less fuel than a blast furnace for black-copper smelting. It also lowers dust generation by about 50%. TBRC's are used in the U.S., Europe and South Africa.

21.1.2 Converting black copper

The impurities in black copper can be divided into two groups – those that are more easily oxidized than copper (Fe, Pb, Sn, Zn) and those that are difficult or

impossible to remove by oxidation (Ni, Ag, Au, platinum group metals). These impurities are removed sequentially by a strategy similar to that for purifying primary copper.

The first step in refining black copper is oxidation, typically in a Peirce-Smith converter, Fig. 1.6. Air is blown into the molten black copper through side tuyeres, oxidizing Fe, Pb, Sn and Zn along with some Ni and Cu. Alloyed copper scrap (the 'light copper' and 'refinery brass' described in Section 20.2) is also added to the converter. Most of its 'impurities' are also oxidized.

This oxidation generates slag containing 30-40% Cu, 8-15% Sn, 3-5% Pb, 3-5% Zn and 2-4% Ni, depending on the composition of the converter feed (Bussmann, 1991). Cu and Ni are recovered by returning the slag to the blast furnace or TBRC.

An offgas is also generated which, when cooled and filtered, yields dust containing PbO, SnO and some ZnO. This dust is usually reduced to recover its Pb and Sn as solder, Fig. 21.1.

Oxidation of black copper provides little heat to the converter (unlike oxidation of matte, Chapter 9). Heat for the converting process must, therefore, be provided by burning hydrocarbon fuel.

21.1.3 Fire refining and electrorefining

The main product of the converter is molten 'rough' copper, 95-97% Cu. It is added to a hearth or rotary refining furnace for final, controlled oxidation before casting it as anodes. High Cu scrap (Numbers 1 and 2, Section 20.2) is also often added to the anode furnace for melting and casting as anodes (Nelmes, 1987; Hanusch and Bussmann, 1995; Jiang, 1997; Nolte, 1997). Plant practice is similar to that for fire refining of primary copper, Chapter 15.

Because the availability of Number 1 and Number 2 scrap is much larger than that of lower grade material, several recycling facilities accept only higher grade material. This allows them to skip smelting/converting and do only fire refining (Rundquist, 1997).

If the only input material to the fire refining furnace is Number 1 scrap, no electrorefining is needed. The output can be directly cast as tough-pitch billet or bar for mechanical use (Rundquist, 1997). However, the rough copper in Fig. 21.1 usually contains nickel or tin, which is never completely removed by oxidation converting. It may also contain appreciable amounts of gold, silver and platinum group metals from the original scrap.

Recovery of these metals is important to the profitability of a recycling facility. As a result, the anode furnace product is almost always cast as anodes for electrorefining. The impurity level in secondary anodes is higher than that in most anodes from primary smelting operations. As a result, electrolyte purification facilities need to be larger (Nelmes, 1987). Otherwise, plant practice is similar to that described in Chapter 16.

The principal electrorefining products are high purity cathode copper, nickel sulphate from electrolyte purification and anode slimes. The slimes contain:

- (a) Cu, which is recycled to the electrorefinery in sulfuric acid solution, Appendix C
- (b) Ag, Au and Pt-metals which are recovered in a precious metal plant, on-site or elsewhere.

21.2 Scrap Processing in Primary Copper Smelters

21.2.1 Smelting scrap in primary smelting furnaces

Melting of high-Cu scrap in primary converting furnaces is commonplace. Heat for the melting is provided by the converter's exothermic Fe and S oxidation reactions, Reaction (9.1). High-Cu grade scrap is also melted in anode furnaces, but this requires considerable hydrocarbon fuel.

Low-Cu scrap is more difficult to process in a primary smelter. It doesn't contain enough Cu for melting in converters or anode furnaces and, unlike concentrate, it is a net energy consumer in the smelting furnace.

Also, it often cannot be broken up into the fine pieces needed for a smelting furnaces concentrate oxidation system, e.g. a flash furnace concentrate burner, Fig. 5.2. Smelting scrap in a flash furnace is particularly difficult.

There are, however, several primary smelting furnaces that are well adapted to smelting scrap, i.e.:

Isasmelt furnace, Chapter 8

Noranda smelting furnace, Chapter 7 (Bedard *et al.*, 1991; Reid, 1999)

reverberatory furnace (Kikumoto *et al.*, 2000)

top blown rotary converter (Lehner and Vikdahl, 1998).

The electric furnace is also well adapted to scrap smelting because of its very small offgas output (Marnette *et al.*, 1994).

21.2.2 Scrap in Mitsubishi Process smelting/converting

The Mitsubishi smelting/converting system is used extensively for treating various types of scrap, Oshima *et al.*, (1998). The pathways taken by scrap in the Naoshima Mitsubishi smelter are shown in Fig. 21.2.

Particulate scrap is mixed with concentrate and blown into the smelting furnace through its rotating lances. Larger scrap pieces are charged to the smelting and converting furnaces through roof and wall chutes. Mitsubishi converting is particularly exothermic, allowing large amounts of scrap to be melted in the converting furnace, Chapter 10.

The very largest chunks of scrap (e.g. anode molds) are fed into the smelter's anode furnaces through their large mouths. They are too large to be charged to the Mitsubishi furnaces.

Small-size shredded scrap can also be added in limited quantities to flash furnaces (Maeda, *et al.*, 2000). In fact, the smelting furnace is preferred to the converter for feeding electronic scrap, due to its plastic content. There are two reasons for this:

- (a) the plastic has fuel value which provides heat for smelting
- (b) when burned intermittently, plastic often gives off smoke and other particulates which might escape through the mouth of a Peirce-Smith converter, adversely affecting workplace hygiene. Burned in a sealed flash furnace, these particulates are efficiently captured by dust collection devices, Chapter 14.

The amount of non-plastic-coated low-grade scrap that can be fed to a smelting furnace is limited, due to its net heat requirement. As a result, much of it has to be treated in a converting furnace (Oshima, *et al.*, 1998).

21.2.3 Scrap additions to converters and anode furnaces

The quality of scrap copper fed to primary converters is similar to that fed to secondary Peirce-Smith converters – low-alloy scrap, Number 1 and Number 2 scrap if available, compressed turnings and anode scrap. Low-grade material and plant reverts may also be fed if their plastic content is not too large (Oshima, *et al.*, 1998). Converters are usually net heat generators, so they require coolants (e.g. bare copper) rather than heat producers (e.g. plastic coated copper).

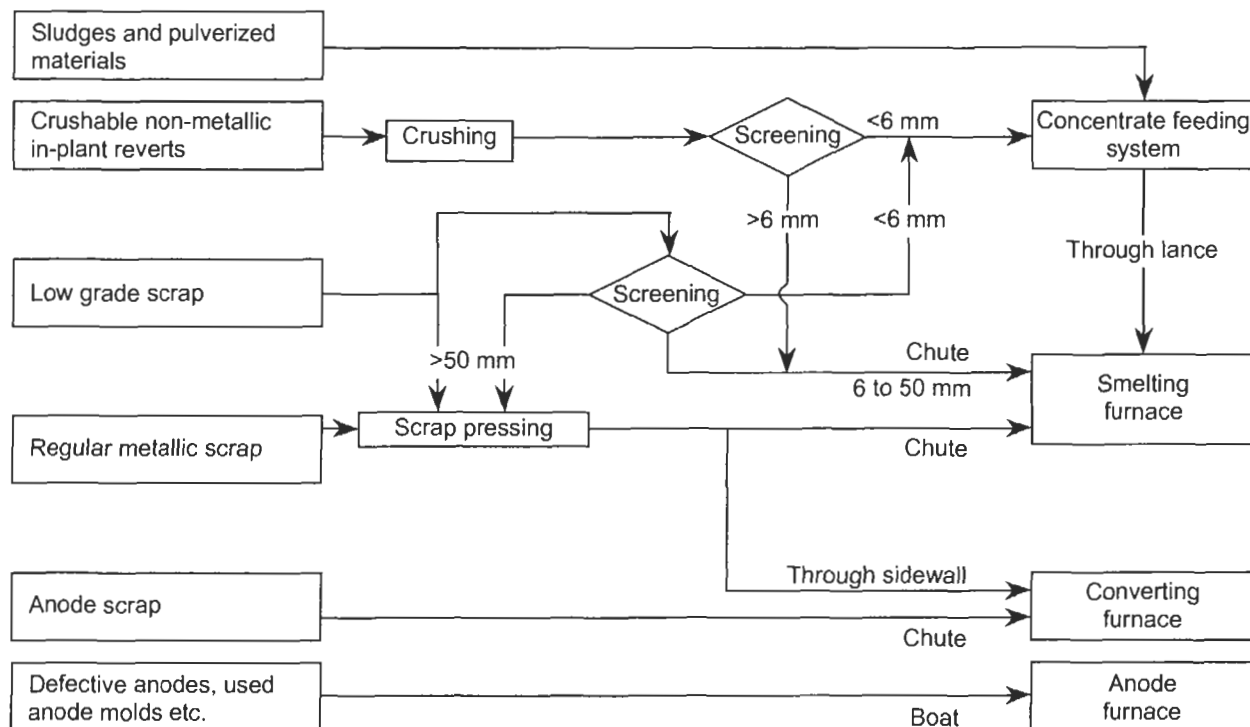


Fig. 21.2. Scrap smelting in the Mitsubishi smelter, Naoshima (Oshima *et al.*, 1998). Low Cu-grade particulate scrap is fed into the smelting furnace through its rotating lances. Larger scrap is fed through roof and sidewall chutes. Large high-grade scrap is fed into the anode furnace.

Scrap additions to anode furnaces are generally limited to physically defective anodes, used anode molds and Number 1 scrap. Even for these, the converter is preferable up to the limit of its exothermic heat production.

21.3 Summary

Copper scrap is smelted in primary (concentrate) and secondary (scrap) smelters. Primary smelters mainly smelt concentrate. Some, however, are well adapted to smelting all grades of scrap. Smelters with Isasmelt, Mitsubishi, Noranda, reverberatory and top blown rotary converter smelting furnaces are particularly effective.

Scrap is also extensively recycled to the converters in primary smelters. The heat from the converter's exothermic Fe and S oxidation reactions is particularly useful for melting scrap, especially if considerable oxygen is used for the oxidation reactions.

Secondary scrap smelters use blast furnaces, top blown rotary converters and electric furnaces for smelting low-Cu grade scrap. The main smelting product is molten 'black' copper (80% Cu), which is converted to 'rough' copper (96% Cu) then fire refined and cast into anodes (98.5% Cu).

These processes can't completely remove Ni and Sn from Cu, so the refining furnace product must be electrorefined. Electrorefining also recovers Ag, Au and Pt-group metals.

Secondary copper refining is similar to primary copper refining. However, scrap may contain more impurities than concentrates so larger electrolyte purification and slimes treatment facilities may be required.

Scrap recycling slows the rate at which the earth's copper resources are being depleted. It also avoids (i) energy expenditure in mining and milling and (ii) mining and milling waste products. It is advantageous in every respect.

Suggested Reading

Bedard, M., Chapados, M. and Kachaniwsky, G. (1991) Advances in technology for complex custom feed material treatment at Noranda. *CIM Bull.*, **84** (948), 64-69.

Jolly, J.L.W. (1997) World Copper Scrap Markets and Trends. In *World Conf. Copper Recycl.*, International Copper Study Group, Lisbon, 11 pp.

Nelmes, W.S. (1987) Current trends in smelting and refining of secondary copper materials. *Trans. Inst. Min. Metall., Sect. C*, **96**, C151 C155.

Nolic, A. (1997) Metallurgical utilization of reusable products from the recycling industry in a secondary copper smelter. In *EPD Congress 1997*, ed. Mishra, B., TMS, Warrendale, PA, 377 400.

Oshima, E., Igarashi, T., Hasegawa, N. and Kumada, H. (1998) Recent operation for treatment of secondary materials at Mitsubishi Process. In *Sulfide Smelting '98*, ed. Asteljöki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 597 606.

Yoshida, T., Tateiwa, H., Tanno, F., Kahata, M. and Seto, H. (1999) Cu recycling from low Cu containing waste. In *REWAS '99, Vol. II*, ed. Gaballah, I., Hager, J. and Solozabal, R., TMS, Warrendale, PA, 1799 1806.

References

Bedard, M., Chapados, M. and Kachaniwsky, G. (1991) Advances in technology for complex custom feed material treatment at Noranda. *CIM Bull.*, **84** (948), 64 69.

Bussmann, H. (1991) Reprocessing of copper alloy scrap in a modified converter process. In *Copper 91/Cobre 91, Vol. IV Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C., Luraschi, A. and Newman, C.J., The Metallurgical Society of CIM, Montreal, Canada, 321 326.

Custovic, E., Fleischer, G., Kammell, R. and Lumbke, U. (1987) Copper recovery from secondary materials in the shaft furnace with used automobile-tire additions. *Conserv. Recyc.*, **10**, 93 98.

Hanusch, K. and Bussmann, H. (1995) Behavior and removal of associated metals in the secondary metallurgy of copper. In *Third Int. Symp. Recycling of Metals and Engineered Materials*, ed. Queneau, P.B. and Peterson, R.D., TMS, Warrendale, PA, 171 188.

Hedlund, L. (1995) Flexible recycling with Boliden technology. In *Third Int. Symp. Recycling of Metals and Engineered Materials*, ed. Queneau, P.B. and Peterson, R.D., TMS, Warrendale, PA, 155 162.

Jiang, K. (1997) Copper Recycling in China. In *World Conf. Copper Recycl.*, International Copper Study Group, Lisbon, 9 pp.

Kikumoto, N., Abe, K., Nishiwaki, M. and Sato, T. (2000) Treatment of industrial waste material in reverberatory furnace at Onahama Smelter. In *EPD Congress 2000*, ed. Taylor, P.R., TMS, Warrendale, PA, 19 27.

Lehner, T. and Vikdahl, A. (1998) Integrated recycling of non-ferrous metals at Boliden Ltd. Rönskärs Smelter. In *Sulfide Smelting '98*, ed. Asteljöki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 353 362.

Maeda, Y., Inoue, H., Kawamura, S. and Ohike, H. (2000) Metal recycling at Kosaka Smelter. In *Fourth Int. Symp. Recycling of Metals and Engineered Materials*, ed. Stewart, D.L., Stephens, R. and Daley, J.C., TMS, Warrendale, PA, 691 700.

Marnette, W., Kersten, L. and Kramer, U. (1994) The new electric furnace of Norddeutsche Affinerie. In *Pyrometallurgy for Complex Materials and Wastes*, ed. Nilmani, M., Lehner, T. and Rankin, W.J., TMS, Warrendale, PA, 359 367.

Nelmes, W.S. (1987) Current trends in smelting and refining of secondary copper materials. *Trans. Inst. Min. Metall., Sect. C*, **96**, C151 C155.

Nolte, A. (1997) Metallurgical utilization of reusable products from the recycling industry in a secondary copper smelter. In *EPD Congress 1997*, ed. Mishra, B., TMS, Warrendale, PA, 377 400.

Nolte, A. and Kreymann, R. (1999) Optimization of the blast furnace process in a secondary copper smelter. In *Copper 99/Cobre 99, Vol. V Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J. and Weddick, A.J., TMS, Warrendale, PA, 335 343.

O'Brien, N.M. (1992) Processing secondary copper materials in a top blown rotary converter. In *Copper in the '90s*, Indian Copper Development Centre, Calcutta, 76 80.

Oshima, E., Igarashi, T., Hasegawa, N. and Kumada, H. (1998) Recent operation for treatment of secondary materials at Mitsubishi Process. In *Sulfide Smelting '98*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 597 606.

Reid, R.L. (1999) High-tech low-grade recycling. *Scrap*, **56** (3), 76 80.

Rundquist, K. (1997) Copper's nine lives. *Scrap*, **54** (4), 117 126.

Tobback, H. (1991) The challenge for recycling. In *Copper 91/Cobre 91, Vol. IV Pyrometallurgy of Copper*, ed. Diaz, C., Landolt, C., Luraschi, A. and Newman, C.J., The Metallurgical Society of CIM, Montreal, Canada, 313 320.

CHAPTER 22

Melting and Casting

About 95% of the copper currently produced in the United States has existed as cathode copper at some time during its processing (Edelstein, 2000). The cathodes are produced by electrorefining pyrometallurgical anodes (from ore and scrap) and by electrowinning copper leached from 'oxide' and chalcocite ores. To make it useful, this copper must be melted, alloyed as needed, cast and fabricated.

Much of the fabrication process for copper and its alloys is beyond the scope of this book; see Joseph (1999) for more information. However, melting and casting are often the last steps in a copper smelter or refinery. A discussion of these processes is, therefore, in order.

22.1 Product Grades and Quality

The choice of melting and casting technology is defined by:

- (a) the quality of the input copper
- (b) the required chemistry of the desired product
- (c) the type of final product, e.g. wire or tube.

Table 22.1 lists the *copper cathode* impurity limits specified by various national standards (Joseph, 1999; ASTM B115-00). Customers usually require purer copper than in these specifications. Fortunately, recent adoption of stainless steel cathodes for electrorefining and electrowinning has improved cathode purity to match these customer requirements.

The tightest impurity limits in copper cathode are for selenium, tellurium and bismuth. All three of these elements are nearly insoluble in solid copper. They form distinct grain boundary phases upon casting and solidification.

Table 22.1. Upper impurity limits for copper cathodes as specified in the United States, Great Britain and Chile (IWCC). Impurity limits specified for the Southwire Continuous Rod (SCR) systems are also shown. (ASTM = American Society for Testing and Materials; BS = British Standards; ppm = parts per million.)

Element	ASTM B-115		BS EN 1978	IWCC High Grade	SCR (Southwire) Classification System		
	Grade 1	Grade 2			Class 1	Class 2	Class 3
% Cu+Ag	99.95						
Se (ppm)	2	10	2	2	4	8	10
Te (ppm)	2	5	2	2	0.5	1	2
Bi (ppm)	1	3	2	2	0.5	1	2
Bi+Se+Te (ppm)	3		3	3			
Sb (ppm)	4	15	4	4	0.5	0.1	2
Pb (ppm)	5	40	5	5	4	8	12
As (ppm)	5	15	5	5	0.5	0.1	2
Fe (ppm)	10	25	10	10	10	20	30
Ni (ppm)	10	20			10	20	30
Sn (ppm)	5	10					
S (ppm)	15	25	15	15			
Ag (ppm)	25	70	25	25	0.5	10	30
Co (ppm)					3	5	10
Mn (ppm)					3	5	15
Zn (ppm)					5	20	15
Total (ppm)	65		65	65			

Selenium and tellurium form Cu_2Se and Cu_2Te , while bismuth exists as pure Bi (Zaheer, 1995). These phases are brittle and cause rod cracking and poor drawability.

The Unified Numbering System currently recognizes about 35 grades of wrought 'coppers' (99.3% Cu or better) and six grades of cast coppers (Joseph, 1999). Several of these coppers are alloyed with small amounts of phosphorus to combine with oxygen when they are being welded.

Unalloyed coppers can be divided into two general classes. The first is *tough pitch* copper, which purposefully contains ~250 ppm dissolved oxygen (Table 22.2; ASTM B49-98; Feyaerts *et al.*, 1996).

Dissolving oxygen in molten copper accomplishes two goals. The first is

Table 22.2. Upper impurity limit specifications for *tough pitch* copper in the United States and Great Britain. (CDA = Copper Development Association; ASTM = American Society for Testing and Materials; BS = British Standards; ppm = parts per million.)

Element	CDA Cu-ETP-1 (Grade 1)	CDA Cu-ETP-2 (Grade 2)	ASTM B216-97	BS 1038
%Cu (min.)	99.95	99.90	99.88	99.85
Ag (ppm)	25			
As (ppm)	05		120	0200
Sb (ppm)	04		030	0050
Bi (ppm)	02	005	030	0030
Fe (ppm)	10			0100
Pb (ppm)	05	050	040	0100
Ni (ppm)			500	0500
O (ppm)	60	060	550	1000
Se (ppm)	02		250	0300
S (ppm)	15			
Tc (ppm)	02			
Sn (ppm)				0100
Total (ppm)	65	300		

removal of inadvertently absorbed hydrogen during melting by the reaction:



This reduces the amount of porosity created by $\text{H}_2\text{O}(\text{g})$ formation during casting and welding.

The second is reaction of the oxygen with metallic impurities, precipitating them as oxides at grain boundaries during solidification. These oxide precipitates have a smaller adverse effect on drawability than compounds which would form if oxygen were not present.

Most copper is cast and fabricated as *tough pitch*. Specified limits for its impurities are shown in Table 22.2.

The second class of pure coppers are the *oxygen free* (oxygen free copper [OFC] or oxygen free high conductivity copper [OFHC]) grades. The amount of

oxygen in these grades is so low that no visible amount of Cu_2O is present in the solid copper microstructure. The maximum permissible oxygen level in OFC is 10 ppm. In the best grades it is only 5 ppm (ASTM B49-98; Nogami *et al.*, 1993).

Because no Cu_2O is generated in the grain boundaries, the electrical conductivity of OFC is higher than that of tough pitch copper. As a result, OFC is primarily used for demanding electrical applications, such as bus tube and wave guides (Joseph, 1999).

Specific numbers are unavailable, but the fraction of copper sold as OFC is not large. Koshiba *et al.* (2000) and the Copper Development Association (2001) estimate that OFC accounts for less than two percent of total copper use.

Table 22.3. U.S copper processing in 1999, kilotonnes
(Copper Development Association, 2001).

Processing Facility	Copper processed in 1999, kilotonnes
Wire rod mills	2259.6
Brass mills	1878.2
Foundaries	167.3
Powder plants	18.1
Other	82.8

22.2 Melting Technology

22.2.1 Furnace types

Table 22.3 shows the 1999 distribution of copper in the U.S. by type of processing plant (Copper Development Association, 2001). Over half of copper production is drawn into copper wire, a fraction which remained largely unchanged in the 1990's. Also, about half of the 'brass mill product' shown in Table 22.3 is unalloyed copper. It is mostly fabricated into pipe and tube.

As a result, most current melting and casting technology produces (i) copper rod for drawing into wire or (ii) billets for extrusion to pipe and tube. The vast majority of this copper is tough pitch.

Most tough pitch copper is produced from cathode in Asarco type shaft furnaces, Fig. 22.1, Table 22.4. Ninety-five Asarco furnaces were operating in 1995, processing about half the world's copper (Hugens and DeBord, 1995).

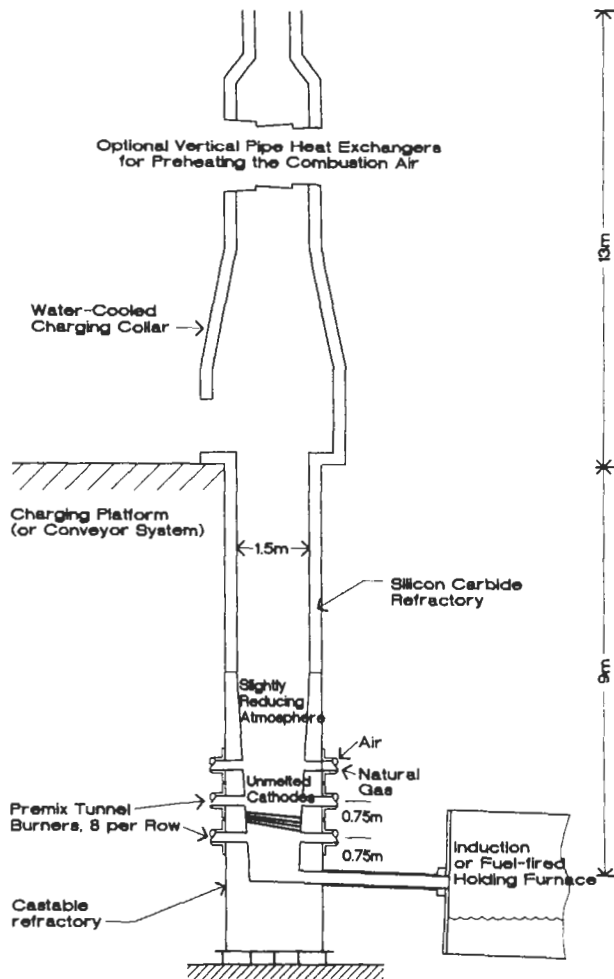


Fig. 22.1. Asarco shaft furnace for melting cathodes. Descending cathodes are melted by ascending combustion gases. Table 22.4 gives industrial operating data

Table 22.4. Operating details of Asarco cathode melting shaft furnaces, 2001.

Melting plant	Nexans Canada Montreal	Phelps Dodge Refinery El Paso, U.S.	Norddeutsche Affinerie Germany	Palabora Mining South Africa
Inputs	cathodes and 'runaround' scrap rod	cathodes	cathodes	cathodes and recycled scrap
Molten copper destination	Hazelett caster & rod mill	Hazelett caster & rod mill	Southwire caster & rod mill	Southwire caster & rod mill
Melting rate, tonnes of copper per hour	48	75	45	35 capacity, 21 operating
Feed system	skip hoist	elevator with automatic trip	forklift truck & skip hoist	forklift truck
Furnace details, m				
height, taphole to charge floor	13	12.2	10	7.9
inside diameter at charge floor	1.7	1.75	1.8	1.6
inside diameter at taphole	1.3	1.37	1.3	1.3
Burner details				
number of burners	23	32	22	23
rows of burners	3	4	3	3
fuel	natural gas	natural gas	natural gas	propane
combustion rate, Nm ³ /hour		2400	1100	50 x 10 ⁶ kJ/h @21.5 t Cu/h
Nm ³ of natural gas burnt per tonne of copper melted	1.9 giga- joules	1.8 giga- joules	26 (furnace only)	2.34 giga- joules
Refractory life, tonnes of copper				
above burners	500 000		500 000	3±0.5 years
below burners	250 000		300 000	3±0.5 years

The furnace operates counter currently, with rising hot hydrocarbon combustion gas heating and melting descending copper cathodes. Natural gas is the usual fuel, Table 22.4. The process is continuous.

An important feature of the furnace is its burner. The burner uses a high-velocity premix flame in a burner tile, accomplishing the premix within the burner itself rather than in an external manifold. This design reduces accretions, shortens downtime for cleaning and allows individual control of each burner.

Automatic burner control using CO analysis of the offgas is a common feature of these furnaces (Schwarze, 1994). The flame is intended to generate a moderately reducing atmosphere, resulting in molten metal with about 50 ppm oxygen and 0.3-0.4 ppm hydrogen. Other impurity concentrations are largely unaffected.

The most common feed to Asarco shaft furnaces is copper cathodes. High-quality scrap is also occasionally melted.

Lower-quality scrap is less suitable for Asarco shaft furnaces, which have no refining ability. As a result, some producers use reverberatory furnaces as an adjunct to their Asarco units (Schwarze, 1994; McCullough *et al.*, 1996). Metal charged to these furnaces can be fire refined. This allows the furnaces to be used for melting lower grade copper and scrap.

Another melting option is the induction furnace, either the channel or coreless type (Schwarze, 1994). Induction furnaces are usually used to melt oxygen free copper, since the absence of a combustion atmosphere prevents oxygen and hydrogen from inadvertently being absorbed into the molten copper.

Feed to induction furnaces which produce oxygen free copper is limited to high-quality cathode and scrap. Melting capacities are generally less than two tonnes per hour (Vaidyanath, 1992; Nogami *et al.*, 1993).

Molten copper from the above described melting furnaces flows into a holding furnace before being directed to continuous casting. This ensures a steady supply of molten copper to the casting machines.

Holding furnaces vary considerably in size and type, but they are usually induction-heated to minimize hydrogen pickup from combustion gases. The copper may also be covered with charcoal to minimize oxygen pickup. Automation of the holding furnace to produce a steady flow of constant temperature metal has become an important part of casting operations (Shook and Shelton, 1999).

Ceramic filters have also begun to appear in copper casting plants, to remove

inclusions caused by erosion of the furnace refractories or precipitation of solid impurities from the molten copper (Strand *et al.*, 1994; Zaheer, 1995).

Introduction of multi-chamber induction furnaces is also a recent development (Bebber and Phillips, 1998). The 'storage' chambers in these furnaces eliminate the need for multiple holding furnaces.

22.2.2 Hydrogen and oxygen measurement/control

As previously mentioned, control of hydrogen and oxygen in molten copper is critical. Oxygen is monitored one of two ways. The first is Leco infrared absorbance, which measures the amount of CO₂ generated when the oxygen in a heated sample of copper reacts with admixed carbon black. This method requires external sample preparation, so does not offer an immediate turnaround.

The second approach is an oxygen sensor, which is applied directly to the molten copper. The electrode potential of the dissolved oxygen in the copper is measured against a reference electrode in the sensor. This relative potential is converted to an equivalent oxygen content in the metal at the measurement temperature. Dion *et al.* (1995) have shown that the two methods yield similar results. The amount of oxygen in the molten copper is controlled by adjusting burner flames and by injecting compressed air into the copper, Table 22.5.

Hydrogen is more difficult to monitor and control. Analysis of solid samples is usual practice (Strand *et al.*, 1994), but efforts have been made to adapt aluminum industry technology to on-line measurement of hydrogen in molten copper (Hugens, 1994).

Hydrogen pickup is minimized by melting the copper with oxidizing flames. However, the molten copper always contains a small amount of hydrogen from entrapped electrolyte in the cathode feed (Chia and Patel, 1992; Back *et al.*, 1993).

22.3 Casting Machines

Casting machines can be divided into three main types:

- (a) billet ('log') casting, for extrusion and drawing to tube, Fig. 22.2
- (b) bar casting, for rolling to rod and drawing to wire, Figs. 22.3, 22.4, Table 22.5
- (c) strip casting, for rolling to sheet and forming of welded tube.

22.3.1 Billet casting

Billet casting is usually performed in vertical direct-chill casters, such as that

shown in Fig. 22.2 (Nussbaum, 1973). Graphite-lined copper or graphite-ceramic molds are used. Diameters up to 30 centimeters are cast (Hugens and DeBord, 1995). Oscillation of the water-cooled molds ($60\text{--}360\text{ min}^{-1}$) improves surface quality and prevents sticking in the mold.

Over the past decade, horizontal casters have begun to replace vertical billet casters, due to their lower cost (Owen, 1990). A recent innovation is horizontal continuous casting of hollow billets (Rantanen, 1995; Taylor, 1992). These billets are rolled directly to tube, eliminating the need for extrusion and piercing. They give a low-cost, high quality product.

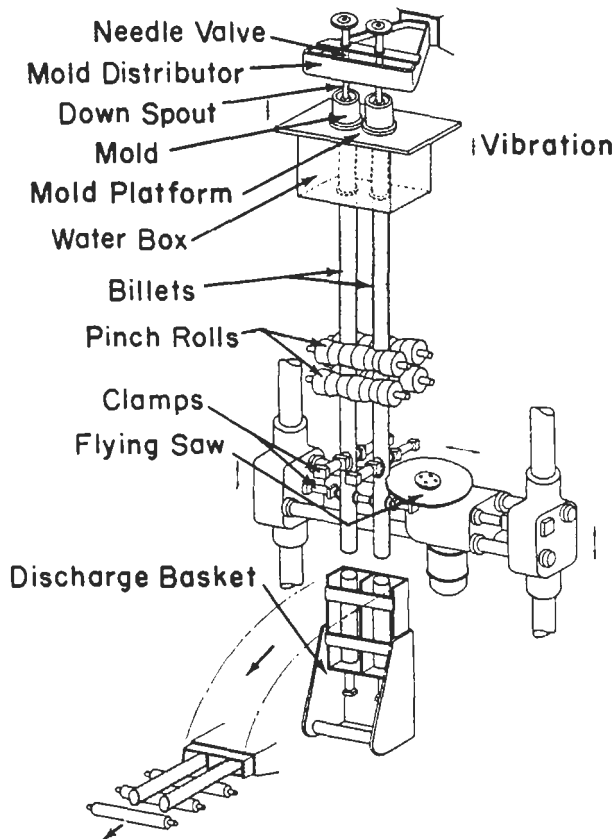


Fig. 22.2. Continuous direct-chill casting machine for casting copper billet (Nussbaum, 1973). Reprinted with permission of TMS.

22.3.2 Bar and rod casting

Copper bar is mostly cast in continuous wheel-and-band and twin-band casting machines, Table 22.5 and Figs. 22.3 and 15.3.

Figure 22.3 shows a Southwire wheel-and-band caster. Its key features are:

- (a) a rotating copper-zirconium alloy rimmed wheel with a mold shape machined into its circumference
- (b) a cold-rolled steel band which moves in the same direction and at the same speed as the wheel circumference.

Molten copper is poured from a 'pour pot' into the mold just as the steel band joins the wheel to form the fourth side of the mold. The wheel and band move together through water sprays as the copper solidifies. After 180-250° of rotation, the band moves off to an idler wheel and the solidified copper bar is drawn away (under minimum tension) to a rolling mill. Pouring to bar separation takes about 0.25 minutes (Adams and Sinha, 1990). The cast bar is removed at about 0.25 m/s. The Properzi casting machine is similar.

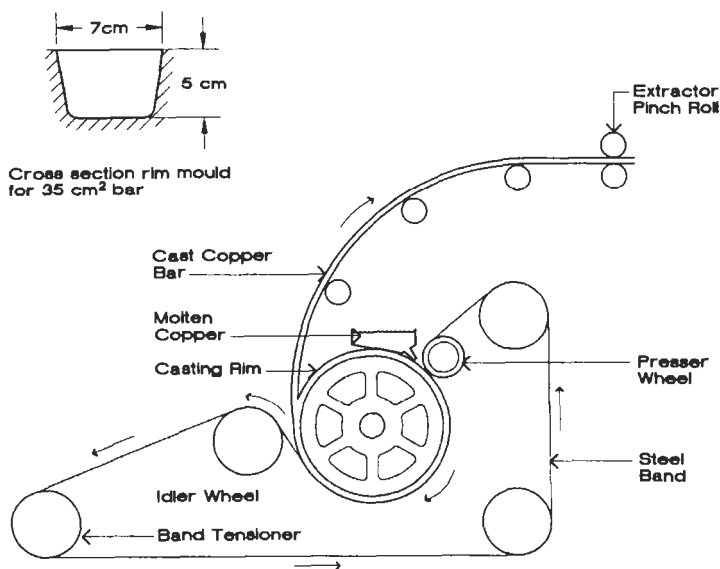


Fig. 22.3. Southwire casting machine for continuously casting copper bar (Adams and Sinha, 1990). The inset shows the cross-section of the rim mold.

The Hazeltett twin-band caster is shown in Fig. 15.3 in its role as an anode-casting machine. Molten copper is fed from a pour pot into the space between two sloped moving steel bands. The bands are held apart by moving alloyed copper dam blocks on each side, creating a mold cavity ranging between 5-15 cm in width and 5-10 cm in thickness. Both separations are adjustable, allowing variable product size. Solidification times are similar to those of the Southwire and Properzi machines (Strand *et al.*, 1994).

The three types of moving-band casting devices have several features in common. All require lubrication of the bands and mold wheel or dam blocks, using silicone oil or acetylene soot (Adams and Sinha, 1990). Leftover soot is removed from the bands after each revolution, then reapplied. This ensures an even lubricant thickness and a constant heat transfer rate.

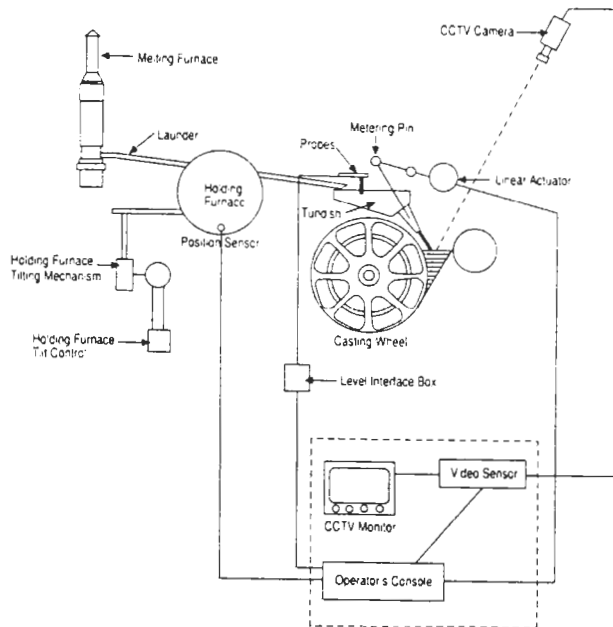


Fig. 22.4. System for controlling molten copper level in Southwire continuous casting machine (Adams and Sinha, 1990). Reprinted courtesy TMS.

Table 22.5. Operating details of Hazeltett and Southwire continuous casting machines, 2001.

Casting plant	Nexans Canada	Phelps Dodge Refinery	Norddeutsche Affinerie	Palabora Mining
Casting machine	Hazeltett twin band	Hazeltett twin band	Southwire wheel & band	Southwire wheel & band
Bar size, cm x cm	7 x 13	7 x 13.2	5.8 x 11.7	2.15 x 15
Casting rate of this bar, tonnes/hour	48	63	45	21.5
Molten copper level control in caster	electromagnetic pool level measurement	electromagn- etic pool level measurement	X-ray	infrared scan- ner
Casting temp., °C	1125	1130	1110-1125	1100-1130
Bar temperature leaving caster, °C	~950	1015	900	890-930
Target O in copper, ppm	250	250	160-250	180-250
measurement technique	Electro-nite cell in launder; Tempolab in holding furnace; Leco on rod	Leco on rod	Leco	Leco on rod
control system	manual	compressed air injection into molten Cu	protective gas, larger or smaller quan- tity	holding fur- nace CO and launder burner CO
Wheel and band details				
wheel diameter, m			3.05	2.44
rotation speed, rpm			1.33	1.8
rim materials			Cu-Cr-Zr	Cu-Cr-Zr
rim life, tonnes of cast copper			100 000	45 000
band material			cold rolled steel	steel
band life			72 hours	1000-1800 t Cu per band
lubrication			Lubro 30 FM	Thermia B (Shell)
Twin band details				
caster length, m	3.7	3.7		
band material	low carbon steel	titanium steel		
life	24 hours	1300 tonnes Cu		
lubrication	oil	Union Carbide Lb-300x oil		
dam block material	Si bronze	Cu with 1.7- 2% Ni & 0.5- 0.9% Si		
dam block life	100 000 tonnes cast copper	~300 hours		

The casters all use similar input metal temperatures, 1110–1130°C, Table 22.5. All require smooth, low-turbulence metal feed into the mold cavity, to reduce defects in the solidified cast bar. Lastly, all require steady metal levels in the pour pot and mold.

Control of mold metal level is done automatically, Fig. 22.4. Metal level in the mold cavity is measured electromagnetically (Hazelett) or with a television camera (Southwire). It is controlled with a stainless-steel metering pin in the pour pot.

Metal level in the pour pot is determined using a conductivity probe or load cell. It is controlled by changing the tilt of the holding furnace which feeds it (Nogami *et al.*, 1993; Shook and Shelton, 1999).

The temperature of the solidified copper departing the machine is controlled to 940–1015°C by varying casting machine cooling-water flow rate.

Common practice for copper cast in the Hazelett, Properzi and Southwire machines is direct feeding of the solidified bar into a rolling machine to give continuous production of copper rod. Southwire Continuous Rod and Hazelett Contirod are prominent (Buch *et al.*, 1992; Hugens and DeBord, 1995; Zaheer, 1995). Both systems produce up to 60 tonnes of 8–14 mm rod per hour, Table 22.5.

22.3.3 Oxygen free copper casting

The low oxygen and hydrogen content of oxygen free copper minimizes porosity when this metal is cast. As a result, the rolling step which is used to turn tough pitch copper bar into rod is not necessary. This has led to the development of processes for direct casting of OFC copper rod. These include both horizontal and vertical casting machines (Joseph, 1999).

Horizontal rod-casting machines use a graphite crucible and a submerged casting die. They generally operate as multi-strand machines. Their capacities are limited to about 0.6 tonnes per hour. They cannot produce very small diameter rod.

Upward vertical casting machines use a vacuum to draw metal into water-cooled graphite-lined dies partially submerged in the molten copper. As it freezes, the rod is mechanically drawn upward and coiled (Eklin, 1999; Rautomead, 2000). It is about the same size as rolled rod.

22.3.4 Strip casting

The development of strip casting for copper and copper alloys parallels

developments in the steel industry, in that continuous processes are favored. The newer the technology, the less rolling is required. One approach taken by small-volume producers is to roll strip from the bar produced by a Hazelett caster (Roller *et al.*, 1999). This can be combined with continuous tube rolling/welding to make optimum use of the casting machine for a mix of products.

However, direct strip casting which avoids rolling is the goal. Current horizontal casters can produce 'thick strip' (15-20 mm), which requires some rolling (Roller and Reichelt, 1994). Development efforts are being made to develop 'thin-strip' (5-12 mm) casting to avoid rolling completely.

22.4 Summary

The last step in copper extraction is melting and casting of electrorefined and electrowon cathodes. The main products of this melting and casting are:

- (a) continuous rectangular bar for rolling to rod and drawing to wire
- (b) round billets ('logs') for extrusion and drawing to tube
- (c) flat strip for rolling to sheet and forming into welded tube.

The copper in these products is almost always 'tough pitch' copper, i.e. cathode copper into which ~250 ppm oxygen has been dissolved during melting/casting. This dissolved oxygen:

- (a) ensures a low level of hydrogen in the copper and thereby avoids steam porosity during casting and welding
- (b) ties up impurities as innocuous grain boundary oxide precipitates in the cast copper.

The remainder of unalloyed copper production is in the form of oxygen free high conductivity copper with 5 to 10 ppm dissolved oxygen. This copper is expensive to produce so it is only used for the most demanding high conductivity applications. It accounts for less than 2% of copper production.

These pure copper products account for about 70% of copper use. The remainder is used in the form of copper alloy, mainly brass and bronze.

The principal melting tool for cathodes is the Asarco shaft furnace. It is thermally efficient and provides good oxygen-in-copper control. Its molten copper is mainly cast:

- (a) as rectangular bar in continuous wheel-and-band and twin-band casters
- (b) as round billets ('logs') in horizontal and vertical direct chill casters.

The bar casters are especially efficient because their hot bar can be fed directly into continuous rod-rolling machines.

The quality of cathode copper is tested severely by its performance during casting, rolling and drawing to fine wire. Copper for this use must have high electrical conductivity, good drawability and good annealability. These properties are all favored by maximum cathode purity.

Suggested Reading

Adams, R. and Sinha, U. (1990) Improving the quality of continuous copper rod. *Journal of Metals*, **42**(5), 31-34.

Hugens, J.R. and DeBord, M. (1995) Asarco shaft melting and casting technologies '95. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Chen, W.J., Díaz, C., Luraschi, A. and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 133-146.

Joseph, G. (1999) *Copper: Its Trade, Manufacture, Use and Environmental Status*, ed. Kundig, K.J.A., ASM International, Materials Park, OH, 141-154; 193-217.

Schwarze, M. (1994) Furnace systems for continuous copper rod production. *Wire Industry*, **61** (731), 741-743; 748.

References

Adams, R. and Sinha, U. (1990) Improving the quality of continuous copper rod. *Journal of Metals*, **42** (5), 31-34.

American Society for Testing and Materials (1997) Standard specification for tough pitch fire-refined copper – refinery shapes (B216-97). In *Annual Book of Standards, Section 2, Nonferrous Metal Products*, ASTM, Philadelphia, PA.

American Society for Testing and Materials (1998) Standard specification for copper rod drawing stock for electrical purposes (B49-98). In *Annual Book of Standards, Section 2, Nonferrous Metal Products*, ASTM, Philadelphia, PA.

American Society for Testing and Materials (2000) Standard specification for electrolytic cathode copper (B115-00). In *Annual Book of Standards, Section 2, Nonferrous Metal Products*, ASTM, Philadelphia, PA.

Back, E., Paschen, P., Wallner, J. and Wobking, H. (1993) Decrease of hydrogen and oxygen contents in phosphorus-free high conductivity copper prior to continuous casting. *BIIM*, **138**, 22-26.

Bebbler, H. and Phillips, G. (1998) Induction furnace technology for horizontal casting. *Metallurgia*, **65**, 349-351.

Buch, E., Siebel, K. and Berendes, H. (1992) Operational experience of newly developed mini copper rod casting and rolling plants, CONTIROD system. *Wire*, **42**, 110 114.

Chia, E.H. and Patel, G.R. (1992) Copper rod and cathode quality as affected by hydrogen and organic additives. *Wire J. Int.*, **25** (11), 67 75.

Copper Development Association (2001) CDA's annual data '00. www.copper.org

Dion, J.L., Sastri, V.S. and Sahoo, M. (1995) Critical studies on determination of oxygen in copper anodes. *Trans. Am. Foundryman's Soc.*, **103**, 47 53.

Edelstein, D.E. (2000) Copper. In *1999 Minerals Yearbook*, United States Geological Survey, <http://minerals.usgs.gov/minerals/pubs/commodity/copper/240499.pdf>.

Eklin, L. (1999) UPGAST—near net shape casting of copper wire rod. In *1999 Conf. Proc. Wire Assoc. Inter.*, Wire Association International, Guilford, CT, 274 277.

Feyaerts, K., Huybrechts, P., Schamp, J., van Humbeeck, J. and Verlinden, B. (1996) The effects of impurities on the recrystallization behavior of tough pitch hot rolled copper rod. *Wire J. Int.*, **29** (11), 68 76.

Hugens, J.R. (1994) An apparatus for monitoring dissolved hydrogen in liquid copper. In *EPD Congress 1994*, ed. Warren, G.W., TMS, Warrendale, PA, 657 667.

Hugens, J.R. and DeBord, M. (1995) Asarco shaft melting and casting technologies '95. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. IV Pyrometallurgy of Copper*, ed. Chen, W.J., Diaz, C., Luraschi, A. and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 133 146.

Joseph, G. (1999) *Copper: Its Trade, Manufacture, Use and Environmental Status*, ed. Kundig, K.J.A., ASM International, Materials Park, OH, 141 154; 193 217.

Koshiba, Y., Masui, T. and Iida, N. (2000) Mitsubishi Materials' high performance oxygen free copper and high performance alloys. In *Second Int. Conf. Processing Mater. Prop.*, ed. Mishra, B. and Yamauchi, C., TMS, Warrendale, PA, 101 104.

McCullough, T., Parghi, R. and Ebeling, C. (1996) Oxy-fuel copper melting for increased productivity and process enhancement. In *Gas Interactions in Nonferrous Metals Processing*, ed. Saha, D., TMS, Warrendale, PA, 221 227.

Nogami, K., Hori, K. and Oshima, E. (1993) Continuous casting of Onahama oxygen-free copper and alloys. In *First Int. Conf. Processing Mater. Prop.*, ed. Henein, H. and Oki, T., TMS, Warrendale, PA, 389 392.

Nussbaum, A.I. (1973) Fully and semi-continuous casting of copper and copper-base alloy billets and slabs. In *Continuous Casting*, ed. Olen, K.R., TMS, Warrendale, Pennsylvania, 73 91.

Owen, M. (1990) High-quality copper billet. *Tube International*, **9** (38), 273 277.

Rantanen, M. (1995) Cast and roll—new copper tube manufacturing technology from Outokumpu. In *Copper 95-Cobre 95 Proceedings of the Third International Conference, Vol. 1 Plenary Lectures, Economics, Applications and Fabrication of Copper*, ed. Diaz, C., Bokovay, G., Lagos, G., Larrivide, H. and Sahoo, M., The Metallurgical Society of CIM, Montreal, Canada, 449 453.

Rautomead, Ltd. (2000) Copper rod and wire — an integrated approach towards optimum quality. *Metallurgia*, **67** (9), 24 25.

Roller, E., Kalkenings, P. and Hausler, K.H. (1999) Continuous narrow strip production line for welded copper tubes. *Tube International*, **18**, 28 31.

Roller, E. and Reichelt, W. (1994) Strip casting of copper and copper alloys. In *Proc. METEC Congress 94, Vol. 1*, Verein Deutscher Eisenhüttenleute, Düsseldorf, Germany, 480 486.

Schwarze, M. (1994) Furnace systems for continuous copper rod production. *Wire Industry*, **61** (731), 741 743; 748.

Shook, A.A. and Shelton, C.A. (1999) Improved rod plant level control with UNAC. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference. Vol. 1 Plenary Lectures, Movement of Copper and Industry Outlook, Copper Applications and Fabrication*, ed. Eltringham, G.A., Piret, N.L. and Sahoo, M., TMS, Warrendale, PA, 293 302.

Strand, C.I., Breitling, D. and DeBord, M. (1994) Quality control system for the manufacture of copper rod. In *1994 Conf. Proc. Wire Assoc. Inter.*, Wire Association International, Guilford, CT, 147 151.

Taylor, J. (1992) Continuous casting of hollow copper billets. *TPQ*, **3** (3), 42 47.

Vaidyanath, L. R. (1992) Producing copper and copper alloy tubes. *Tube International*, **11** (48), 165 166.

Zaheer, T. (1995) Reduction of impurities in copper. *Wire Industry*, **62** (742), 551 553.

CHAPTER 23

Costs of Copper Production

This chapter:

- (a) describes the investment and production costs of producing copper metal from ore
- (b) discusses how these costs are affected by such factors as ore grade, process choice and inflation
- (c) indicates where cost savings might be made in the future.

The discussion centers on mine, concentrator, smelter and refinery costs. Costs of producing copper by leach/solvent extraction/electrowinning and from scrap are also discussed.

The cost data have been obtained from published information and personal contacts in the copper industry. They have been obtained during 2001 and 2002 and are expressed in 2002 U.S. dollars. The data are directly applicable to plants in the U.S.A. They are thought to be similar to costs in other parts of the world.

Investment and operating costs are significantly affected by inflation. Fortunately, U.S. dollar inflation was low during the 1990's and early 2000's, so the cost of producing copper rose slowly.

This is confirmed by the 1982-2001 inflationary index for mining and milling equipment, Fig. 23.1. The basic equation for using this index is:

$$\frac{\text{Cost}_{(\text{year A})}}{\text{Cost}_{(\text{year B})}} = \frac{\text{Index}_{(\text{year A})}}{\text{Index}_{(\text{year B})}} \quad (23.1)$$

(for identical equipment). Fig. 23.1 and Eqn. 23.1 show that 1990's mining and milling equipment costs rose less than 2% per year.

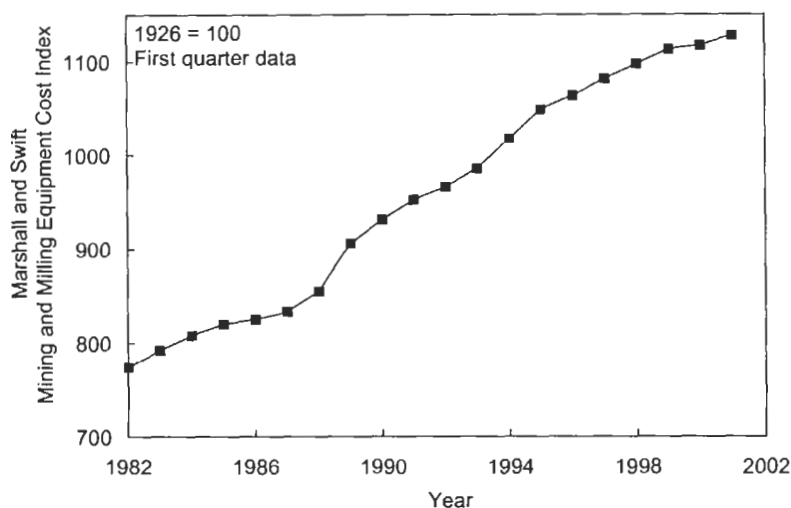


Fig. 23.1. Mining and milling equipment cost index from 1982 to 2001 (Chemical Engineering, 2001).

Accuracy of the cost data

The investment and operating costs in this chapter are at the 'study estimate' level, which is equivalent to an accuracy of $\pm 30\%$ (Bauman, 1964). Data with this accuracy can be used to examine the economic feasibility of a project before spending significant funds for piloting, market studies, land surveys and acquisition (Perry and Chilton, 1973).

23.1 Overall Investment Costs: Mine through Refinery

Table 23.1 lists 'study estimate' investment costs for a mine/concentrator/smelter/refinery complex designed to produce electrorefined cathodes from 0.75% Cu ore. These costs are for a 'green field' (new) operation starting on a virgin site with construction beginning January 1, 2002.

The investment costs are expressed in terms of investment cost per annual tonne of product copper. This is defined by the equation:

$$\text{plant cost} = \frac{\text{investment cost per annual tonne of copper}}{\text{tonne of copper}} \times \frac{\text{plant capacity, tonnes of copper per year}}{\text{tonnes of copper per year}} \quad (23.2).$$

This equation shows, for example, that the investment in an electrolyrefinery

which:

- (a) costs \$500 per annual tonne of copper
- (b) produces 200 000 tonnes of copper per year

will be:

$$\text{investment cost} = \frac{\$500 \text{ per annual tonne of copper}}{200\,000 \text{ tonnes of copper per year}} \times 200\,000 \text{ tonnes of copper per year}$$

or: $\$100 \times 10^6$.

Table 23.1 indicates that the fixed capital investment for a complex which produces electrowrefined copper from 0.75% Cu ore is in the range of \$8500 per annual tonne of copper. To this must be added working capital to cover the initial operating expenses of the complex (about 10% of fixed capital investment, Peters and Timmerhaus, 1968). It means that a new mine/mill/smelter/refinery complex which is to produce 200 000 tonnes of copper per year will cost $\sim \$1900 \times 10^6$.

23.1.1 Variation in investment costs

Mine investment costs vary considerably between mining operations. This is due to differences in ore grades, mine sizes, mining method, topography and ground condition.

Underground mine development costs considerably more than open pit mine development, per annual tonne of mined ore. This, and the high cost of operating underground explain why underground orebodies must contain higher % Cu ore than open pit orebodies.

Table 23.1. Copper extraction *investment* costs. Fixed investment costs for a copper extraction complex, starting with 0.75% Cu ore. The costs are at the 'study estimate' level of accuracy. Cost effects of underground mining and ore grade are discussed in Section 23.1.1.

Facility	Fixed investment cost (\$U.S. per annual tonne of Cu)
Mine (open pit)	3000
Concentrator	2500
Smelter (Outokumpu flash furnace smelting/ converting), including sulfuric acid plant	2500
Electrolytic refinery (excluding precious metals refinery)	500
Total	8500

Ore grade has a direct effect on mine investment costs, \$ per annual tonne of product copper. Consider (for example) two identical orebodies, one containing 0.5% Cu ore and the other 1% Cu ore. Achievement of an identical annual production of Cu requires that the 0.5% Cu ore be mined at twice the rate of the 1% Cu ore. This, in turn, requires:

- (a) about twice as much plant and equipment (e.g. trucks)
- (b) about twice as much investment.

The same is true for the concentrator – it will have to treat 0.5% Cu ore twice as fast as 1% Cu ore – to achieve the same annual production of Cu. This will require about twice the amount of concentrator equipment and about twice the investment.

Smelter investment costs, per annual tonne of copper production, are influenced by *concentrate* grade rather than by ore grade. The higher the % Cu in the concentrate, the smaller the smelter (and smelter investment) for a given annual production of copper. High Cu grade concentrates also minimize smelter *operating* costs (e.g. materials handling costs, fuel consumption costs, gas handling costs) per tonne of copper.

Refinery investment costs are not much affected by mine/concentrator/smelter characteristics. This is because copper refineries treat 99.5% Cu anodes, irrespective of the preceding processes.

23.1.2 Economic sizes of plants

Mines can be economic at any size, depending upon the Cu grade of their ore. Thus, copper mines are operating at production rates between 10 000 tonnes of ore per day (a high Cu grade operation) to 100 000 tonnes per day (a large open-pit low Cu grade operation, EMJ, 1998).

Concentrators vary similarly. A new large concentrator unit typically consists of a semi-autogenous grinding mill, two ball mills and a flotation circuit. It is capable of treating 30 000 to 50 000 tonnes of ore per day (Dufresne, 2000; EMJ, 1998). Larger concentrators consist of multiples of this basic concentrating unit.

Smelters are almost always large because their minimum economic output is that of a single, fully used high intensity smelting furnace (e.g. flash furnace). These furnaces typically smelt 1000 to 3000 tonnes of concentrate per day.

Copper refineries are usually sized to match the anode output of an adjacent smelter. The advantage of one-smelter/one-refinery combination at the same site is shared site facilities, particularly for anode casting and anode scrap re-melting.

A few refineries treat the anodes from several smelters.

23.2 Overall Direct Operating Costs: Mine Through Refinery

Direct operating ('cash') costs (excluding depreciation, capital repayment and income taxes) for mining/concentrating/smeltering/electrorefining are given in Table 23.2. The table shows that the direct operating costs for the major steps are, in descending order, concentration and smelting (about equal); open pit mining; electrorefining; and sales and distribution. Overall direct operating costs for extraction are ~\$1 per kg of copper.

23.2.1 Variations in direct operating costs

The operating costs which vary most are those for mining and concentrating. The amounts of ore which must be handled by these operations, per tonne of Cu, vary directly with % Cu in ore – and this significantly affects operating costs. Also, underground mining costs can be twice those of open pit mining – they must be offset by high % Cu underground ore.

Table 23.2. Copper extraction *operating* costs. Direct operating costs for producing electrorefined copper cathodes from a 0.75% Cu ore (assuming 90% Cu recovery). Maintenance is included. The costs are at the 'study estimate' level. Factors affecting these costs are discussed in Section 23.2.1.

Activity	Direct operating cost (\$U.S. per kg of Cu)
Open pit mining, 0.75% Cu ore @ \$1.6/tonne of ore	0.25
Beneficiation from 0.75% Cu ore to 30% Cu concentrate at shipping point, including tailings disposal @ \$2.5/tonne of ore	0.35
Smelting @ \$80/tonne of 30% Cu concentrate including sulfuric acid production	0.3
Electrolytic refining, excluding precious metals recovery	0.1
Sales and distribution	0.05
Local management and overhead	0.05
Total direct operating cost	1.10

23.3 Total Production Costs, Selling Prices, Profitability

The total cost of producing copper from ore is made up of:

- (a) direct operating costs (Section 23.2)
- (b) finance (indirect) costs, i.e. interest and capital recovery.

A reasonable estimate for (b) is 12% of the total capital investment per year. Based on a fixed capital investment of \$8500 (+ 10% working capital) per annual tonne of copper, this is equivalent to:

\$1100 per tonne of copper*

or

\$1.1 per kg of copper.

Thus the direct (\$1.1) plus indirect (\$1.1) operating costs of producing electrorefined copper in a new operation are of the order of \$2.2 per kg. For a new operation to be profitable, the selling price of copper must exceed these costs.

Mines and plants which have been in operation for many years may have repaid much of their original capital investment. In this case, direct operating costs (plus refurbishing) are the main cost component. This type of operation will be profitable at selling prices of ~\$1.5 per kg of copper.

In summary, the price-profit situation is:

- (a) At copper selling prices above \$2.2 per kg, copper extraction is profitable and expansion of the industry is encouraged. Underground orebodies containing about 1.5 % Cu are viable as are open-pit orebodies containing about 0.75% Cu.
- (b) At selling prices below about ~\$1.5 per kg, some mines and plants are unprofitable. Some operations begin to shut down.

These costs and prices all refer to January 1, 2002. They will increase at about the same rate as the cost index in Fig. 23.1.

The 2001 selling price of copper was about \$1.60 per kg so that direct operating costs were met in most cases. However, the most costly copper operations were unprofitable at this price and several closed, especially in North America.

$$\begin{aligned}
 \text{* Finance charges} &= \frac{\text{finance charges, \$ / year}}{\text{copper production, tonnes / year}} \\
 \text{per tonne of copper} &= \frac{12\% \text{ per year} / 100\% \times \text{total capital investment, \$}}{\text{copper production, tonnes / year}} \\
 &= 0.12 \times (\text{capital investment per annual tonne of copper})
 \end{aligned}$$

23.3.1 Byproduct credits

Many Cu orebodies contain Ag and Au (EMJ, 1998). These metals follow Cu during concentration, smelting and refining. They are recovered during electrorefining (with some additional treatment) and sold. Other orebodies contain MoS_2 which is recovered in the concentrator and sold. The credits (sales minus extra costs for recovery) for these byproducts should be included in project evaluations.

23.4 Concentrating Costs

The investment costs of constructing a Cu concentrator are of the order of \$20 per annual tonne of ore (Dufresne, 2000). This means that a 10×10^6 tonnes of ore per year concentrator will cost $\sim \$200 \times 10^6$.

Table 23.3 breaks concentrator investment costs into major cost components, expressed as a percentage of total investment cost. The largest cost item is the grinding mill/classifier circuit. The grinding mills are expensive. They also require extensive foundations and controls.

Table 23.3. Concentrator *investment* costs. Investment costs for a copper concentrator by section, expressed as a percentage of the total investment cost. Control equipment costs are included in each section.

Section	Percent of total investment cost
Ore handling, storage, conveying equipment	10
Semi-autogenous grinding mill, ball mills and size classifiers	50
Flotation cells and associated equipment	10
Dewatering equipment, tailings dam, concentrate loading facilities	30
Total	100

Concentrator direct *operating* costs (Table 23.4) are of the order of \$2.5/tonne of ore, which is equivalent to about \$0.4/kg of Cu (assuming 0.75% Cu ore and 90% Cu recovery). Grinding is by far the largest operating cost, followed by flotation. Electricity and operating supplies are the largest cost components, Table 23.5.

Grinding and flotation costs vary markedly for different ores. Grinding costs are

Table 23.4. Concentrator *operating costs by activity*. Direct operating costs of producing 30% Cu concentrate from 0.75% Cu ore. Ore cost is not included.

Activity	Cost per tonne of ore (\$U.S.)
Crushing, conveying, storage	0.4
Semi-autogenous grinding, ball mill grinding, size classification	1.3
Flotation	0.4
Dewatering, filtering, drying, storage and loading of concentrate	0.2
Tailings disposal, effluent control, water recycle	0.15
Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)	0.05
Total	2.5

Table 23.5. Concentrator *operating costs by cost component*. Expenditures on energy, manpower, supplies and overhead are shown. Ore cost is not included.

Component	Percent of concentrating cost
Electrical energy	
crushing and grinding	25
flotation and tailings disposal	3
other (including hydrocarbon fuel)	2
	30
Operating labor	5
Maintenance labor	5
Maintenance and operating supplies, including freight and handling	30
Reagents and grinding balls	
reagents and lime	10
grinding media	15
	25
Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)	5
Total	100

high for hard primary ores and low for secondary (altered) ores. Flotation costs are low for simple Cu sulfide ores. They increase with increasing ore complexity.

23.5 Smelting Costs

The investment cost of a new Outokumpu flash furnace/flash converter smelter is ~\$2500 per annual tonne of copper. A smelter designed to produce 200 000 tonnes of new anode copper per year will cost, therefore, about $\$500 \times 10^6$.

Table 23.6 breaks this investment cost into its major components. About 75% of the investment goes into concentrate handling/smelting/converting/anode casting and about 25% into gas handling/sulfuric acid manufacture.

Table 23.6. Smelter *investment* costs. Investment costs of a flash furnace/flash converter smelter by section, expressed as a percentage of total fixed investment cost. The costs include installation and housing of the units.

Item	Percent of smelter cost
Concentrate handling and drying, including delivery of dry concentrate to smelting furnace	10
Oxygen plant	10
Flash furnace	20
Flash converter, including matte granulation and crushing	15
Cu-from-slag recovery equipment (electric furnace or flotation) including barren slag disposal	10
Anode furnaces and anode casting equipment	10
Gas handling system including waste heat boilers, electrostatic precipitators and sulfuric acid plant	25
Total	100

23.5.1 Investment costs for alternative smelting methods

In 2002, there are six major intensive smelting processes available for installing in new smelters or for modernizing old smelters. They are:

Ausmelt	Isasmelt
Mitsubishi	Noranda
Outokumpu flash	Teniente.

Each has been installed during the late 1990's and early 2000's. Each appears to be competitive for new and replacement smelting units.

23.5.2 Smelter operating costs

Table 23.7 shows the direct costs of operating an autothermal, oxygen-enriched

Table 23.7. *Smelter operating costs by activity.* Direct operating costs for producing anodes from 30% Cu concentrate in a flash smelting/flash converting smelter, including maintenance. Concentrate cost is not included.

Activity	Cost, \$U.S. per tonne of concentrate
Concentrate reception, storage and delivery to dryer	5
Flash furnace smelting including concentrate drying, gas handling and delivery of 70% Cu crushed matte granules to flash converting	20
Flash converting including delivery of molten copper to anode furnaces	20
Cu recovery from smelting slag	15
Anode-making including desulfurization and deoxidation of molten copper, anode casting and loading for transport to electrorefinery	5
Sulfuric acid plant including acid storage and loading of rail cars and trucks. Costs of treating 'acid plant blowdown' and credit for sulfuric acid are included	10
Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)	5
Total	80

Table 23.8. *Smelter operating costs by cost component.* Expenditures on manpower, utilities and supplies in a flash smelting/flash converting smelter, by percentage. Concentrate cost is not included.

Component	Percent of smelting cost
Oxygen	10
Operating manpower, including supervision	20
Maintenance manpower, including supervision	10
Electricity (<i>excluding</i> electricity used for making oxygen)	10
Hydrocarbon fuel	5
Flux and refractories	5
Other maintenance supplies	35
Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)	5
Total	100

Outokumpu flash smelting/flash converting smelter. The total is about \$80 per tonne of concentrate. For a 30% Cu concentrate this is equivalent to about \$0.3 per kg of new copper anodes.

Table 23.8 breaks down these direct operating costs into labor, fuel, oxygen and supplies. Labor and maintenance supplies are shown to be the largest items.

The 1980 edition of this book suggested that smelter investment and operating costs could be minimized by maximizing the use of industrial oxygen in smelting.

Oxygen enrichment of smelting furnace blasts continued to increase during the 1990's to the point where most smelting furnaces now operate with little hydrocarbon fuel. This has minimized fuel costs. It has also minimized offgas quantities (per tonne of copper produced) and gas handling/acid making investment and operating costs.

23.6 Electrorefining Costs

The investment cost of a new electrorefinery using stainless steel cathode technology is ~\$500 per annual tonne of electrorefined cathodes. This means that a refinery producing 200 000 tonnes per year of cathodes will cost of the order of $\$100 \times 10^6$.

Table 23.9. Electrorefinery *investment* costs. Investment costs of components in an electrolytic copper refinery expressed as a percentage of the total fixed investment cost.

Component	Percent of total fixed investment cost
Anode reception, weighing, straightening, lug milling, sampling equipment	10
Production electrorefining equipment including stainless steel blanks, polymer concrete cells, transformers, rectifiers, electrical distribution system	55
Electrolyte circulation and purification equipment including filters, heaters, pumps, storage tanks, reagent addition equipment, electrowinning cells	15
Cathode handling equipment including stripping, washing, weighing, sampling and bundling equipment	5
Anode (and purchased) scrap melting and anode casting equipment – including Asarco shaft furnace, holding furnace, pouring equipment and Hazelett anode caster	15
Total	100

Table 23.10. Electrorefinery *operating* costs by activity. Direct operating costs including maintenance, for producing electrorefined cathode 'plates' from anodes in a stainless steel blank electrorefinery. Anode cost is not included.

Activity	Cost, \$U.S. per kg of cathode Cu
Anode reception, weighing, straightening, lug milling, delivery to tankhouse*	0.010
Production electrorefining, including cell cleaning, electrolyte purification and reagent addition, delivery of cathodes to washing and delivery of 'slimes' to Cu/precious metal recovery plant	0.050
Cathode handling including stripping, washing, weighing, quality control and delivery to loading docks	0.010
Anode scrap washing and melting, purchased scrap melting, anode casting and anode delivery to tankhouse	0.010
Cu recovery from slimes	0.005
Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)	0.005
Total	0.090

* In some cases this is a smelter activity

Table 23.11. Electrorefinery *operating* costs by cost component. Expenditures on manpower, electricity and supplies (excluding anodes and scrap), by percentage. Anode cost is not included.

Component	Percentage of electrorefining cost
Operating manpower, including supervision	30
Maintenance manpower, including supervision	10
Electricity	30
Maintenance materials	20
Reagents and fossil fuel	5
Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)	5
Total	100

The relative investment costs of various sections of a refinery are shown in Table 23.9. The production electrorefining section (including stainless steel blanks) is by far the largest investment cost component of the refinery.

The direct costs of producing electrorefined cathodes in an electrolytic refinery are ~\$0.1 per kg of cathode copper, Table 23.10. The main components of that cost are manpower, electricity and maintenance, Table 23.11.

23.7 Production of Copper from Scrap

Chapter 20 showed that copper scrap varies in grade from 99.5+% Cu (manufacturing wastes) to 5% Cu (recycled mixed-metal scrap). The high-grade manufacturing wastes require only reclamation, melting, casting and marketing which costs of the order of \$0.10/kg of copper. Low-grade scrap, on the other hand, requires reclamation, sorting, smelting, refining and marketing, which costs about \$0.5 per kg of copper, Table 23.2. Intermediate grade scrap treatment lies between these two extremes.

For scrap recovery to be profitable, the difference between refined copper sales price and scrap purchase price must exceed these treatment charges. If it doesn't, scrap is held off the market.

23.8 Leach/Solvent Extraction/Electrowinning Costs

The investment and operating costs of heap leach/solvent extraction/electrowinning plants are listed in Tables 23.12 and 23.13. The costs are shown to be considerably lower than those for conventional concentration/smelting/refining complexes. This accounts for the rapid adoption of leaching in the 1990's, especially in Chile.

Table 23.12. Heap leach/solvent extraction/electrowinning *investment* costs. Fixed investment costs for a heap leach/solvent extraction/electrowinning plant. The plant produces copper cathode plates ready for shipment from 0.75% Cu 'oxide' ore. Stainless steel cathodes and polymer concrete cells are used. Mine investment cost is not included.

Component	\$U.S. per annual tonne of copper
Heap leach system including leach pad, crusher, agglomerating drum, on-off heap building and removal equipment, piping, pumps, solution collection ponds etc.	1600
Solvent extraction plant including mixer-settlers, pumps, piping, storage tanks and initial extractant and diluent	400
Electrowinning plant including electrical equipment, polymer concrete cells, rolled Pb-Sn-Ca anodes, stainless steel cathodes, cranes, cathode stripping, washing and handling equipment	700
Utilities and infrastructure	500
Engineering services, contingency, escalation etc.	300
Total (Dufresne, 2000)	3500

Table 23.13. Direct *operating* costs of a heap leach/solvent extraction/electrowinning system. The plant produces copper cathode plates ready for shipment from 0.75% Cu 'oxide' ore. Stainless steel cathodes and polymer concrete cells are used. Ore cost is not included.

Item	\$/kg of copper
Heap leach operation including crushing, acid curing, agglomeration, on-off heap construction/removal, solution delivery and collection	0.10
Sulfuric acid	0.05
Solvent extraction plant operation, including maintenance	0.03
Reagent make-up: extractant, diluent, guar and $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$	0.04
Electrowinning tankhouse operation, delivering cathode plates to loadout platform	0.15
Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)	0.03
Total	0.40

Unfortunately, chalcopyrite ore (the world's largest source of copper) cannot be processed by heap leach/solvent extraction/electrowinning, Chapter 17. Chalcopyrite ores must be treated by conventional concentration/smelting/refining/refining, irrespective of cost.

The small investment requirement of leach/solvent extraction/electrowinning plants is due to the small equipment and infrastructure requirements of these processes. Specifically, leaching and solvent extraction require much less equipment than concentrating, smelting, converting and anode making.

An interesting aspect of pyrometallurgical and hydrometallurgical copper extraction is sulfuric acid production and use. Hydrometallurgical copper extraction requires sulfuric acid (Chapter 17) – pyrometallurgical copper processing produces it (Chapter 14).

Companies with both processes benefit significantly from this synergistic effect, especially if the operations are close together.

23.9 Profitability

The key to a profitable mine-to-market copper operation is, of course, a large, high Cu-grade orebody. Such an orebody maximizes copper production per tonne of ore mined, moved and processed.

Optimal use of an orebody requires that each part of the orebody be processed by

its most efficient method, e.g. leaching or concentrating/smeltering. Separation of the orebody into milling ore, leaching ore, leaching 'waste' and unleachable waste is crucial for profitable utilization of the resource.

Mechanization, automation and computer control optimize resource utilization and profitability throughout the mine-to-market sequence. In-pit crushing and conveyor ore transport, computer controlled semi-autogenous mill/ball mill grinding and flotation; oxygen-enriched continuous smelting/converting; and mechanized stainless steel cathode/polymer concrete cell electrowinning and electrowinning have all contributed to lower costs, enhanced resource utilization and improved profitability.

23.10 Summary

The total direct plus indirect cost of producing electrorefined copper from ore by conventional mining/concentration/smeltering/refining is in the range of \$1.5 to \$2.2 per kg of copper.

The total direct plus indirect cost of producing electrowon copper cathodes from 'oxide' and chalcocite ores (including mining) is in the range of \$0.7 to \$1.5 per kg of copper.

Copper extraction is distinctly profitable when the selling price of copper is ~\$2.5 per kg. It is unprofitable for some operations when the selling price falls below \$1.5 per kg. At the former price, the industry tends to expand. At the latter, it begins to contract.

References

- Bauman, H.C. (1964) *Fundamentals of Cost Engineering in the Chemical Industry*, Reinhold Book Corporation, New York, NY, Chapter 1.
- Chemical Engineering* (2001) (McGraw-Hill Publishing Company, New York, NY), data obtained from July issues, 1983-2001.
- Dufresne, M. W. (2000) The Collahuasi copper project, Chile. *CIM Bulletin*, **93**, 25-30.
- EMJ (1998) Bajo de la Alumbrera, Argentina's first mining mega-project. *E&MJ*, **199**(5), pp. 46WW-54WW.
- Perry, R.H. and Chilton, C.H. (1973) *Chemical Engineer's Handbook, Fifth Edition*, McGraw-Hill Book Company, New York, NY, 25-12 to 25-47.
- Peters, M.S. and Timmerhaus, K.D. (1968) *Plant Design and Economics for Chemical Engineers. Second Edition*, McGraw-Hill Book Company, New York, NY.

Appendix A

Stoichiometric Data for Copper Extraction

Compound	MW, kg/kg mol	% Metal	%O or S
Al ₂ O ₃	101.96	52.9	47.1
CH ₄	16.04	74.9	25.1
C ₂ H ₆	30.07	79.9	20.1
CO	28.01	42.9	57.1
CO ₂	44.01	27.3	72.7
CaCO ₃	100.09	56.0% CaO	44.0% CO ₂
CaO	56.08	71.5	28.5
Cr ₂ O ₃	151.99	68.4	31.6
CuCO ₃ :Cu(OH) ₂	221.12	57.5	5.4 C 0.9 H 36.2 O
(CuCO ₃) ₂ :Cu(OH) ₂	344.67	55.3	7.0 C 0.6 H 37.1 O
Cu ₂ Cl(OH) ₃	213.57	59.5	16.6 Cl 1.4 H 22.5 O
CuFeS ₂	183.51	34.6 Cu 30.4 Fe	35.0
Cu ₅ FeS ₄	501.82	63.3 Cu 11.1 Fe	25.6
CuO	79.55	79.9	20.1
Cu ₂ O	143.09	88.8	11.2
CuSiO ₃ :2H ₂ O	175.66	36.2	2.3 H 27.3 O 34.2 SiO ₂
CuS	95.61	66.5	33.5
Cu ₂ S	159.15	79.9	20.1
CuSO ₄	159.60	39.8	40.1 O 20.1 S
CuSO ₄ :CuO	239.15	53.1	33.5 O 13.4 S
CuSO ₄ :2Cu(OH) ₂	354.72	53.7	1.1 H 36.1 O 9.0 S

Compound	MW, kg/kg mol	% Metal	%O or S
CuSO ₄ ·3Cu(OH) ₂	452.29	56.2	1.2 H 35.4 O 7.1 S
Cu ₂ SO ₄	223.15	57.0	28.6 O 14.4 S
FeO	71.85	77.7	22.3
Fe ₂ O ₃	159.69	69.9	30.1
Fe ₃ O ₄	231.54	72.4	27.6
FeS	87.91	63.5	36.5
FeS _{1.14}	92.40	60.4	39.6
FeS ₂	119.97	46.6	53.4
FeSO ₄	151.90	36.8	42.1 O 21.1 S
Fe ₂ (SO ₄) ₃	399.87	27.9	48.0 O 24.1 S
H ₂ O	18.02	11.2	88.8
MgCO ₃	84.31	47.8% MgO	52.2% CO ₂
MgO	40.30	60.3	39.7
NiO	74.69	78.6	21.4
NiS	90.75	64.7	35.3
Ni ₃ S ₂	240.25	73.3	26.7
NiSO ₄	154.75	37.9	41.4 O 20.7 S
PbO	223.20	92.8	7.2
PbS	239.30	86.6	13.4
PbSO ₄	303.30	68.3	21.1 O 10.6 S
SiO ₂	60.08	46.7	53.3
SO ₂	64.06	50.0	50.0
SO ₃	80.06	40.0	60.0
ZnO	81.38	80.3	19.7
ZnS	97.44	67.1	32.9
ZnSO ₄	161.44	40.5	39.6 O 19.9 S

APPENDIX B

Lesser-Used Smelting Processes

The years following publication of the third edition of this book saw several matte smelting technologies fall into disfavor or fail to gain widespread adoption. This appendix provides a thumbnail sketch of these lesser-used smelting processes.

B.1 Reverberatory Furnace

Reverberatory smelting furnaces have been used for over a century. They dominated Cu smelting through the 1960's. Figure B.1 illustrates the 'reverber'. It is heated by hydrocarbon fuel combustion.

Concentrate (moist, dry or roasted*) and flux are fed through feedholes along the

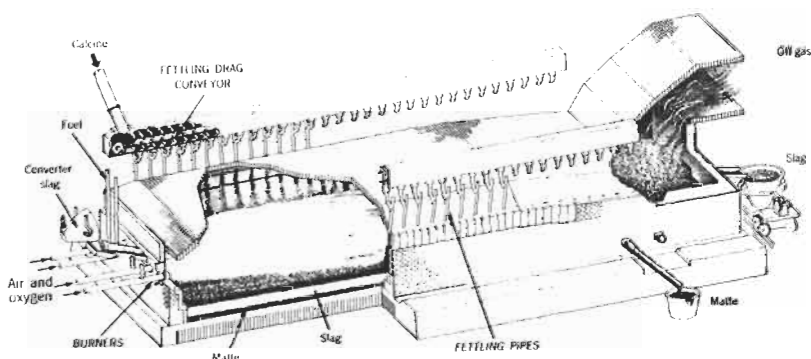


Fig. B.1. Reverberatory furnace for producing molten Cu-Fe-S matte from sulfide concentrates and 'roasted' calcines*. (Boldt and Queneau, 1967, courtesy Inco Ltd.)

*Roasted concentrate (calcine) is concentrate which has been oxidized (i) to remove sulfur as SO_2 and (ii) to oxidize iron to iron oxide (Biswas and Davenport, 1994). The results of the roasting are (i) efficient SO_2 capture from the roaster offgas and (ii) production of high %Cu matte during reverberatory and electric furnace smelting. Flash (and other) oxidation smelting processes have largely eliminated roasting from the smelter flowsheet.

Table B.1. Physical and operating details of reverberatory furnaces at Onahama, Japan, 2001. The furnaces smelt 33% Cu concentrate to molten 43% Cu matte.

Smelter	Onahama Smelting & Refining, Japan
Number of furnaces	2
Hearth size, w x l x h, m	a) 9.73 × 33.55 × 3.69 b) 11.1 × 33.27 × 4.00
slag layer thickness, m	0.6-0.9
matte layer thickness, m	0.4-0.6
active slag tapholes	1
active matte tapholes	4
Burner details	
number of burners	6
endwall or roof	endwall
combustion 'air' temperature °C	(a) 300; (b) 30
volume% O ₂ in combustion 'air'	21-27
fuel consumption kg per tonne of new concentrate	200 coal
oxygen consumption kg per tonne of new concentrate	110
Feed details	
type of charge	moist concentrate
% moisture in charge	8
Feed, tonnes/day (dry basis)	
new concentrate	1060 (33% Cu)
silica flux	30
recycle reverberatory furnace dust	60
converter dust	6
molten converter slag	910
reverts	50
other	
Production, tonnes/day	
matte, tonnes/day	1030 (43% Cu)
slag, tonnes/day	1010 (0.65% Cu)
mass% SiO ₂ /mass% Fe	0.91
Cu recovery, reverberatory slag	none
Cu recovery, converter slag	recycle to reverb
offgas, thousand Nm ³ /hour	180
vol% SO ₂ , leaving furnace	1
dust production, tonnes/day	60 (all recycled)
matte/slag temperatures, °C	1120/1280

sides of the roof. They form 'banks' along the sides of the furnace. Concentrate and flux at the edge of the banks react with hot combustion gas and air in the furnace, generating molten matte, molten slag and offgas, Chapter 4.

The smelting is continuous. Matte and slag are tapped intermittently through separate tapholes. The matte is sent to converting. The slag is discarded.

The length of a reverb is 3 to 4 times its width, which gives the slag and matte considerable time to separate. Its slags are dilute in Cu (~0.6%). They are discarded without slag recovery treatment. Molten converter slag is treated for Cu recovery.

Because hydrocarbon combustion gas contains little O₂, the reverb is primarily a melting furnace. It does not oxidize concentrates well. As a result, it produces low-grade mattes, 40 to 50% Cu. Also, the smelting reactions are slow because the concentrate is not intimately mixed with air and combustion gas as in flash and other recent smelting furnaces. This results in poor use of the energy generated by concentrate oxidation and a large requirement for hydrocarbon fuel.

Burning of this hydrocarbon fuel generates a large quantity of offgas, especially if air is used for the combustion. This and the reverb's slow rate of concentrate oxidation give offgas with only about 1% SO₂. This offgas is difficult to treat in a sulfuric acid plant, and simply releasing it to the environment is unacceptable in most parts of the world.

The result of this is that only about 10 of the 30 reverberatory furnaces operating worldwide in 1994 are still operating in 2002.

An interesting use of the reverberatory furnace is for smelting automobile shredding residue, Fig. 20.3, mixed in the concentrate feed (Kikumoto *et al.*, 2000). The residue's organic component acts as fuel to supplement that provided by oxy-fuel burners. The furnace's offgas (~1% SO₂) is treated for SO₂ capture in a gypsum (CaSO₄·2H₂O) plant. SO₂ capture is efficient.

Although the reverberatory smelting furnace is gradually disappearing, hearth furnaces are still used widely for melting intermediate grade copper scrap. Oxy-fuel burners are used to improve furnace efficiency and reduce offgas volume (McCullough *et al.*, 1996; Beene, *et al.*, 1999).

B.2 Electric Furnace

Electric furnace Cu matte smelting flourished in the 1970's (Biswas and Davenport, 1980, 1994). Most, however, closed due to their high electricity cost.

The best-known Cu electric furnace smelters are those in:

Dzhezkasgan, Kazakstan
 Ronnskar, Sweden (Isaksson and Lehner, 2000)
 Mufulira, Zambia (Zambia, 2002).

The Dzhezkasgan smelter treats siliceous concentrates, the others treat normal Cu concentrate feed.

Like the reverberatory furnace, the electric furnace (Fig. B.2) is mainly a melting unit. Energy is provided by passing electric current between self-baking carbon electrodes suspended in the furnace's molten slag layer. Resistance of the slag to current flow heats the slag and melts roof-charged concentrate (dry or roasted) and flux.

Smelting is continuous. Matte and slag are tapped intermittently through separate tapholes in the furnace sidewalls. The matte (50-60% Cu) is tapped and sent to converting. The slag (0.5 to 1% Cu) is discarded. Molten converter slag is treated for Cu recovery.

Although its use as a Cu smelting unit is diminished, the electric furnace is still used extensively for recovering Cu from molten slags. This use is discussed in Chapter 11.

The electric furnace is also used for smelting dried and roasted Cu-Ni concentrates. Its advantage for this application is its reducing environment, which encourages Co and Ni to report to matte rather than slag (Aune and Strom, 1983, Voermann et al., 1998).

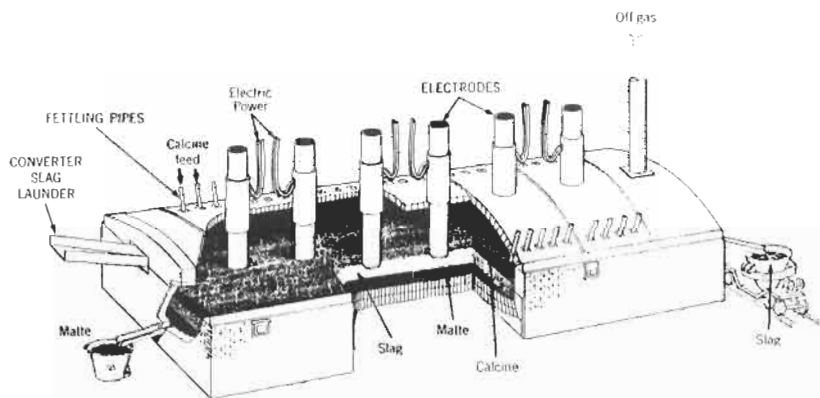


Fig. B.2. Electric furnace for producing molten Cu-Fe-S matte from dry sulfide concentrates and 'roasted' calcines. (Boldt and Qucneau, 1967, courtesy Inco Ltd.)

Table B.2. Physical and operating details of electric furnace at Ronnskar, Sweden, 1993. The furnace smelts 27% Cu calcine to molten 51% Cu matte.

Smelter	Boliden Limited Ronnskar, Sweden
Number of electric furnaces	1
Hearth size, w x l x h, m	7 × 24 × 5
slag layer thickness, m	1.5
matte layer thickness, m	0.8
active slag tapholes	2
active matte tapholes	2
Electrical details	
furnace power rating, kW	23 000
usual applied power, kW	19 000
usual current, A	38 000
usual voltage between electrodes, V	180 (towards melt)
number of electrodes	6
diameter, m	1.2
material	self baking
normal immersion in slag, m	0.1
electrode consumption, kg/tonne of new calcine	1.9
electrical energy consumption kWh/tonne of new calcine	300
Feed details	
type of charge	roasted concentrate (calcine)
Feed, tonnes/day (dry basis)	
calcine	930 (27% Cu)
silica flux	95
recycle smelting furnace dust	70
converter dust	15
molten converter slag	300
reverts	140
dried ashes (secondary feed)	260
Production	
matte, tonnes/day	580 (51% Cu)
slag, tonnes/day	830 (1.3% Cu)
mass% SiO ₂ /mass% Fe	0.93
Cu recovery, electric furnace slag	Zn fuming/settling
Cu recovery, converter slag	in electric smelting furnace
offgas production, Nm ³ /minute	580
vol% SO ₂ , leaving furnace	4.5
dust production, tonnes/day	70 (all recycled)
matte/slag/offgas temperatures, °C	1180/1250/800

B.3 Vanyukov Furnace

The Vanyukov furnace (Figure B.3) is a submerged-tuyere type of smelting furnace like the Noranda and Teniente furnaces in Chapter 7. It was developed in the 1970's in the former Soviet Union. It is currently used by one Kazak smelter and two Russian smelters (Bystrov, *et al.*, 1992, 1995).

Vanyukov matte smelting entails:

- (a) charging moist concentrate (up to 8% H₂O), reverts, flux and occasionally lump coal through two roof ports, Fig. B.3
- (b) blowing oxygen enriched air (50-95% O₂, 9.2 atmospheres gage) through submerged side tuyeres (Fig. 9.1b) into the furnace's molten slag layer.

The tuyeres are located ~0.5 m below the slag surface.

Smelting is continuous. The furnace always contains layers of molten matte and slag. The smelting reactions are similar to those in Noranda and Teniente smelting furnaces, Chapter 7.

Matte and slag are tapped intermittently through tapholes at opposite ends of the furnace. Weirs are provided to give quiet matte/slag separation near the slag taphole.

Matte grade is 48 to 56% Cu, slag Cu content is 0.5 to 0.7% Cu. SO₂-in-offgas is 25 to 65% SO₂ depending upon blast oxygen enrichment and hydrocarbon combustion rate.

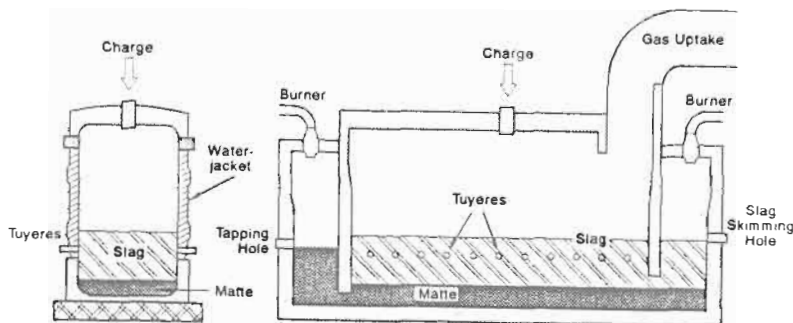


Fig. B.3. Sketch of Vanyukov matte smelting furnace (Kellogg and Diaz, 1992).

Table B.3. Operating details of Vanyukov furnace at Balkash, Kazakhstan, 1993.

Smelter	Balkash, Kazakhstan
Furnace size, inside brick	
width × length × height, m	2 × 10 × 6
bath volume, m ³	
Feed details, tonnes/day	
concentrate	~1800 (15% Cu)
flux	
Blast details	
number of operating tuyeres	16
tuyere diameter, cm	2
tuyere depth in slag, m	
total blast flowrate, Nm ³ /h	16 000
volume% O ₂ in blast	93
blast temperature	ambient
blast velocity at tuyere tip, m/s	
Production details	
matte grade, %Cu	45
slag % Cu from smelting furnace	1.5-2
Cu-from-slag recovery systems	
Vanyukov slag	electric furnace (0.7% Cu after settling)
converter slag	reverberatory furnace
offgas production, Nm ³ /hour	33 000
volume% SO ₂ in offgas	30
dust production, tonnes/day	20
Oxygen and fuel consumption	
oxygen (98% O ₂), kg/tonne of new concentrate	~300
natural gas, Nm ³ /tonne of new concentrate	0 (autothermal)

Unlike the rotatable Noranda and Teniente furnaces, the Vanyukov furnace is stationary. The advantages of this are a directly connected gas collection system and no moving parts. The disadvantage is that the Vanyukov furnace cannot lift its tuyeres above the slag for maintenance and repair or in a blower emergency.

Bystrov *et al.* (1992, 1995) report, however, that the stationary tuyeres are not a problem and that Vanyukov furnace availability is over 95%.

B.4 Shaft Furnace

When the first edition of *Extractive Metallurgy of Copper* was published in 1976, about ten copper producers were operating shaft (blast) furnaces to smelt lump sulfide agglomerates. In 2001, the only shaft furnaces still in use are those at the Legnica and Glogow smelters in Poland (Czernecki *et al.*, 1998). These furnaces survive because of:

- (a) their unusual concentrates:

low in Fe and S
high in organic carbon
self fluxing.

These concentrates require little Fe and S oxidation, little hydrocarbon fuel and little or no fluxing.

- (b) their high levels of As and Pb in concentrate and recycle converter slag. The reducing atmosphere of the shaft furnace encourages volatilization of As and Pb rather than oxidation. This permits As and Pb to concentrate in the shaft furnace offgas from which they are collected and sent elsewhere for recovery.

The charge to the shaft furnaces consists of briquetted concentrate (fine particles would be blown out of the furnace), solid converter slag, and some metallurgical coke. Three products result:

- (a) molten matte containing 58–63% Cu, 3–6% Pb, and 0.15–0.3% As
- (b) molten slag with < 0.5% Cu
- (c) 'slime' from a wet scrubber system analyzing 40% Pb, 5% Zn, and up to 5% As.

The matte is sent to converting, the slag to discard and the slime to byproduct metal recovery.

The main deficiencies of the shaft furnace for 'normal' Cu-Fe-S concentrates are:

- (a) its large production of dilute SO₂ offgas
- (b) the necessity of briquetting or sintering its concentrate feed
- (c) its requirement for metallurgical coke.

The shaft furnace will, therefore, probably only be used for unusual concentrates such as those smelted in Legnica and Glogow.

References

- Aune, J.A., and Strom, K.H., (1983) Electric sulfide smelting technology: Elkem Engineering Division's new processing/design concept for the 80's, in *Advances in Sulfide Smelting, Vol. 2: Technology and Practice*, ed Sohn, H.Y., George, D.B., and Zunkel, A.D., TMS, Warrendale, PA, 635 657.
- Beene, G., Mponda, E., and Syamujulu, M. (1999) Breaking new ground—recent developments in the smelting practice at ZCCM Nkana smelter, Kitwe, Zambia, in *Copper 99—Cobré 99, Vol. V—Smelting Operations and Advances*, ed. George, D.B., Chen, W.J., Mackey, P.J., and Weddick, A.J., TMS, Warrendale, PA, 205 220.
- Biswas, A.K. and Davenport, W.G. (1976, 1980, 1994) *Extractive Metallurgy of Copper*, Elsevier Science Press, New York, NY.
- Boldt, J.R. and Queneau, P. (1967) *The Winning of Nickel*, Longmans Canada Limited, Toronto, Canada.
- Bystrov, V.P., Fyodorov, A.N., Komkov, A.A., and Sorokin, M.L. (1992) The use of the Vanyukov process for the smelting of various charges, in *Extractive Metallurgy of Gold and Base Metals*, Australasian Institute of Mines and Metallurgy, Parkville, Vic., 477 482.
- Bystrov, V.P., Komkov, A.A., and Smirnov, L.A. (1995) Optimizing the Vanyukov process and furnace for treatment of complex copper charges, in *Copper 95—Cobre 95, Vol. IV—Pyrometallurgy of Copper*, ed. Chen, W. J., Diaz, C., Luraschi, A., and Mackey, P.J., The Metallurgical Society of CIM, Montreal, Canada, 167 178.
- Czernecki, J., Suisse, Z., Gizicki, S., Dobranski, J. and Warmuz, M. (1998) Problems with elimination of the main impurities in the KGHM Polska Miedz S.A. copper concentrates from the copper production cycle (shaft furnace process, direct blister smelting in a flash furnace), in *Sulfide Smelting '98, Current and Future Practices*, ed. Asteljoki, J.A. and Stephens, R.L., TMS, Warrendale, PA, 315 343.
- Isaksson, O. and Lechner, T. (2000) The Ronnskar smelter project: production, expansion, start-up. *JOM*, **52** (8), 26 29.
- Kellogg, H.H., and Diaz, C. (1992) Bath smelting processes in non-ferrous pyrometallurgy: An overview, in *Savard/Lee International Symposium on Bath Smelting*, ed. Brimacombe, J.K., Mackey, P.J., Kor, G.J.W., Bickert, C., and Ranade, M.G., TMS, Warrendale, PA, 39 63.
- Kikumoto, N., Abe, K., Nishiwaki, M., and Sato, T. (2000) Treatment of industrial waste material in reverberatory furnace at Onahama smelter, in *EPD Congress 2000*, ed. Taylor, P.R., TMS, Warrendale, PA 19 27.
- McCullough, T., Parghi, R., and Ebeling, C. (1996) Oxy-fuel copper melting for increased productivity and process enhancement, in *Gas Interactions in Nonferrous Metals Processing*, ed. Saha, D., TMS, Warrendale, PA, 221 227.

Voermann, N., Vaculik, V., Ma, T., Nichols, C., Roset, G., and Thurman, W. (1998) Improvements to Stillwater Mining Company's smelting furnace yielding increased capacity and productivity, in *Sulfide Smelting '98: Current and Future Practices*, ed. Asteljoki, J.A., and Stephens, R.L., TMS, Warrendale, PA, 503-518.

Zambia Consolidated Copper Mines, Ltd. (2001) www.zccm.com.zm/html/index4.html.

APPENDIX C

Copper Recovery from Anode Slimes

Electrorefining of the anodes produced by pyrometallurgical processes generates a byproduct known as anode slimes. These slimes are the un-dissolved portion of the corroding anode. They are a fine material which (i) falls to the bottom of the electrorefining cell and (ii) adheres to the corroding anode. They are recovered by washing them from the final 'scrap' anodes (Section 16.7) and by sluicing them from the bottom of the drained refining cells. They are processed to recover their Cu and precious metals.

The composition of the slimes varies according to the composition of the anodes. However, most contain significant amounts of copper (15–35%), antimony, arsenic, bismuth, gold, lead, nickel, platinum metals, selenium, silver, and tellurium (Cooper, 1990; Davenport *et al.*, 1999; Wesstrom, 2000). About 0.3% of an anode's copper ends up in the slimes (Hoffmann, 2000). The Cu is present largely as Cu_2O and metallic copper. It is also combined with Ag and Se/Te in various compounds and solid solutions.

A complete description of slimes processing is beyond the scope of this book. (See Cooper (1990) and Järvinen (2000) for more information.) However, Cu recovery is the first step in slimes treatment, so a brief discussion of this technology is warranted.

Most Cu in anode slimes is removed by leaching the slimes with dilute sulfuric acid (50–300 kg $\text{H}_2\text{SO}_4/\text{m}^3$), aerated to oxidize Se and Te (Cooper, 1990, Chen and Dutrizac, 1993). The leaching extracts most of the Cu from the slimes, with the exception of slimes high in Ni or Se. Concentrated sulfuric acid improves Cu extraction from these slimes. Gold, silver and platinum-group metals are not dissolved. They remain in the de-coppered slimes and are recovered in a byproducts recovery plant.

The Cu-rich pregnant leach solution is first treated to precipitate Te as Cu_2Te , by adding copper metal shavings or granules. Filtered Te-free solution is then returned to the electrolyte purification section of the copper electrorefinery (Section 16.5.1) where:

- (a) its Cu is electrowon from solution
- (b) its impurities are removed.

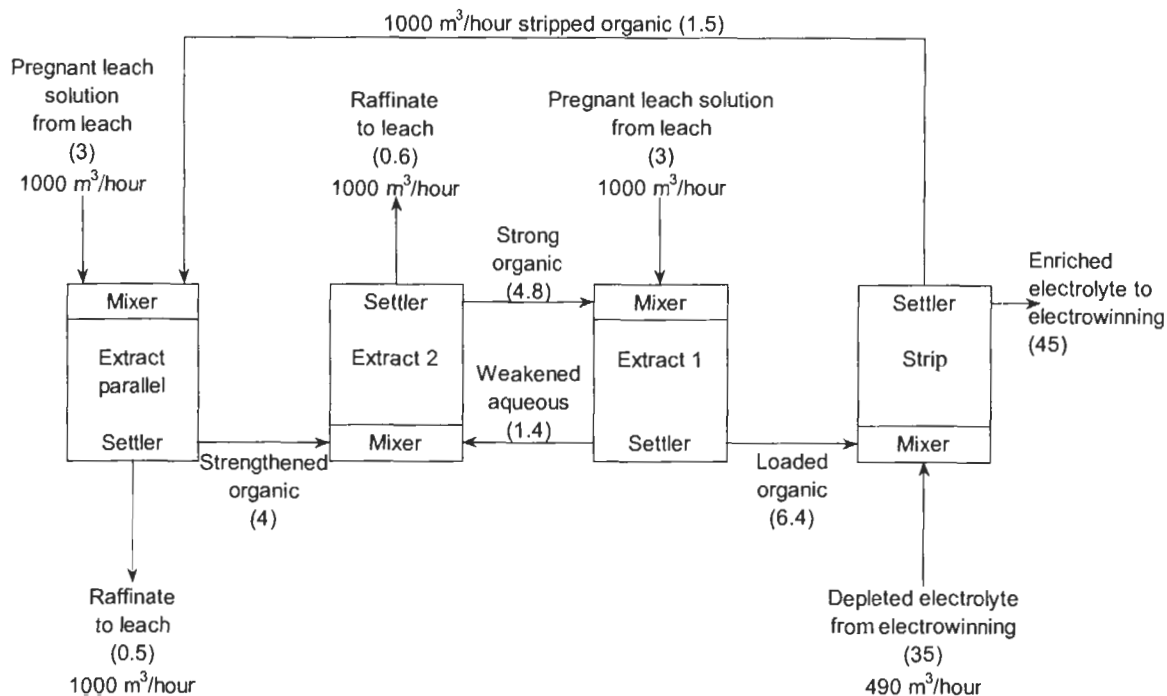
The past decade has seen an increase in the use of pressure leaching for decopperizing anode slimes (Hoffmann, 2000). Pressure leaching improves reaction kinetics and overall Cu recovery. Autoclave temperatures of 125–150°C and oxygen partial pressures of 12–24 atmospheres gage are used. Given the relatively small masses involved, batch processing is standard.

In addition to recovering nearly all the Cu from the anode slimes, pressure leaching also extracts most of the As and Ni (Järvinen, 2000). These elements are also removed in the electrolyte purification section of the copper electrolyrefinery, Section 16.5.1.

References

- Chen, T.T. and Dutrizac, J.E. (1993) Mineralogical changes occurring during the decopperizing and deleading of Kidd Creek copper refinery anode slimes. In *Paul E. Queneau International Symposium on Extractive Metallurgy of Copper, Nickel and Cobalt, Vol. I, Fundamental Aspects*, ed. Reddy, R.G. and Weizenbach, R.N., TMS, Warrendale, PA, 377 401.
- Cooper, W.C. (1990) The treatment of copper refinery anode slimes. *JOM*, **42** (8), 45 49.
- Davenport, W.G., Jenkins, J., Kennedy, B. and Robinson, T. (1999) Electrolytic copper refining – 1999 world tankhouse operating data. In *Copper 99-Cobre 99 Proceedings of the Fourth International Conference, Vol. III Refining and Electrowinning of Copper*, ed. Dutrizac, J.E., Ji, J. and Ramachandran, V., TMS, Warrendale, PA, 3 76.
- Hoffman, J.E. (2000) Process and engineering considerations in the pressure leaching of copper refinery slimes. In *EPD Congress 2000*, ed. Taylor, P.R., TMS, Warrendale, PA, 397 410.
- Järvinen, O. (2000) Outokumpu process for the precious metal refining from copper anode slime. In *EPD Congress 2000*, ed. Taylor, P.R., TMS, Warrendale, PA, 511 514.
- Wesstrom, B.C. (2000) Pressure leaching of copper refinery slimes. In *EPD Congress 2000*, ed. Taylor, P.R., TMS, Warrendale, PA, 503 509.

Appendix D. Sketch of Series-Parallel Solvent Extraction Circuit. The circuit gives a high rate of copper transfer to electrolyte but with some loss of Cu-from-pregnant solution extraction efficiency. The bracketed numbers are Cu concentration, kg/m³.



Appendix E. Extended list of Chinese copper refineries and their capacities

City	Province	2002 Refining capacity, kilotonnes cathode Cu/year
Bayin	Gangxu	60
Beijing	Beijing	10
Changjiang	Hainan	5
Changsha	Hunan	5
Changzhou	Jiangsu	32
Chengdu		3
Chongqing	Sichuan	15
Dabizhuang		26
Daye	Hubei	110
Fuyang	Zhejiang	10
Ghuangzhou	Guandong	20
Guixi,	Jiangxi	250
Harbin	Heilongjiang	3
Huludao	Liaoning	80
Jiangpu	Jiangsu	5
Jinchang		70
Jinlong	Anhui	140
Jinquan	Gansu	70
Kunming	Yunnan	180
Luoyang	Hunan	50
Shanghai	Huangpu	80
Shanghai 2	Jiangsu	16
Shenyang,	Liaoning	60
Shenyang smelter		100
Shenyang	Xixing	30
Tianjin	Heilongjiang	23
Tonling II	Anhui	250
Wuhu	Anhui	60
Xiaoshigou	Hebei	5
Yantai	Shandong	30
Zhongtiaoshan	Shanxi	20
Zhuzhou	Hunan	10

Index

(Italicized numbers indicate illustrations)

- Acid manufacture, sulfuric 217
- Air Liquide shrouded injector (converter) tuyere 148
- Alloys, copper, % of Cu use 380
- Al_2O_3 in smelter concentrates, fluxes, slags and dusts 61
- Ammonia leaching process 302
 - Arbiter 302
 - Escondida 302
- Anodes, electrowinning 253-260, 254, 275
 - automatic weight control 255
 - casting 253, 254
 - continuous 256, 257, 259
 - composition 271
 - deplating time (life) 274
 - flowsheet, refining 266
 - Hazelett (Contilanol) 256, 257, 259
 - passivation 282
 - periodic current reversal avoids 282
 - preparation machine 255
 - improves refining 256
 - scrap 272
 - flowsheet, 266
 - quantity 274
 - slimes 270, 413
- Anodes, electrowinning 330
 - composition 330
 - manufacture 330
 - recent developments 337
 - Ti sandwich anode 336, 337
 - size 329, 332
- Anode furnace 247, 248
 - scrap additions to 250, 362
 - tuyere 248
- Anode scrap 272
 - quantity 274
- Antimony in
 - anodes 271
 - blister copper 140
 - cathode copper 271
 - converter slag 140
 - electrolyte 276
 - removal from 276
 - matte 140
- Antimony behavior
 - during smelting 69
 - during fire refining 260
 - flash 86
 - Isasmelt 125
 - Mitsubishi 211
 - Noranda smelting 107
 - Teniente smelting 115
 - during Peirce-Smith converting 137
 - during fire refining 260
 - during electrowinning 270
 - electrode potential 272
 - removal from electrolyte 276
- Antimony ASTM specifications
 - cathodes 368
 - tough pitch copper 369
- Arsenic concentrations in
 - anodes 271
 - blister copper 140
 - cathode copper 271
 - electrolyte 276
 - removal from 276
 - matte 140
- Arsenic behavior
 - during smelting 69
 - flash 86
 - Isasmelt 125
 - Mitsubishi 211
 - Noranda smelting 107
 - Teniente smelting 115
 - during Peirce-Smith converting 137
 - during fire refining 260
 - during electrowinning 270, 271
 - electrode potential 272
 - removal from electrolyte 276
 - during slimes treatment 414
- Arsenic ASTM specifications
 - cathodes 368
 - tough pitch copper 369
- Asarco cathode melting furnace 370, 371
 - gas composition control 373
 - industrial data 372
- ASTM specifications, copper 368, 369
- Ausmelt process 119
 - converting 127
 - smelting 119
 - industrial data 122, 123

- installations worldwide 126
- Autogenous grinding 35, 37
- Automatic control
 - anode casting 255
 - bar casting 377
 - flotation 50
 - grinding 38, 39
 - Inco flash smelting 98, 99
 - Mitsubishi smelting/converting 211
 - Noranda smelting 108
 - Outokumpu flash smelting 83, 84
 - Teniente smelting 113
- Bacterial leaching 291
 - optimum conditions for 292
- Ball mill 35
 - energy use 37
 - industrial data 37
- Beneficiation of Cu ores 31 (*see also*
 - Concentration of Cu ores and
 - Flotation of Cu ores)
- Beryllium 108
- Bismuth concentrations in
 - anodes 271
 - blister copper 140
 - cathode copper 271
 - ASTM specification 368
 - converter slag 140
 - electrolyte 276
 - removal from 276
 - matte 140
 - smelting dust 87
 - tough pitch copper ASTM
 - specification 369
- Bismuth behavior
 - anodes, makes brittle 137
 - during smelting 69
 - flash 86
 - Isasmelt 125
 - Mitsubishi 211
 - Noranda smelting 107
 - Teniente smelting 115
 - during Peirce-Smith converting 137
 - during fire refining 260
 - during electrorefining 270
 - electrode potential 272
 - removal from electrolyte 276
- Bismuth ASTM specifications
 - cathodes 368
 - tough pitch copper 369
- Blast (shaft) furnace
 - for concentrate smelting 410
 - for scrap smelting 355
- Blister copper
 - composition 140, 249
 - blisters in 247
 - impurity removal from 260
 - O in 249
 - production of (converting) 131
 - refining of 247
 - S in 249
- BS specifications, copper 368, 369
- Cadmium behavior
 - during flash smelting 86
- Calcine, roaster 403
- Calcium in electrowinning anodes 330
- Canvas coverings, electrorefining cells 264
- CaO in Peirce-Smith converter slags 140
- CaO in smelter concentrates, fluxes, slags and dusts 61
 - optimum in silicate slags 59, 60
- CaO-base slag 206
 - advantages 163, 206
 - Cu₂O in 161, 207
 - for flash converting 163
 - liquid composition range 207
 - Mitsubishi converting 161, 206
 - phase diagram 207
 - viscosity 161
- Casting copper
 - anodes 253, 254, 257, 259
 - continuous (Hazelett Contilanol) 256
 - industrial data 258
 - bar for rolling to rod 376, 376, 377, 378
 - billets (logs) 374, 375
 - direct chill 374, 375
 - oxygen free copper 379
 - Hazelett 256, 257, 377
 - industrial data 258, 378
 - Southwire 376, 376, 377
 - industrial data 378
 - strip 379
- Catalyst for converting SO₂ to SO₃ 227

- (*see also* Sulfuric acid manufacture)
- cesium lowers ignition temp. 229
- degradation and initiation temperatures 228
- supported liquid phase 227
- Cathodes
 - electrorefining 273, 275 10, 264, 267, 268, 269
 - cathode copper composition 271, 274
 - ASTM specification 368
 - copper starting sheet 273
 - industrial data 275
 - purity maximization 280
 - stainless steel 273
 - advantage 284
 - electrowinning 329, 331
 - copper product composition 332, 335
 - industrial data 332
 - purity maximization 335
 - melting 370
- Cells
 - electrorefining 272, 283, 264, 267, 268, 269
 - electrolyte flow into 273, 274
 - polymer concrete 278, 283, 264
 - electrowinning 329, 331
 - electrolyte flow into 332
- Chlorine in electrolytes
 - electrorefining 274, 276, 277
 - electrowinning 334, 332
- CLEAR leaching process 302
- Coal in smelting
 - flash 79, 86
 - Isasmelt 120, 123
 - Noranda 105
- Coal for reducing Cu from slag 177, 179
- Cobalt
 - electrode potential 272
 - electrorefining, behavior during 270
 - in electrorefining electrolyte 270
 - removal from 276
 - electrowinning, added to electrolyte 334, 335, 332
 - decreased requirement with sandwich anodes 337
 - purpose 334
 - smelting, behavior during 86, 406
- Coke
 - for reducing Cu from slag 177, 179
 - in smelting
 - flash 86
 - Noranda 105
 - in Noranda continuous converting 167
- Comminution of copper ores 31 (*see also* Crushing, Grinding)
- energy requirements 37
- Concentrates
 - Cu content 48, 61 (*see also specific smelting processes*)
 - slag concentrate 182
 - dewatering, moisture content 52
 - drying 80
 - steam 80
 - particle size 34, 37
 - slag concentrate 182
 - production of 31
 - flotation 42
 - smelting in converter 146
- Concentration of Cu ores 31
 - flotation 42
 - industrial data 37, 48
 - plant location and size 18, 388
 - cost 391
 - efficiency 48
- Continuous casting of copper 256, 374
 - anodes (Hazelett) 256, 257, 259
 - industrial data 258
 - direct chill casting
 - Hazelett process 256, 257, 377
 - anodes 256
 - industrial data 258
 - bar for rolling 377
 - industrial data 378
 - Southwire process 376, 376
 - control 379, 377
 - industrial data 378
- Control
 - casting 377, 379
 - converting 141
 - flotation 50
 - in-process stream analysis 52
 - grinding 38, 40
 - smelting
 - direct to copper 190
 - Outokumpu flash 83, 84
 - Inco flash 97, 99

- Isasmelt 126
- Mitsubishi 211
- Noranda 108
- Teniente 113
- Continuous converting
 - flash 162
 - Mitsubishi 157
 - Noranda 166
- Converting of copper matte 131, 155
 - (*see also* Peirce-Smith converting)
 - blister copper product 140
 - Cu-Cu₂S system 135
 - continuous 155
 - flash 162
 - Mitsubishi 157
 - Noranda 166
 - converters for
 - Ausmelt 127
 - flash 162, 162
 - Hoboken 150
 - Mitsubishi 157, 158
 - Noranda 166, 166
 - Peirce-Smith 8, 137, 132, 133, 135
- Copper
 - anode 249, 253, 271
 - black 355
 - blister 249
 - casting 253, 374 (*see also* Casting copper)
 - costs of production 385
 - density, liquid 190
 - electrorefined 271, 274
 - ASTM specification 368
 - BS specification 368
 - industrial compositions 271, 274
 - electrowon compositions 332, 335
 - extraction costs 385
 - impurities, effect on 367, 368
 - losses in slags 173
 - melting 370
 - melting point 135
 - minerals 19
 - leaching 291
 - oxygen-free 369
 - price 28
 - profitable 389, 399
 - production by country 20
 - production, world 21, 17
 - recovery from slag 176 (*see also* Slags, copper recovery from)
 - scrap 341, 355
 - automobile 348
 - cable and wire 346
 - electronic 350
 - specifications 342, 344
 - tough pitch 368
 - ASTM specification 368
 - BS specification 368
 - oxygen content 369, 378
 - uscs 18
- Copper losses
 - dusts 61, 68, 86
 - Cu recovery from 86
 - slags 173
 - copper recovery from 176 (*see also* Slags, copper recovery from)
 - flotation tailings 48
- Copper, oxygen free 369
- Copper recovery from scrap (recycling)
 - 341, 355 (*see also* Scrap, recovery of copper from)
 - automobile 348
 - cable and wire 346
 - electronic 350
- Copper recovery from slag 176
 - settling 176
 - flotation 181
- Costs of copper extraction 385
 - accuracy, estimated level of 386
- Cost index (mining equipment) 386
- Covered electrolytic cells save energy 264
- Crushing of copper ore 31
 - for leaching 299, 296, 297
 - for flotation 31
 - flowsheet 32
 - of grinding mill oversize 35
 - gyratory crusher 33, 36
 - industrial data 37
 - product size 37
- Crushing matte for flash converting 162
 - particle size 162
- Cuprex leaching process 302
- Cut-off grade (mine) 19
- Cymet leaching process 302
- Density
 - copper, liquid 190
 - electrolytes 316

- matte 65
- slag 63
- solvent extraction liquids 316
- Diluents for solvent extraction 312
- Direct-to-copper smelting
 - flash furnace 187 (*see also* Flash furnace direct-to-copper smelting)
 - ideal process 187, 188
 - Mitsubishi 199
- Drying concentrate 80
 - dewatering 52
 - fluid bed dryer 96
 - rotary dryer 80
 - steam dryer 80
- Dust evolution
 - smelting 68 and converting 136 (*see also* industrial data for each process)
 - smelting dust composition 61
- Electrical conductivities
 - matte 65
 - slag 63
- Electric furnace matte smelting 405, 406
- Electric furnace recovery of Cu from
 - slags 176, 178
 - industrial data 179
- Electrolytic tough pitch copper 369
- Electrolyte
 - electrorefining 273
 - addition agents 277
 - removal of impurities 276
 - electrowinning 332, 335
 - control of impurities 332, 336
- Electromotive series 272
- Electrorefining of copper 265, 266
 - additions to electrolyte 277
 - anodes 272, 267
 - composition 271
 - anode passivation 282
 - avoidance 282
 - anode deplating time (life) 274
 - anode scrap 266, 272, 274
 - canvas cell covers 264
 - cathodes
 - copper starter sheet 273
 - stainless steel 273, 267
 - advantages of 284
 - edge strips for 273, 264, 267
 - cathode copper purity 271, 274
 - maximization of 280
 - cathode plating time 274
 - cells 278
 - polymer concrete 278, 264, 268
 - chemical reactions, 266
 - Chinese refineries, list of 416
 - chlorine added to electrolyte 277, 274
 - covered cells save energy 264
 - copper production, worldwide 20
 - refinery locations 24
 - Chinese 416
 - economic size 388
 - electrochemical potentials 272
 - electrolyte 273-276
 - composition 273-276
 - filtering 274, 275
 - flowrate 273, 274
 - industrial 274
 - purification 281, 274, 276
 - temperature 278, 274
 - energy requirement 274, 283
 - flowsheet 266
 - grain refining agents 277
 - control of 277
 - impurity behavior 269
 - silver 270
 - industrial data 274
 - inspection, short circuit 279
 - leveling agents 277
 - control of 277
 - location 18
 - map of world's refineries 24
 - passivation of anodes 282
 - periodic reversal of current 282
 - production, world 21
 - reagent control 277
 - scrap, anode 272, 266
 - percent of anode feed 274
 - recycle of 272
 - scrap, electrorefining of 359
 - flowsheets 14, 356
 - short circuits 282
 - causes 282
 - inspection for 279
 - slimes from anodes 413
 - Cu recovery from 270, 280, 413
 - stainless steel cathodes 273, 264, 267

- temperature 278, 274, 276
- voltage 269, 274
- Electrowinning of copper 327, 290
 - acid mist suppression 329
 - anodes for 330
 - calcium, purpose 330
 - tin, purpose 330
 - titanium sandwich 337, 336
 - cathodes 330
 - copper starter sheets 330
 - stainless steel 330
 - chlorine effect on 334
 - cathode copper purity 332, 335
 - maximization 335
 - cells 329, 331
 - polymer concrete 329, 278
 - cobalt addition to electrolyte 334, 332
 - decreased by titanium anodes, 337
 - copper production worldwide 21
 - current density 330, 332
 - current efficiency 332, 335
 - maximizing 335
 - electrolyte 334, 332
 - chlorine in 334
 - maximum 334
 - cobalt addition 334, 332
 - purpose 334
 - decreased by Ti anodes, 337
 - composition 332, 334
 - distribution in cells 331
 - flowrate 332
 - filtering 334, 332
 - flotation of organics from 332, 334
 - guar addition 334
 - automatic control 334
 - purpose 334
 - advantage 334
 - impurities (Cl, Fe, Mn) 332
 - controlled by coalescence and solvent extraction
 - washing 312
 - controlled by electrolyte bleeding 336
 - organics removal from 334
 - production (solvent extraction) 307
 - temperature 332
 - energy requirement 328, 332
 - industrial data 332
 - lead contamination of cathode
 - copper 332
 - minimization 335
 - map of plants 26, 27
 - new anodes for 337, 336
 - advantages 337
 - organic additions to electrolyte 334
 - automatic control 334
 - production, world 21
 - reactions 328
- Energy requirements (*see industrial data for specific processes*)
- Escondida leaching process 302
- Extractants for solvent extraction 310
 - concentrations 310, 318
 - diluents for 312
- Ferrite slag ($\text{CaO-Cu}_2\text{O-Fe}_2\text{O}_3$ system) 206, 207
- Ferrosilicon reduces slag 177
- Fire refining of molten copper 247, 248
 - antimony and arsenic removal 260
 - casting anodes 253, 254
 - continuous (Hazelett) 256, 257
 - industrial data 250, 258
 - chemical reactions 252
 - copper product from 249
 - hearth furnace refining 252
 - hydrocarbons for 253
 - impurity behavior during 260
 - industrial data 250
 - lead removal 260
 - O-in-copper measurement 249
 - purpose 247
 - rotary furnace refining 247, 248
 - scrap additions 250
 - time 250
- Flash converting 162, 162
 - industrial data 164
- Flash furnace direct-to-copper smelting 187
 - advantages 187
 - concentrate, flux, matte, slag and dust compositions 61
 - concentrate grade limitation 194
 - control 190
 - copper composition 191
 - Cu-in-slag concentration 193

- limits applicability 194
- recovery of Cu 193
- foaming, avoidance of 192
- impurity behavior 195
- industrial data 191
- reactions 189
- Flash furnace matte smelting, Inco 91
 - 92
 - burner, concentrate 92, 91
 - control 98, 99
 - concentrate, flux, matte, slag and dust compositions 61
 - converter slag recycle to 100
 - industrial data 94
 - magnetite deposition 100
 - offgas treatment 96
- Flash furnace matte smelting, Outokumpu 73, 6, 75
 - burner, concentrate 75, 76
 - control 83, 84
 - concentrate, flux, matte, slag and dust compositions 61
 - concentrate burner 75, 76
 - cooling jackets 75
 - drying concentrate 80
 - dust recovery and recycle 82
 - hydrometallurgy treatment 87
 - hearth and wall protection 85
 - impurity behavior during 86
 - industrial data 78
 - magnetite deposition 85
 - matte grade, optimum 84
 - offgas treatment 82
 - refractories 74
 - steam concentrate dryer 80
- Flotation of Cu ores 31, 42
 - cells for 43, 49, 50
 - chemistry 42
 - dewatering 52
 - collectors 42, 43, 44
 - column cell 49
 - control 50
 - cost 399
 - Cu recovery efficiency 48
 - differential 44
 - efficiency 48
 - equipment for, 43, 49, 50
 - flowsheets 32, 47
 - froth and frothers 46
 - gold recovery 48
 - industrial data 48
 - Cu recovery efficiency 48
 - in-stream chemical analysis 52
 - mechanical cell 49
 - Jameson cell 50
 - modifiers 44
 - CaO 44
 - SO₂ 45
 - molybdenite recovery 53, 48
 - particle size for 33
 - effect on Cu recovery 34
 - pH effect 44, 45
 - reagents for 42
 - quantities 48
 - regrind for 46, 47
 - sensors 51
 - tailings disposal 52
- Flotation recovery of Cu from slag 181
 - advantages 183
 - efficiency 182
 - industrial data 182
- Flowsheets
 - acid plant blowdown treatment 225
 - automobile scrap, copper recovery from 349
 - cable and wire, copper recovery from 347
 - copper extraction from oxide ores 3, 290
 - copper extraction from scrap 14, 356
 - copper extraction from sulfide ores 2
 - concentration of Cu ores 32
 - flotation 47
 - electrorefining 266
 - flash smelting/converting 162
 - flash smelting control
 - Inco 99
 - Outokumpu 84
 - flotation 47
 - grinding 32
 - control 40
 - heap leach/solvent extraction/electrowinning 290
 - hydrometallurgy 3, 290
 - ideal smelting 188
 - leaching 3, 290
 - materials cycle 343
 - Mitsubishi smelting/converting 200
 - scrap additions to 362
 - scrap (materials) cycle 343

- pyrometallurgy 2
- scrap general flowsheet 14
- scrap (low grade) treatment 356
- solvent extraction
 - general 308
 - series 318, 321
 - series-parallel 415
- sulfuric acid manufacture 221
 - acid plant blowdown treatment 225
 - SO₂ – SO₃ conversion and SO₃ absorption 232
 - wire and cable scrap, copper recovery from 347
- Fluxes
 - fire refining for impurity removal 260
 - CaCO₃ for Mitsubishi converting 160, 203, 205, 200
 - CaO for flash converting 163, 164, 162
 - silica
 - for Peirce-Smith converting 143
 - industrial 140
 - optimum 143
 - for smelting 61
 - purpose 57, 58
 - industrial compositions 61
- Garr gun 143
- Gases, effluent 219 (*see also* specific processes)
 - sulfuric acid manufacture from 217
 - treatment of 218
 - flowsheet 221
- Gold
 - anodes, in 271
 - anode slimes, in 413
 - recovery from 413
 - byproduct of copper production 86
 - byproduct credit for 391
 - cathode copper (electrorefined) in 271
 - converting, behavior during 137
 - electrode potential 272
 - electrorefining, behavior during 270
 - flux choice, based on 143
 - smelting, behavior during 86
 - slimes (anode), in 413
- Grinding 33
 - autogenous 35, 37
 - ball mill 35
 - control 38, 40
 - energy requirements 37
 - flowsheets 32, 40
 - grinding media 35
 - industrial data 37
 - matte for flash converting 162
 - particle size 162
 - particle size from 37
 - hydrocyclone controls 38, 39
 - measurement and control 38-42, 40
 - optimum 34
 - regrind ball mill 46, 48, 47
 - semi-autogenous mill 35, 37, 36
 - slag for Cu recovery 181
 - particle size 182
- Hazelett casting 256
 - anodes 256, 257, 259
 - advantages 259
 - half thickness lugs 258
 - industrial data 258
 - traveling shear 256, 259
 - bar for rod making 377
 - industrial data 378
- Heap leaching 289
 - acid (H₂SO₄) consumption 296, 297
 - acid cure 299
 - aceration of sulfide heaps 299
 - agglomeration 299
 - optimum conditions 299
 - bacteria assistance 291
 - optimum conditions for 292, 300
 - chemistry
 - 'oxide' minerals 291
 - chalcocite 291
 - sulfides 293
 - crushing for 299
 - efficiency 296
 - flowsheets 3, 290
 - heaps for 294, 297
 - base 295
 - on-off 294
 - advantages 294
 - permanent (multilift) 294
 - industrial data 297

- leachable minerals 293
- lixiviant 290, 296, 299
- maps 26, 27
- optimum conditions for 300
- ore preparation 298
- pregnant leach solution from 297
 - collection of 298
 - transfer of Cu to electrolyte 307
- reactions 291, 292
- Hoboken converter 150
- Hydrocyclone particle size control 38, 39
- Hydrogen in copper 369, 374
- Hydrometallurgical extraction of Cu
 - 289, 307, 327
 - chalcopyrite 293
 - concentrates 302
 - chemistry 291
 - chalcocite 291, 292
 - 'oxide' minerals 290, 291
 - sulfide minerals 293
 - concentrate leaching 302
 - cost 397
 - electrowinning 327 (see also Electro-winning)
 - flowsheets 3, 290
 - leaching 289-293
 - heap leaching 289
 - optimization of mine operation by 398
 - solvent extraction 307 (see also Solvent extraction transfer of Cu from pregnant leach solution to electrolyte)
- Hydrometallurgical treatment of smelter dusts 87
- Impurity behavior
 - converting 137, 140, 146
 - electrorefining 269
 - silver 270
 - fire refining 260
 - scrap smelting and converting 357, 356
 - smelting 69
 - flash 86
 - direct-to-copper 195
 - Isasmelt 125
 - Mitsubishi 211
 - Noranda 107
 - Teniente 115
- Inco flash smelting 91, 92 (see also Flash furnace matte smelting, Inco)
- Intec halide leaching process 302
- Interfacial tension, matte-slag 65
- Iron, concentration in:
 - anodes, electrorefinery 271
 - blister copper 140
 - cathode copper, electrorefinery 271
 - ASTM specification 368
 - cathode copper, electrowon 332, 335
 - concentrates 61
 - converter raw materials and products 140, 138
 - dust, smelting 61
 - electrorefining electrolyte 276
 - removal from 276
 - electrowinning electrolyte 332
 - control of 332, 336
 - flux, converting 140
 - flux, smelting 61
 - matte 61
 - scrap copper, removal from 349, 359
 - slag, smelting 61
 - slag, converting 140
 - smelter raw materials and products 61
- Iron, behavior during:
 - converting 133, 144
 - electrorefining 270
 - electrode potential 272
 - electrowinning 335, 336
 - smelting, concentrate 57
 - smelting, scrap 356
 - solvent extraction 312
 - treatments to avoid transfer to electrolyte 332
- Isasmelt process 119, 121
 - concentrate, flux, matte, slag and dust compositions 61
 - industrial data 122
 - lance 120, 124
 - swirl plates 124, 125
 - purpose 125
 - matte/slag separation 120
 - reactions 125
 - smelter locations 126
 - SO₂ in offgas 123

- Lance Mitsubishi converting, 157, 158
 lance rotates 161
 Lance, smelting
 Isasmelt/Ausmelt 120, 121, 124
 Mitsubishi 200
 lance rotates 201
 swirl plate 124
 Leaching of Cu ores 289 (*see also* Heap leaching)
 Heap leaching)
 Leaching
 ammonia 302
 Arbiter 302
 bacterial 291
 chalcopryrite concentrates 302
 chemistry 289
 CLEAR 302
 Cuprex 302
 Cymet 302
 Escondida 302
 halide 302
 heap 298 (*see also* Heap leaching)
 Intec 302
 pressure-oxygen 302
 Lead
 anodes, electrowinning 330
 Pb-Sn-Ca rolled 330
 behavior during
 converting 137
 direct-to-copper smelting 192-195
 electrorefining 270, 271
 electrowinning 335
 fire refining 260
 scrap smelting 356, 357
 smelting 69
 direct-to-copper 192-195
 flash 86
 Isasmelt 125
 Mitsubishi 211
 Noranda 107
 Teniente 115
 blister copper, removal from 260
 concentrations in:
 anodes, electrorefining 271
 cathode copper, electrorefining 271
 ASTM specification 368
 cathode copper, electrowinning 333, 335
 tough pitch copper, ASTM spec-
 ification 369
 electrode potential 272
 Magnetite
 CaO-Cu₂O-Fe₃O₄ phase diagram 207
 melting point 207
 reduction by carbon 86, 177
 by ferrosilicon 177
 refractory protection by 83, 85, 100
 saturation in silica slags, phase diagram 62
 slags, solubility in
 CaO based phase diagram 207
 SiO₂ based phase diagram 62
 viscosity increased by 177
 Manganese in:
 electrowinning 332, 335
 solvent extraction 312
 Maps
 electrorefineries 24
 Chinese (list of) 416
 electrowinning plants 26, 27
 smelters 22
 Marshall and Swift mining and milling
 equipment cost index 386
 Materials cycle 341, 343
 Matte (Cu-Fe-S)
 Cu-S phase diagram 135
 Cu₂S-FeS phase diagram 64
 density 65
 electrical conductivity 65
 immiscible with slag 57
 interfacial tension 65
 O content 61, 64, 140
 viscosity 65
 Matte grade (%Cu) smelting 61 (*see also* specific processes)
 affects % Cu in slag 69
 choice 68
 %Cu in slag, affected by 69
 industrial data 61
 Matte/slag separations, phase diagram 58
 Matte smelting 5, 57 (*see also* Smelting to matte and specific matte smelting processes)
 Melting of cathode copper 370
 Asarco furnace 370, 371
 industrial data 372

- induction furnace for oxygen free copper 373
- Milling (crushing, grinding, flotation)
 - 31 (*see also* Concentration of Cu ores)
 - ore 31
 - flowsheets 32, 47
 - slag 181
- Minerals of copper 19
 - compositions (stoichiometry) 401
 - general 19
 - hydrometallurgy 291
- Mining copper ores
 - blasting 34
 - costs 387, 389
 - cut-off grades 19
 - mine locations 17
 - production statistics 20
- Mining equipment cost index 386
- Mitsubishi continuous smelting/
 - converting process 199
 - CaO-Cu₂O-Fe₃O₄ slag for 206, 207
 - 207
 - control 211
 - converting furnace 157, 158
 - electric furnace 203, 202
 - impurity behavior 211
 - industrial data 204, 205
 - converter 160, 204
 - flowsheets 200
 - scrap addition 362
 - lances 201
 - matte grade 210
 - matte and copper siphons 158, 202
 - reactions 208
 - scrap smelting by 361, 362
 - smelting furnace 201, 202
- Mixer-settlers, solvent extraction 312, 12, 313
 - construction materials 314
 - industrial data 314
 - picket fences in 316
 - purpose 316
- Nickel
 - behavior during
 - electric furnace smelting 406
 - electrorefining 270
 - electrode potential 272
 - scrap smelting 359
 - smelting 69, 86
 - concentrations in:
 - anodes, electrorefining 271
 - cathode copper, electrorefining 271
 - ASTM specification 368
 - electrolyte, electrorefining 276
 - removal from 276
 - sulfate byproduct from 276
 - scrap, removal from 359
 - tough pitch copper, ASTM specification 369
- Noranda continuous converting process
 - 166, 166
 - control 169
 - industrial data 167
 - reactions 168
- Noranda smelting process 103, 7, 104
 - concentrates, dry through tuyeres 106
 - control 108
 - impurity behavior 107
 - industrial data 105
 - scrap smelting in 107
 - tuyere pyrometer for 109
- Obsolete scrap 344
- Offgases 219 (*see also specific processes*)
 - sulfuric acid manufacture from 217
 - treatment of 217
 - flowsheet 221
- Old (obsolete) scrap 344
 - industrial distribution 345
- Oleum 235, 240
- Ores of copper
 - %Cu 1, 48, 296
 - cut-off grade 19
 - minerals 19
- Outokumpu flash smelting 73 (*see also* Flash furnace matte smelting, Outokumpu)
 - Outokumpu direct-to-copper flash smelting 187 (*see also* Flash furnace direct-to-copper smelting)
 - Outokumpu flash converting 162
 - industrial data 164

- Oxide copper minerals 291
 - leaching of 291
- Oxygen enrichment (*see also* specific processes and industrial data tables)
 - converting 144
 - advantages 144
 - upper limit 145
 - shrouded tuyere overcomes 148
 - direct-to-copper smelting 189, 191
 - smelting 67
 - advantages 67
- Oxygen in copper
 - anodes, electrorefining 249, 271
 - continuous converting copper 160, 164
 - converter 'blister' copper 140
 - direct-to-copper smelting copper 191
 - oxygen free copper 369
 - tough pitch copper 378
 - ASTM specification 369
- Oxygen in matte 61, 64
- Oxygen manufacture 81

- Passivation of electrorefining anodes 282
- Peirce-Smith converting 131
 - alternatives 148
 - campaign life 138, 147
 - maximizing 147
 - concentrate smelting in 146
 - converter 8, 132, 133, 135
 - copper blow 134
 - copper in slag 138-140
 - recovery of 179, 182
 - end point determinations 144
 - feed matte compositions 61, 138, 140
 - flux, optimum 143
 - precious metals in 143
 - high pressure shrouded tuyeres for 148, 149
 - impurity behavior 136
 - industrial data 138
 - offgas collection 141
 - oxygen enrichment of blast 144, 138
 - product copper composition 140
 - productivity maximization 145, 147
 - reactions 131
 - scrap additions 138, 146
 - maximizing 146
 - slag 133, 138, 140
 - copper recovery from 179, 182
 - blow 133
 - formation rate 143
 - temperature control 141
 - temperature choice 141, 142
 - measurement 143
- tuyeres 141, 133
 - accretion buildup 141, 142
 - high pressure tuyere prevents 148, 149
 - tuyere pyrometer 143
- Periodic current reversal, electrorefining
 - avoids passivation 282
- Phase diagrams
 - CaO-Cu₂O-FeO_n 207
 - Cu-S 135
 - Cu₂S-FeS 64
 - FeO-Fe₂O₃-SiO₂ 62
 - FeO-FeS-SiO₂ 58
- Platinum group metal behavior during:
 - anode slimes treatment 413
 - converting 137
 - electrorefining 270, 271
 - smelting 69
- Platinum mesh – Pb composite
 - electrowinning anode 336, 337
- Polymer concrete electrolytic cells 278
 - electrorefining, 264, 268, 278, 283
 - electrowinning 329
- Price, copper 28
 - profitable 389, 398
- Production of copper 17, 17
 - by country 20
 - electrorefining 20, 24
 - China 416
 - electrowinning 20, 26
 - Chile 27
 - mining 20
 - smelting 20, 23
- Profitability of copper extraction 389, 398

- Recycling of copper scrap 341, 355 (*see also* Scrap, copper recovery from)
- Refinery locations 24
 - Chinese 416
 - map 24

- production statistics 20, 25
- Refining, electrolytic 265 (*see also* Electrorefining of copper)
- Refining, fire 247 (*see also* Fire refining of molten copper)
- Refractories (*see also* specific processes)
 - converting 137
 - consumption 138
 - protection by magnetite 85
 - smelting 74, 91, 104 (*see also* *specific smelting processes*)
- Reverberatory matte smelting 403
- Roasting for smelting 403
- Rod production
 - bar casting and rolling 376
 - industrial data 378
 - oxygen free copper 379
 - Hazelett 377
 - Southwire 376, 376, 377
- Scrap, copper recovery from 341, 355
 - anode furnaces, in 361, 362
 - automobile scrap 348, 349
 - black copper 359
 - cable 346, 347
 - converting of 358
 - blast (shaft) furnace 355, 356
 - cable 346, 347
 - categories of scrap 342, 345
 - collection and physical processing 341
 - converting black copper 359
 - electronic 350
 - fire refining 359
 - home (run around) 342
 - Mitsubishi process 361, 362
 - new 342
 - Noranda process 107
 - old (obsolete) 344
 - industrial data 345
 - Peircc-Smith converters in 361
 - physical separation processes 341
 - in primary smelters 360
 - refining (fire and electrolytic) 359
 - smelting processes for 355
 - black copper 356, 357
 - converting of 358
 - blast (shaft) furnace 355
 - chemical reactions 357
 - fire refining 359
 - flowsheet 356
 - primary smelter 360
 - secondary smelter 355
 - shaft (blast) furnace 355
 - top blown rotary converter 358
 - wire 346, 347
- Selenium behavior during:
 - converting 137
 - electrorefining 270
 - slimes (anode) treatment 413
 - smelting 69, 86, 115
- Selenium in copper
 - anodes 271
 - cathode copper 271
 - ASTM specification 368
 - tough pitch ASTM specification 369
- Selenium in anode slimes 413
- Semi-autogenous grinding 35, 36
 - energy use 37
 - industrial data 37
- Shaft (blast) furnace smelting
 - concentrate 410
 - scrap 355
- Shrouded high pressure tuyere,
 - converting 148, 149
- Silver, behavior during
 - converting 137
 - electrorefining 270, 271
 - smelting 69, 86
- Silver in copper
 - anodes 271
 - cathode copper 271
 - ASTM specification 368
 - tough pitch ASTM specification 369
- Slags 59 (*see also* following items)
- Slags, CaO based 206
 - advantages 161
 - CaO-Cu₂O-FeO_n phase diagram 207
 - disadvantages 163
 - flash converting 163
 - industrial data 164
 - melting points 207
 - Mitsubishi converting 161, 207
 - industrial data 160
 - viscosity 161
- Slags, copper concentrations in
 - after electric furnace settling 179
 - after solidification/flotation 182

- converting 140
 - industrial data 138
 - direct-to-copper smelting slag 193
 - industrial data 191
 - limits use of 194
 - matte grade effect on 69
 - minimization 175
 - smelting 61, 69
 - industrial data 61 (*see also specific processes*)
- Slags, copper losses in 173
 - minimization 175
- Slags, copper recovery from settling 176
 - furnace for 178
 - industrial data 179, 180
 - solidification/flotation 181
 - industrial data 182
- Slags, SiO₂ based converter 140
 - industrial data 138
 - density 63
 - electrical conductivity 63
 - FeO-Fe₂O₃-SiO₂ phase diagram 62
 - FeO-FeS-SiO₂ phase diagram 58
 - ionic structure 59, 60
 - interfacial tension 65
 - melting point 62
 - smelting industrial data 61
 - structure 59, 60
 - surface tension 63
 - viscosity 62, 63
 - equation 63
- Slimes, anode (electrorefining) 270
 - Cu recovery from 413
 - pressure leaching 414
- Smelters
 - cost 393
 - locations and capacities 23
 - map 22
 - production statistics 21
- Smelting to matte 57
 - Ausmelt 119
 - blast (shaft) furnace 410
 - chemistry 57
 - converter, smelting in 146
 - copper losses during 173
 - dusts from 61
 - electric furnace 405
 - flash furnace, Inco 91
 - flash furnace, Outokumpu 73
 - fluxes for 61
 - heats of reaction 5
 - Isasmelt process 119
 - matte from 61, 64
 - minor element behavior 69
 - Mitsubishi process 199
 - Noranda process 104
 - oxygen enrichment during 67
 - reactions 5, 57
 - reverberatory 403
 - shaft (blast) furnace 410
 - slags from 59, 61
 - viscosity 63
 - Teniente 110
 - Vanyukov furnace 408
- Smelting direct to copper metal 187
- Solvent extraction transfer of Cu from pregnant leach solution to electrolyte 307, 290, 308, 318
 - acid concentration effect 309
 - aqueous carryover, minimization of 312
 - purpose 312
 - chemistry 309
 - coalescence prevents impurity carryover to electrolyte 312
 - 'crud' 322
 - densities, aqueous and organic phases 316
 - diluents for 312
 - extractants for 310, 310
 - concentration in organic 314
 - calculation 318
 - flowsheets 308, 318, 321, 415
 - industrial data 314
 - mixer-settlers for 12, 313
 - reactions 309
 - solvent removal from electrolyte 334
 - washing, prevents impurity carryover to electrolyte 312
- Southwire continuous bar casting 376, 376
 - control 379, 377
 - industrial data 378
- Stainless steel cathode blanks 273, 267
 - advantages 281
 - construction 273
 - edge strips 273
 - electrorefining 273

- electrowinning 330
 - sizes 274
 - support design 273
 - surface description 273
 - Steam concentrate drier 80
 - Stokes' Law (matte settling) 174
 - Submerged tuyere smelting
 - Noranda 104,
 - Teniente 110
 - Vanyukov 408
 - Sulfur, capture and fixation of 217
 - Sulfur in copper
 - anodes (electrorefining) 271
 - cathode copper
 - ASTM specification 368
 - electrorefinery 271
 - electrowinning 332, 335
 - minimization of 335
 - source of 335
 - converter (blister) copper 249
 - continuous converting copper
 - flash 164, 165
 - Mitsubishi 160
 - Noranda 167
 - Cu-S phase diagram 135
 - direct-to-copper smelting 191, 192
 - electrorefining behavior 270, 271
 - fire refining removal of 252
 - Sulfur dioxide (SO₂)
 - air standards for 218
 - capture efficiency 220
 - concentration in smelter gases 219
 - (*see also* individual processes, industrial data)
 - converter offgas 219
 - smelting furnace offgas 219
 - liquid, production of 241
 - Sulfuric acid concentration
 - electrorefining electrolyte 274, 276
 - electrowinning electrolyte 334, 332
 - solvent extraction influenced by 309
 - lixiviant (heap leach) 296
 - pregnant leach solution 296, 314
 - raffinate 314
 - Sulfuric acid manufacture 217
 - blowdown (drying effluent) 224
 - catalysts for 227
 - cesium lowers initiation temperature 229
 - industrial arrangement 233
 - cleaning offgas 222-224
 - cooling offgas 222
 - heat recovery 223
 - double absorption 231, 232
 - industrial data 234
 - drying offgas 224, 226
 - efficiency 237
 - flowsheets 221, 232
 - industrial data 234
 - products, principal 240
 - reactions 227
 - recent developments 240
 - single absorption 233
 - industrial data 238
 - SO₂ to SO₃ oxidation 227, 231
 - catalysts for 227
 - ignition temperature 228
 - cesium lowers ignition temperature 229
 - degradation temperature 228
 - flowsheet 232
 - heat exchangers for 239, 232
 - heat recovery during 241
 - heatup paths 237, 238
 - industrial data 234-236
 - reactions 227, 228
 - SO₂ capture efficiency 237
 - SO₃ absorption 230
 - equipment for 239
 - reactions 230
- Surface tension, slag 63
- Tailings from flotation
 - Cu content (ore flotation) 48
 - Cu content (slag flotation) 182
 - dewatering 52
 - storage 52
- Tellurium
 - in anodes 271
 - in cathode copper 271
 - ASTM specification 368
 - behavior during electrorefining 270
 - behavior during slimes leaching 414
- Temperatures (*see* individual processes, industrial data)
 - measurement and control
 - copper casting, Southwire 379, 377

- converting 141
 - tuyere pyrometer for 143
 - Inco flash smelting 99, 99
 - Mitsubishi process 213
 - Noranda converting 169
 - Noranda smelting 108
 - Outokumpu
 - direct-to-copper smelting 192
 - flash smelting 85, 84
 - Teniente smelting 113
 - shell thermography 114
- Teniente matte smelting 110
 - impurity behavior 114
 - industrial data 112
 - matte grade, high 115
 - seed matte (used less) 110
 - tuyere concentrate injection 111
- Tin concentrations
 - electrorefining anodes 271
 - electrorefining cathode copper 271
 - ASTM specification 368
 - electrowinning anodes 330
 - tough pitch copper ASTM
 - specification 369
- Tin behavior during:
 - electrorefining 270
 - electrode potential 272
 - scrap smelting 356-359
- Titanium
 - new electrowinning anodes 337
- Tough pitch copper 369
- Tuyere
 - anode furnace 249, 248
 - Noranda converter 166
 - Noranda smelting furnace 104
 - Peirce-Smith converter 137, 133
 - accretion buildup 141, 142
 - high pressure shrouded tuyere for
 - 148, 149
 - advantages 148
 - punching 141, 8
 - Teniente smelting furnace 110
 - Vanyukov smelting 408
 - facture 227
 - cesium 229
 - degradation temperature 228
 - dust accumulation affects 229
 - initiation temperature 228
- Vanyukov smelting 408
- Viscosity
 - matte 64
 - slag
 - CaO based 206
 - SiO₂ based 62, 63
 - composition effects 63
 - temperature effect 63
- Waste heat boiler 222, 223
- Water cooling (smelting furnace) 75, 93
- White metal (high grade matte) 134, 135
- Zinc, behavior during:
 - converting 137
 - electrorefining 271
 - smelting
 - concentrate smelting 69
 - Isasmelt 125
 - Mitsubishi 211
 - Outokumpu flash 86
 - Noranda 107
 - Teniente 115
 - scrap smelting 356-359, 356
- Zinc concentration in
 - cathode copper, electrorefining
 - SCR specification 368
 - scrap smelting products 357
- Uses, copper and copper alloys 18
 - oxygen free copper 370
- V₂O₅ catalysts for sulfuric acid manu-

	1 (IA)																
1	1 H 1.0079 Hydrogen		2 (IIA)														
2	3 Li 6.94 ₁ Lithium		4 Be 9.01218 Beryllium														
3	11 Na 22.98977 Sodium		12 Mg 24.305 Magnesium		3 (IIIA)	4 (IVA)	5 (VA)	6 (VIA)	7 (VIIA)	8	9(VIIIA)						
4	19 K 39.098 ₁ Potassium		20 Ca 40.08 Calcium		21 Sc 44.9559 Scandium	22 Ti 47.9 ₀ Titanium	23 V 50.9415 Vanadium	24 Cr 51.996 Chromium	25 Mn 54.9380 Manganese	26 Fe 55.84 ₇ Iron	27 Co 58.9332 Cobalt						
5	37 Rb 85.467 ₈ Rubidium		38 Sr 87.62 Strontium		39 Y 88.9059 Yttrium	40 Zr 91.22 Zirconium	41 Nb 92.9064 Niobium	42 Mo 95.94 Molybdenum	43 Tc (98) Technetium	44 Ru 101.0 ₇ Ruthenium	45 Rh 102.9055 Rhodium						
6	55 Cs 132.9054 Cesium		56 Ba 137.33 Barium		57 La 138.905 ₅ Lanthanum	72 Hf 178.4 ₉ Hafnium	73 Ta 180.947 ₉ Tantalum	74 W 183.8 ₅ Wolfram	75 Re 186.207 Rhenium	76 Os 190.2 Osmium	77 Ir 192.2 ₂ Iridium						
7	87 Fr (223) Francium		88 Ra 226.0254 Radium		89 Ac 227.0278 Actinium	Lanthanide Metals											
					Actinide Metals												
						58 Ce 140.12 Cerium	59 Pr 140.9077 Praseodymium	60 Nd 144.2 ₄ Neodymium	61 Pm (145) Promethium	62 Sm 150.4 Samarium							
						90 Th 232.0381 Thorium	91 Pa 231.0359 Protactinium	92 U 238.029 Uranium	93 Np 237.0482 Neptunium	94 Pu (244) Plutonium							

18 (VIII B)

										2 He 4.00260 Helium
										13 (IIIB) 14 (IVB) 15 (VB) 16 (VIB) 17 (VIIB)
										5 B 10.81 Boron
										6 C 12.011 Carbon
										7 N 14.0067 Nitrogen
										8 O 15.999 ₄ Oxygen
										9 F 18.998403 Fluorine
										10 Ne 20.17 ₉ Neon
										13 Al 26.98154 Aluminum
										14 Si 28.085 ₅ Silicon
										15 P 30.97376 Phosphorus
										16 S 32.06 Sulphur
										17 Cl 35.453 Chlorine
										18 Ar 39.94 ₈ Argon
10 Ni 58.70 Nickel	11 (IB) Cu 63.54 ₆ Copper	12 (IIB) Zn 65.38 Zinc	31 Ga 69.72 Gallium	32 Ge 72.5 ₉ Germanium	33 As 74.9216 Arsenic	34 Se 78.9 ₆ Selenium	35 Br 79.904 Bromine	36 Kr 83.80 Krypton		
46 Pd 106.4 Palladium	47 Ag 107.868 Silver	48 Cd 112.41 Cadmium	49 In 114.82 Indium	50 Sn 118.6 ₉ Tin	51 Sb 121.7 ₅ Antimony	52 Te 127.6 ₀ Tellurium	53 I 126.9045 Iodine	54 Xe 131.30 Xenon		
78 Pt 195.0 ₉ Platinum	79 Au 196.9665 Gold	80 Hg 200.5 ₉ Mercury	81 Tl 204.3 ₇ Thallium	82 Pb 207.2 Lead	83 Bi 208.9804 Bismuth	84 Po (209) Polonium	85 At (210) Astatine	86 Rn (222) Radon		

63 Eu 151.96 Europium	64 Gd 157.2 ₅ Gadolinium	65 Tb 158.9254 Terbium	66 Dy 162.5 ₀ Dysprosium	67 Ho 164.9304 Holmium	68 Er 167.2 ₆ Erbium	69 Tm 168.9342 Thulium	70 Yb 173.0 ₄ Ytterbium	71 Lu 174.96 ₇ Lutetium
95 Am (243) Americium	96 Cm (247) Curium	97 Bk (247) Berkelium	98 Cf (251) Californium	99 Es (252) Einsteinium	100 Fm (257) Fermium	101 Md (258) Mendelevium	102 No (259) Nobelium	103 Lr (260) Lawrencium

EXTRACTIVE METALLURGY OF COPPER

'...an invaluable publication to anyone involved with the copper industry.'
NFB Abstracts

This book has become the authority on copper extraction – from ore to pure, cast copper. The fourth edition is a near-total rewrite of the now out of print third edition (1994, reprinted in 1996). Its strongest features are its completely updated year 2001 industrial data, its emphasis on new, efficient processes and its up-to-date references. While it still emphasizes flash smelting, it also devotes considerable space to submerged tuyere smelting, lance smelting and continuous converting, processes which have all had a significant impact on copper extraction over the last decade. Its electrorefining and electrowinning text and data clearly reflect the switch to stainless steel cathode technology and polymer concrete cells. Its heap leaching section has been expanded to include on-off heap technology, heap aeration and crushing/agglomeration with an improved understanding of the underlying chemical reactions. Lastly, sulfur dioxide capture and sulfuric acid manufacture are explained clearly in terms of their catalytic chemical reactions, industrial equipment and sulfur-capture efficiency.

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