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### Elements

- **He**: Helium
- **Ne**: Neon
- **Ar**: Argon
- **Kr**: Krypton
- **Xe**: Xenon
- **Rn**: Radon
Elsevier Titles of Related Interest

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Extractive Metallurgy of Copper

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FOURTH EDITION

PERGAMON
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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/Cobre 99 (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 SO₂ collection and sulphuric acid manufacture. SO₂ capture has continued to grow in importance – only a few smelters now emit their SO₂ 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 benefication and advancing through roasting, smelting, converting, refining, casting and quality control. Hydrometallurgy and its associated processes are introduced just before electrorefining 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 a 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 (CuFeS₂), bornite (Cu₅FeS₄) and chalcocite (Cu₂S). 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, Cu₂S.

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. *Principally Isasmelt/Ausmelt, reverberatory, shaft, electric, and Vanyukov smelting. -------Two furnaces, worldwide.
Overview

$\text{H}_2\text{SO}_4$ leach solution, recycle from solvent extraction

Make-up $\text{H}_2\text{SO}_4$

10 kg $\text{H}_2\text{SO}_4$/m$^3$, 0.3 kg Cu/m$^3$

Ore 'heap'

Collection dam

1 to 6 kg Cu/m$^3$

Solvent extraction

Electrolyte, 40 kg Cu/m$^3$

Electrowinning

Stripped cathode plates

Melting

Molten copper, <20 ppm impurities
~250 ppm oxygen

Continuous casting

Fabrication and use

**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 m$^3$) 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:

\[ 2\text{CuFeS}_2 + \frac{13}{4}\text{O}_2 \rightarrow \text{Cu}_2\text{S}_\frac{1}{2}\text{FeS} + \frac{3}{2}\text{FeO} + \frac{5}{2}\text{SO}_2 \]  
\[ \text{in oxygen enriched air} \quad \text{molten matte} \quad 1220^\circ\text{C} \]

\[ \Delta H^\circ_{25^\circ\text{C}} = -450 \text{ MJ/kg mol CuFeS}_2 \]

\[ 2\text{FeO} + \text{SiO}_2 \rightarrow 2\text{FeO} \cdot \text{SiO}_2 \]
\[ \text{silica flux} \quad \text{molten slag} \quad 1250^\circ\text{C} \]

\[ \Delta H^\circ_{25^\circ\text{C}} = -20 \text{ MJ/kg mole FeO.} \]

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.

SO\textsubscript{2}-bearing offgas (10 to 60% SO\textsubscript{2}) is also generated. SO\textsubscript{2} 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 SO\textsubscript{2} 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 7 m 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\textsubscript{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:

\[
2\text{FeS} + 3\text{O}_2 + \text{SiO}_2 \rightarrow 2\text{FeO} \cdot \text{SiO}_2 + 2\text{SO}_2 + \text{heat}
\]

in molten flux molten slag offgas

(b) the blister copper forming stage:

\[
\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu}^0 + 2\text{SO}_2 + \text{heat}
\]

in liquid molten copper offgas

Coppemaking (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-Fe-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). SO₂ offgas escapes the system unless the hoooding 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.
Roughly 1m x 1m. 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 $\text{H}_2\text{SO}_4$ (150 to 200 kg/m$^3$) and $\text{CuSO}_4$ (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:

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

The ores most commonly treated this way are:

(a) 'oxide' copper minerals, e.g. carbonates, hydroxy-silicates, sulfates, hydroxy-chlorides
(b) chalcocite, Cu2S.

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:

\[
\text{CuO} + \text{H}_2\text{SO}_4 \rightarrow \text{Cu}^{++} + \text{SO}_4^{2-} + \text{H}_2\text{O} \quad (1.5).
\]

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

\[
\text{Cu}_2\text{S} + \frac{5}{2}\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{Cu}^{++} + 2\text{SO}_4^{2-} + \text{H}_2\text{O} \quad (1.6).
\]

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/m³ and 0.5 to 5 kg
H₂SO₄/m³ 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:

(a) extracting Cu from an impure leach solution into a Cu-specific organic extractant
(b) separating the Cu-loaded extractant from the Cu-depleted leach solution
(c) stripping Cu from the loaded extractant into 185 kg H₂SO₄/m³ electrolyte.

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

The solvent extraction process is represented by the reaction:

\[
\text{Cu}^{++} + 2RH \rightarrow R_2\text{Cu} + 2H^+ \\
\text{aqueous \hspace{1cm} organic \hspace{1cm} in \hspace{1cm} aqueous \hspace{1cm} extractant \hspace{1cm} extractant}
\]

It shows that a low-acid aqueous phase causes the organic extractant to 'load' with Cu (as R₂Cu). 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$^{2+}$ 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 electrowinning except that the anode is an inert lead alloy.

The cathode reaction is:

\[
\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}^0 \quad \text{(in electrolyte \ to \ metal \ deposit \ on \ cathode)}
\]

The anode reaction is:

\[
\text{H}_2\text{O} \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \quad \text{(gas \ evolution \ on \ anode)}
\]

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.
Contaminated copper scrap (88 - 99% Cu) → Low-grade copper scrap (10 - 88% Cu) → Black copper (80+% Cu) → Rough copper (95+% Cu) → Fire refining + anode casting → Anodes (99.5% Cu) → Electrorefining → Cathodes → Melting → Melted copper, <20 ppm impurities ~250 ppm oxygen → Continuous casting → Continuous casting

High quality copper alloy scrap (99+%Cu) → Induction or fuel-fired furnace → Brasses, bronzes, etc. → Shaft or hearth furnace → Continuous casting → Fabrication and use by producers

Fabrication and use by
pipe, tube , sheet

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**


**References**

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).

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.
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>
<thead>
<tr>
<th>Type</th>
<th>Common minerals</th>
<th>Chemical formulae</th>
<th>Theoretical % Cu</th>
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<td>bornite</td>
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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.

<table>
<thead>
<tr>
<th>Country</th>
<th>Mine production</th>
<th>Smelter production</th>
<th>Refinery production</th>
<th>Electrowon production</th>
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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: Kiveet furnace. (s: smelting; c: converting; cu: direct to copper furnace. *Annual production, kilotonnes of copper per year.

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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.

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* 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.

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<td>10</td>
<td>29 Chiquicamata, Chile, 2</td>
<td>115</td>
</tr>
<tr>
<td>3 Pinto Valley, AZ</td>
<td>7</td>
<td>30 Zaldivar, Chile</td>
<td>145</td>
</tr>
<tr>
<td>4 Miami (BHP), AZ</td>
<td>12</td>
<td>31 Escondida Oxidos, Ch.</td>
<td>130</td>
</tr>
<tr>
<td>5 Miami (PD), AZ</td>
<td>73</td>
<td>32 El Salvador, Chile</td>
<td>12</td>
</tr>
<tr>
<td>6 Ray, AZ</td>
<td>46</td>
<td>33 Bi0 Cobre, Chile</td>
<td>10</td>
</tr>
<tr>
<td>7 Silver Bell, AZ</td>
<td>23</td>
<td>34 Manto Verde, Chile</td>
<td>42</td>
</tr>
<tr>
<td>8 Sierrita, AZ</td>
<td>23</td>
<td>35 Dos Amigos, Chile</td>
<td>3</td>
</tr>
<tr>
<td>9 San Manuel, AZ</td>
<td>23</td>
<td>36 Andacollo, Chile</td>
<td>20</td>
</tr>
<tr>
<td>10 Morenci AZ 4S X, 3E W</td>
<td>420</td>
<td>37 El Soldado, Chile</td>
<td>8</td>
</tr>
<tr>
<td>11 Tyrone, NM</td>
<td>74</td>
<td>38 Los Broncos, Chile, 2</td>
<td>30</td>
</tr>
<tr>
<td>12 Chino, NM</td>
<td>68</td>
<td>39 Pudahuel, Chile</td>
<td>18</td>
</tr>
<tr>
<td>13 Cananea, Mexico</td>
<td>55</td>
<td>40 El Teniente, Chile</td>
<td>8</td>
</tr>
<tr>
<td>14 La Caridad, Mexico</td>
<td>22</td>
<td>41 Chingola, Zambia</td>
<td>110</td>
</tr>
<tr>
<td>15 Tintaya, Peru</td>
<td>34</td>
<td>42 Nkana, Zambia</td>
<td>14</td>
</tr>
<tr>
<td>17 Toquepala, Peru</td>
<td>56</td>
<td>43 Chambishi, Zambia</td>
<td>15</td>
</tr>
<tr>
<td>18 Cerro Verde, Peru</td>
<td>60</td>
<td>43a Bwana Mkubwa</td>
<td>25</td>
</tr>
<tr>
<td>19 Cerro Colorado, Ch.</td>
<td>130</td>
<td>44 Hellenic Cu, Cyprus</td>
<td>5</td>
</tr>
<tr>
<td>20 Collahuasi, Chile</td>
<td>50</td>
<td>45 Kokkola, Finland</td>
<td>21</td>
</tr>
<tr>
<td>21 Quebrada Blanca, Ch.</td>
<td>83</td>
<td>46 Nifty, Australia</td>
<td>21</td>
</tr>
<tr>
<td>22 Tocopilla, Chile</td>
<td>5</td>
<td>47 Mt Gordon, Australia</td>
<td>50</td>
</tr>
<tr>
<td>22a El Tesoro</td>
<td>75</td>
<td>48 Mt Cuthbert, Australia</td>
<td>4</td>
</tr>
<tr>
<td>23 El Abra, Chile</td>
<td>225</td>
<td>49 Cloncurry, Australia</td>
<td>6</td>
</tr>
<tr>
<td>24 Lomas Bayas, Chile</td>
<td>60</td>
<td>50 Port Pirie, Australia</td>
<td>5</td>
</tr>
<tr>
<td>25 Michilla, Chile</td>
<td>60</td>
<td>51 Olympic Dam, Aus.</td>
<td>20</td>
</tr>
<tr>
<td>26 Radomiro Tomic, Ch.</td>
<td>256</td>
<td>52 Girilambone, Australia</td>
<td>18</td>
</tr>
<tr>
<td>27 Ivan Zar, Chile</td>
<td>10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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


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


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 is 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 m$^3$ of 13 cm iron or steel balls per 0.85 m$^3$ 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.
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.

<table>
<thead>
<tr>
<th>Concentrator</th>
<th>Candaleria, Chile</th>
<th>Mexicana de Cobre, Mexico</th>
<th>Bagdad Copper, Arizona</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ore treated per year, tonnes</strong></td>
<td>25 000 000</td>
<td>27 360 000</td>
<td>31 000 000</td>
</tr>
<tr>
<td><strong>Ore grade, %Cu</strong></td>
<td>0.9 – 1.0</td>
<td>0.522</td>
<td>0.4</td>
</tr>
<tr>
<td><strong>Crushing</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>primary gyratory crusher</td>
<td>one</td>
<td>2</td>
<td>one</td>
</tr>
<tr>
<td>diameter × height, m</td>
<td>1.52 × 2.26</td>
<td>1.52 × 2.26</td>
<td>1.5 × 2.26</td>
</tr>
<tr>
<td>power rating, kW</td>
<td>522</td>
<td>375 at ~600 RPM</td>
<td>450</td>
</tr>
<tr>
<td>product size, m</td>
<td>0.1–0.13</td>
<td>0.15</td>
<td>0.2</td>
</tr>
<tr>
<td>energy consumption, kWh per tonne of ore</td>
<td>0.3 (estimate)</td>
<td>3.0</td>
<td></td>
</tr>
<tr>
<td>secondary crushers</td>
<td>no</td>
<td>6</td>
<td>no</td>
</tr>
<tr>
<td><strong>First stage grinding</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mill type</td>
<td>semi-autogenous</td>
<td>ball mills</td>
<td>autogenous</td>
</tr>
<tr>
<td>number of mills</td>
<td>2</td>
<td>12</td>
<td>5</td>
</tr>
<tr>
<td>diameter × length, m</td>
<td>11 × 4.6</td>
<td>5 × 7.3</td>
<td>10 × 4</td>
</tr>
<tr>
<td>power rating each mill, kW</td>
<td>12 000</td>
<td>4000</td>
<td>4500</td>
</tr>
<tr>
<td>rotation speed, RPM</td>
<td>9.4–9.8</td>
<td>~13.8</td>
<td>10</td>
</tr>
<tr>
<td>vol. % 'steel' in mill</td>
<td>12–15</td>
<td>32</td>
<td>0</td>
</tr>
<tr>
<td>ball size, initial</td>
<td>12.5 cm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ball consumption</td>
<td>0.3 kg/tonne ore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>feed</td>
<td>70% ore, 30%H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>product size</td>
<td>80% &lt;140 μm</td>
<td>80% &lt;215 μm</td>
<td>83% ore, 17% H₂O</td>
</tr>
<tr>
<td>oversize treatment</td>
<td>22% ore recycle through two 525 kW crushers</td>
<td></td>
<td></td>
</tr>
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<td>energy consumption, kWh per tonne of ore</td>
<td>7.82</td>
<td></td>
<td>8</td>
</tr>
<tr>
<td><strong>Second stage grinding</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mill type</td>
<td>ball mills</td>
<td>ball mills</td>
<td>ball mills</td>
</tr>
<tr>
<td>number of mills</td>
<td>4</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>diameter × length, m</td>
<td>6 × 9</td>
<td>4.3 × 7.3</td>
<td>4.7 × 6.7</td>
</tr>
<tr>
<td>power rating each mill, kW</td>
<td>5600</td>
<td></td>
<td>2200</td>
</tr>
<tr>
<td>rotation speed, RPM</td>
<td>~15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>vol. % 'steel' in mill feed</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>product size</td>
<td>80% &lt;58 μm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>energy consumption, kWh per tonne of ore</td>
<td>7 (estimate)</td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Hydrocyclones</td>
<td>14 Krebs (0.5 m diameter)</td>
<td>6</td>
<td>2 to 3</td>
</tr>
<tr>
<td>Particle size monitor</td>
<td>yes (0.85 m diameter)</td>
<td></td>
<td>no</td>
</tr>
</tbody>
</table>

Concentrating Copper Ores
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\% \(\text{H}_2\text{O}\), 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.
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.
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>
<thead>
<tr>
<th>Sensing instruments</th>
<th>Symbol</th>
<th>Purpose</th>
<th>Type of device</th>
<th>Use in automatic control system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore tonnage weight-meter</td>
<td>O</td>
<td>Senses feed rate of ore into grinding circuit</td>
<td>Load cells, conveyor speed</td>
<td>Controls ore feed rate</td>
</tr>
<tr>
<td>Water flow gages</td>
<td>W</td>
<td>Sense water addition rates</td>
<td>Rotameters</td>
<td>Control water/ore ratio in grinding mill feed</td>
</tr>
<tr>
<td>On-stream particle size analyzer</td>
<td>S</td>
<td>Senses a critical particle size parameter (e.g. percent minus 150 μm) on the basis of calibration curves for the specific ore</td>
<td>Measure ultrasound energy loss in de-aerated pulp (Outokumpu, 2002a)</td>
<td>Controls water addition rate to hydrocyclone feed (which controls the particle size of the final grinding circuit product)</td>
</tr>
<tr>
<td>Hydrocyclone feed sump level indicator</td>
<td>L</td>
<td>Senses changes of pulp level in sump; triggers alarms for impending overflow</td>
<td>Bubble pressure tubes; electric contact probes; ultrasonic echoes; nuclear beam</td>
<td>Controls rate of ore input into grinding circuit (prevents over-loading of ball mills or hydrocyclones)</td>
</tr>
<tr>
<td>Ball mill load</td>
<td></td>
<td>Senses mass of ore in ball mill</td>
<td>Load cells; sound, bearing pressures; power draw</td>
<td>Controls rate of ore input into grinding circuit</td>
</tr>
</tbody>
</table>
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-
Concentrating Copper Ores

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.:

\[
\text{S} = \text{O} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{C} - \text{H} \\
\text{K}^+ \quad \text{S}^\text{2-}
\]

(Potassium amyl xanthate)
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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.
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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:

(a) up to pH 5 (acid pulp): CuFeS₂, PbS and FeS₂ all float
(b) between pH 5 and pH 7.5 (neutral pulp): CuFeS₂ and PbS float while FeS₂ is depressed
(c) between pH 7.5 and pH 10.5 (basic pulp): only CuFeS₂ 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 SO₃²⁻. It is produced by bubbling SO₂ 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.

<table>
<thead>
<tr>
<th>Concentrator</th>
<th>Candaleria, Chile</th>
<th>Mexicana de Cobre</th>
<th>Bagdad Copper, AZ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore treated per year, tonnes</td>
<td>25 000 000</td>
<td>27 360 000</td>
<td>31 000 000</td>
</tr>
<tr>
<td>Concentrate, tonnes/year</td>
<td>416 496</td>
<td>385 000</td>
<td></td>
</tr>
<tr>
<td>Ore grade, %Cu</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>sulfide</td>
<td>0.9-1.0</td>
<td>0.522</td>
<td>0.4</td>
</tr>
<tr>
<td>'oxide'</td>
<td>0.058</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Concentrate grade, % Cu</td>
<td>29-30</td>
<td>28.08</td>
<td>30.5</td>
</tr>
<tr>
<td>Tailings grade, % Cu</td>
<td>0.096</td>
<td>0.039</td>
<td></td>
</tr>
<tr>
<td>Cu recovery to concentrate, %</td>
<td>95% Cu</td>
<td>82% Au</td>
<td>87% Mo</td>
</tr>
</tbody>
</table>

**Rougher-scavenger flotation**

<table>
<thead>
<tr>
<th>Feed</th>
<th>Cyclone overflow</th>
<th>Cyclone overflow</th>
<th>Cyclone overflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of cells</td>
<td>24</td>
<td>140</td>
<td>78</td>
</tr>
<tr>
<td>volume of each cell, m³</td>
<td>85 and 128</td>
<td>38 and 14</td>
<td>18</td>
</tr>
<tr>
<td>cell type</td>
<td>Eimco</td>
<td>OK 38 and Wemco</td>
<td>OK and Wemco</td>
</tr>
<tr>
<td>mass% solids in feed</td>
<td>29</td>
<td>9.6-10.5</td>
<td>10.3</td>
</tr>
<tr>
<td>pH</td>
<td>10.4</td>
<td>9.6-10.5</td>
<td>10.3</td>
</tr>
<tr>
<td>collector</td>
<td>SF 323</td>
<td>thionocarbamate</td>
<td>Na ethyl xanthate</td>
</tr>
<tr>
<td>oily collector, kg/t of ore</td>
<td>~0.0065</td>
<td>0.018</td>
<td>0.009</td>
</tr>
<tr>
<td>frother</td>
<td>MIBC</td>
<td></td>
<td>Cytec 547</td>
</tr>
<tr>
<td>kg/t of ore</td>
<td>0.03</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>CaO, kg/t of ore</td>
<td>0.7</td>
<td>0.024</td>
<td>0.86</td>
</tr>
<tr>
<td>residence time, minutes</td>
<td>-20</td>
<td>10.5</td>
<td></td>
</tr>
</tbody>
</table>

**Cleaner flotation**

<table>
<thead>
<tr>
<th>Feed</th>
<th>Rougher concentrate</th>
<th>Cleaner tails</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of cells</td>
<td>32</td>
<td>30</td>
</tr>
<tr>
<td>volume of each cell, m³</td>
<td>14</td>
<td>2.8</td>
</tr>
<tr>
<td>cell type</td>
<td>Denver</td>
<td>Wemco/agitair</td>
</tr>
<tr>
<td>mass% solids in feed</td>
<td>20</td>
<td>13</td>
</tr>
<tr>
<td>pH</td>
<td>12.0-12.3</td>
<td>11.5</td>
</tr>
<tr>
<td>reagents</td>
<td>0.002</td>
<td>CaO</td>
</tr>
<tr>
<td>residence time, minutes</td>
<td>2.5</td>
<td></td>
</tr>
</tbody>
</table>

**Cleaner-scavenger flotation**

<table>
<thead>
<tr>
<th>Feed</th>
<th>Cleaner tails</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of cells</td>
<td>64</td>
</tr>
<tr>
<td>volume of each cell, m³</td>
<td>14</td>
</tr>
<tr>
<td>cell type</td>
<td>Denver</td>
</tr>
<tr>
<td>mass% solids in feed</td>
<td>20</td>
</tr>
<tr>
<td>pH</td>
<td>12-12.3</td>
</tr>
<tr>
<td>reagents</td>
<td>none</td>
</tr>
<tr>
<td>Na ethyl xanthate</td>
<td></td>
</tr>
</tbody>
</table>

**Re-cleaner flotation**

<table>
<thead>
<tr>
<th>Feed</th>
<th>Cleaner froth</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of cells</td>
<td>16</td>
</tr>
<tr>
<td>cell volume, m³</td>
<td>14</td>
</tr>
<tr>
<td>cell type</td>
<td>Column</td>
</tr>
<tr>
<td>mass% solids in feed</td>
<td>35</td>
</tr>
<tr>
<td>pH</td>
<td>12.0-12.3</td>
</tr>
<tr>
<td>reagents</td>
<td>none</td>
</tr>
<tr>
<td>Na ethyl xanthate</td>
<td></td>
</tr>
<tr>
<td>residence time, minutes</td>
<td>14.7</td>
</tr>
</tbody>
</table>
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 sheers 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...
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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.

<table>
<thead>
<tr>
<th>Sensing instrument</th>
<th>Purpose</th>
<th>Type of Device</th>
<th>Use in automatic control</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-stream particle size monitor</td>
<td>Senses particle size after grind and regrind mills</td>
<td>Ultrasonic energy loss or laser beam</td>
<td>Controls water addition rates to hydrocyclone feed (which controls final grind size)</td>
</tr>
<tr>
<td>In-stream X-ray analysis for Cu</td>
<td>Determines % Cu in solids of various process streams (especially feed, tailing and concentrate)</td>
<td>X-ray energy dispersive analysis with probes in process streams</td>
<td>Controls collector, frother, modifier and water addition rates throughout the circuit. Adjusts valves in flotation cells to alter pulp levels</td>
</tr>
<tr>
<td>Flotation cell pulp level sensor</td>
<td>Determines pulp level in flotation cells</td>
<td>Float level, hydrostatic pressure, conductivity</td>
<td>Adjusts valves in flotation cells to maintain froth depths prescribed by supervisory computer</td>
</tr>
<tr>
<td>Pulp mass-flow gage and % solids-in-pulp gage</td>
<td>Determine mass and volumetric flow rates of process streams</td>
<td>Magnetic induction, Doppler effects, ultrasonic energy loss</td>
<td>Determine recycle flows in flotation circuit, permit optimization of recycle streams</td>
</tr>
</tbody>
</table>
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
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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. Molybdenite 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 (MoS₂) 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 MoS₂ 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 MoS₂ are ~70% overall (~90% in the MoS₂ 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**


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

**References**


Concentrating Copper Ores


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


4.1 Why Smelting?

Beneficiation of copper ores produces concentrates consisting mostly of sulfide minerals, with small amounts of gangue oxides (Al₂O₃, CaO, MgO, SiO₂). Theoretically, this material could be directly reacted to produce metallic Cu by oxidizing the sulfides to elemental copper and ferrous oxide:

\[
\begin{align*}
\text{CuFeS}_2 + \frac{5}{2} \text{O}_2 & \rightarrow \text{Cu}^{\circ} + \text{FeO} + 2\text{SO}_2 \quad (4.1) \\
\text{Cu}_2\text{S} + \text{O}_2 & \rightarrow 2\text{Cu}^{\circ} + \text{SO}_2 \quad (4.2) \\
\text{FeS}_2 + \frac{5}{2} \text{O}_2 & \rightarrow \text{FeO} + 2\text{SO}_2 \quad (4.3).
\end{align*}
\]

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:

\[
\text{Cu}_2\text{S} + \frac{3}{2} \text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{SO}_2 \quad (4.4).
\]

When this happens, the Cu₂O 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 SiO₂ 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, \( i.e. \):

\[
\text{CuFeS}_2 + O_2 + \text{SiO}_2 \rightarrow \text{Cu-Fe-S} + \text{FeO-SiO}_2 + \text{SO}_2
\]

\[\text{matte} + \text{slag}\]  \hspace{1cm} (4.5)

\[70\% \text{SiO}_2 + \text{single liquid}\]

\[60\% \text{SiO}_2 + \text{two liquids}\]

\[50\% \text{SiO}_2 + \text{single liquid}\]

\[40\% \text{SiO}_2 + \text{two liquids}\]

\[30\% \text{SiO}_2 + \text{single liquid}\]

\[20\% \text{SiO}_2 + \text{solid FeO}\]

\[10\% \text{SiO}_2 + \text{liquid + solid FeO}\]

\[1200^\circ C\]

Fig. 4.1. Simplified partial phase diagram for the Fe-O-S-SiO\(_2\) system showing liquid-liquid (slag-matte) immiscibility caused by SiO\(_2\) (Yazawa and Kameda, 1953). The heavy arrow shows that adding SiO\(_2\) to an oxy-sulfide liquid causes it to split into FeS-rich matte and FeS-lean slag. The compositions of points A and B (SiO\(_2\) 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          | FeO      | FeS      | SiO₂     | CaO     | Al₂O₃ | Cu₂S |
| FeS-FeO-SiO₂   | “A” Slag       | 54.82   | 17.90   | 27.28   |         |      |      |
|                | “B” Matte      | 27.42   | 72.42   | 0.16    |         |      |      |
| FeS-FeO-SiO₂ + CaO | Slag       | 46.72   | 8.84    | 37.80   | 6.64    |      |      |
|                | Matte          | 28.46   | 69.39   | 2.15    |         |      |      |
| FeS-FeO-SiO₂ + Al₂O₃ | Slag     | 50.05   | 7.66    | 36.35   | 5.94    |      |      |
|                | Matte          | 27.54   | 72.15   | 0.31    |         |      |      |
| Cu₂S-FeS-FeO-SiO₂ | 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:

\[
\text{FeO} + \text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4(s)
\]  (4.6).

\[\text{Si} = \text{Si}; \quad \text{O} = \text{O}; \quad \text{Ca}^{+2} \text{ or Mg}^{+2} \]

---

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

<table>
<thead>
<tr>
<th>Smelter &amp; process</th>
<th>Concentrate</th>
<th>Flux</th>
<th>Matte</th>
<th>Slag</th>
<th>Dust</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu  Fe  S  SiO&lt;sub&gt;2&lt;/sub&gt; other</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;  Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; other</td>
<td>Cu  Fe  S  O</td>
<td>Cu  SiO&lt;sub&gt;2&lt;/sub&gt; total Fe  Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; S  Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; other</td>
<td>Cu  Fe  S  SiO&lt;sub&gt;2&lt;/sub&gt; other</td>
</tr>
<tr>
<td>Caraiha</td>
<td>32  23  28  9</td>
<td>98  2</td>
<td>62  12  22</td>
<td>1.8  31  42  16  0.5</td>
<td>1  29  7  Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 2  CaO 1</td>
</tr>
<tr>
<td>Outokumpu flash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Norddeutsche</td>
<td>33  24  31  5</td>
<td>85-95 5  CaO 2</td>
<td>65  12  22</td>
<td>1.5  32  39  5  0.6  4</td>
<td>1  26  15  12  3  Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 2  CaO 1</td>
</tr>
<tr>
<td>Outokumpu flash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toyo,</td>
<td>32  25  30  6</td>
<td>73  10  Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 4  Fe  Cu 2</td>
<td>63  10  22</td>
<td>1.3  33  37  13  0.6  5</td>
<td>1  20  15  9  7  CaO 2</td>
</tr>
<tr>
<td>Outokumpu flash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chino</td>
<td>29  25  32  7</td>
<td>90  4  Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 4</td>
<td>59  16  23  Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 4</td>
<td>0.8  34  43  4  1  3</td>
<td>1  30  17  12  7  CaO 2</td>
</tr>
<tr>
<td>Inco flash</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Caletones</td>
<td>32  25  30  6</td>
<td>95  2  3</td>
<td>74  4  20  other 1</td>
<td>6  27  38  16  2.7  4</td>
<td>1  34  6  11  4  Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 1  other 3</td>
</tr>
<tr>
<td>Teniente</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Port Kembla</td>
<td>31  28  31  5</td>
<td>96</td>
<td>72  6  20</td>
<td>2  30  46  15  0.8  2</td>
<td>1  34  23  23  7  Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 2</td>
</tr>
<tr>
<td>Noranda</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sterlite, India</td>
<td>30  28  31  9</td>
<td>85  1  4</td>
<td>63  13</td>
<td>0.7  29  44  3  0.7  4.9</td>
<td>1  33  32  10</td>
</tr>
<tr>
<td>Isasmelt</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Olympic Dam</td>
<td>41  16  25  3</td>
<td>95  1  Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; 2</td>
<td>99  0.8  0.4</td>
<td>20  15  30  0.1  3</td>
<td>1  36  14  3  SO&lt;sub&gt;4&lt;/sub&gt; 30</td>
</tr>
<tr>
<td>OK flash direct-to-copper</td>
<td>to to to to</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>56  23  30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gresik</td>
<td>32  25  31  9</td>
<td>90  3  1</td>
<td>68  8  22</td>
<td>0.7  33  39  2  0.5  5</td>
<td>1  63  9  19  1</td>
</tr>
<tr>
<td>Mitsubishi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Onsan</td>
<td>32  23  29  8</td>
<td>82  4  Fe  5</td>
<td>69  8  22</td>
<td>0.9  34  38  3  0.4  5</td>
<td>5  17  5  9  1  0.3</td>
</tr>
<tr>
<td>Mitsubishi</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Onahama</td>
<td>33  23  28  7</td>
<td>88  4  Fe 1.3  CaO 0.7</td>
<td>44  26  26</td>
<td>0.7  32  37  3  1  5</td>
<td>1  13  13  5  24  CaO 3</td>
</tr>
<tr>
<td>Reverberatory</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Extensive oxidation and lower smelting temperatures encourage the formation of Fe₂O₃ 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 (Fe₂SiO₄). 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:

\[ VR = \frac{A}{B} \]  

(4.7)
\[ A = (\%\text{Si}_2\text{O}_3) + 1.5(\%\text{Cr}_2\text{O}_3) + 1.2(\%\text{ZrO}_2) + 1.8(\%\text{Al}_2\text{O}_3) \]  

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

Utigard and Warczok related \( VR \) to viscosity by regression analysis against their existing database, obtaining:

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

Fig. 4.4 shows the effect of temperature and composition on the viscosity of \( \text{FeO}, \text{Fe}_2\text{O}_3, \text{SiO}_2 \) slags.

The specific gravity of smelting slags ranges between 3.3 and 3.7. It decreases with increasing \( \text{Fe}_2\text{O}_3 \) and \( \text{SiO}_2 \) 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\(^{-1}\) cm\(^{-1}\) (Ziołek and Bogacz, 1987; Hejja et al., 1994). It increases with \( \text{Cu} \) and iron oxide content and with basicity.

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$_2$S 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.

![Cu$_2$S-FeS phase diagram](image)

**Fig. 4.5.** Cu$_2$S-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 – ~0.003 kg/m·s vs. 0.2-1 kg/m·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$_2$S-FeS mattes ranges from 0.33–0.45 N/m, increasing with Cu$_2$S 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$_2$S. 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$_2$S 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$_2$S).

Matte specific electrical conductances are 200 to 1000 ohm$^{-1}$ 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:

$$
\text{CuFeS}_2 + O_2 \rightarrow \text{Cu-Fe-S} + \text{FeO} + \text{SO}_2
$$

(matte)

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:

$$
\text{Cu}_2\text{S} + \frac{3}{2} O_2 \rightarrow \text{Cu}_2\text{O} + \text{SO}_2
$$

(4.4).
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$_2$S in the matte:

\[
\text{FeO} + \text{Cu}_2\text{S} \rightarrow \text{FeS} + \text{Cu}_2\text{O}
\]

(4.12).

This reaction is not thermodynamically favored ($K_{eq} \approx 10^{-4}$ 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$_2$O 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:

\[
3\text{FeO} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4(s)
\]

(4.13).

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

\[
\text{FeO} + \text{SiO}_2 \rightarrow \text{FeO} \cdot \text{SiO}_2
\]

molten slag

(4.14).

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, ~1250°C.

A new method for contacting concentrate and O₂ 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 Cu₂O in the slag by the reverse of Reaction (4.12):

\[
\text{FeS} + \text{Cu}_2\text{O} \rightarrow \text{FeO} + \text{Cu}_2\text{S}
\]

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% Cu₂S equivalent). At higher levels, the activity of Cu₂S 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 SO₂ 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 SiO₂, with a small amount of ferric oxide. Small amounts of Al₂O₃, 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. SiO₂/Fe mass ratios are usually 0.7–0.8.

4.5.3 Offgas

The offgas from smelting contains SO₂ generated by the smelting reactions, N₂ from the air used for oxidizing the concentrate and small amounts of CO₂, H₂O and volatilized impurity compounds. The strength of the offgas is usually 10 to 60 vol% SO₂. The strength depends on the type of O₂-containing gas used for smelting, the amount of air allowed to leak into the furnace and the grade of matte produced. Volume% SO₂ 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/Nm³). 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.

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

* 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


References


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. CuFeS₂) react rapidly with the O₂ 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 (~100 μm) produced by froth flotation.

The products of flash smelting are:

(a) molten Cu-Fe-S matte, ~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% SO₂.

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

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Caraiba Metais S/A Dias d'Avila, Brazil</th>
<th>Norddeutsche Affinerie, Hamburg, Germany</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Startup date</strong></td>
<td>1982</td>
<td>1972</td>
</tr>
<tr>
<td><strong>Size, inside brick, m</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hearth: w x l x h</td>
<td>6.8 x 24.3 x 2.9</td>
<td>6 x 20 x 3</td>
</tr>
<tr>
<td>reaction shaft</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diameter</td>
<td>5.5</td>
<td>6</td>
</tr>
<tr>
<td>height above settler roof</td>
<td>6.1</td>
<td>7.5</td>
</tr>
<tr>
<td><strong>gas uptake</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diameter</td>
<td>5.1</td>
<td>4 x 8</td>
</tr>
<tr>
<td>height above roof</td>
<td>10</td>
<td>10</td>
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<tr>
<td>slag layer thickness</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>matte layer thickness</td>
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<td>0.2-0.5</td>
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<td>active slag tapholes</td>
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<td>2</td>
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<td>active matte tapholes</td>
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<td>4</td>
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<td>concentrate burners</td>
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<td><strong>Feed details, tonnes/day</strong></td>
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<td></td>
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<tr>
<td>new concentrate (dry)</td>
<td>2001 (32% Cu)</td>
<td>2850 (33% Cu)</td>
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<tr>
<td>silica flux</td>
<td>71 to 150</td>
<td>300-350</td>
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<td>oxygen</td>
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<td>recycle flash furnace dust</td>
<td>120</td>
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<td>converter dust</td>
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<td>revert</td>
<td>60</td>
<td>150 (ladle sculls, slimes, various dusts</td>
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<td>other</td>
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<td>375 molten converter slag</td>
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<td><strong>Blast details</strong></td>
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<td>200</td>
<td>ambient</td>
</tr>
<tr>
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<td>60</td>
<td>50-60</td>
</tr>
<tr>
<td>flowrate, thousand Nm³/hr</td>
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<td>40</td>
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<tr>
<td><strong>Production details</strong></td>
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<tr>
<td>matte, tonnes/day</td>
<td>1000 (62% Cu)</td>
<td>1450 (65% Cu)</td>
</tr>
<tr>
<td>slag, tonnes/day</td>
<td>950 (1.7% Cu)</td>
<td>1600 (1.5% Cu)</td>
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<td>mass% SiO₂/mass% Cu</td>
<td>0.74</td>
<td>0.85</td>
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<td>Cu recovery, flash slag</td>
<td>electric furnace</td>
<td>electric furnace</td>
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<td>Cu recovery, converter slag</td>
<td>electric furnace</td>
<td>recycle to flash furnace</td>
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<td>vol. % SO₂, leaving furnace</td>
<td>24</td>
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<td>dust production, tonnes/day</td>
<td>101-120</td>
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<td>1230/1310/1350°C</td>
<td>1210/1220/1350°C</td>
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<td><strong>Fuel inputs, kg/hour</strong></td>
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<tr>
<td>hydrocarbon fuel burnt</td>
<td>oil 400 + natural</td>
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<tr>
<td>in reaction shaft</td>
<td>gas, 400 Nm³/hour</td>
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<tr>
<td>hydrocarbon fuel</td>
<td>oil, 600</td>
<td>oil, 1000; no coke</td>
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<td>in settler burners</td>
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<tr>
<th>Nikko Mining Saganoseki, Japan</th>
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<th>LG Nikko Onsan, Korea</th>
<th>Kennecott Utah Copper, U.S.A.</th>
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<tr>
<td>$6.8 \times 20.1 \times 2.2$</td>
<td>$6.7 \times 19.9 \times 2.5$</td>
<td>$4.87 \times 20 \times 2.15$</td>
<td>$7.7 \times 23.9 \times 1.9$</td>
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<td>6.2</td>
<td>6</td>
<td>4</td>
<td>7</td>
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<td>5.9</td>
<td>6.4</td>
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<td>3.6</td>
<td>5.0</td>
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<td>8.4</td>
<td>11.9</td>
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<td>4</td>
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</tr>
<tr>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>3123 (34.8% Cu)</td>
<td>2190 (31.7% Cu)</td>
<td>1445 (31% Cu)</td>
<td>2815 (27.1% Cu)</td>
</tr>
<tr>
<td>191</td>
<td>320</td>
<td>122</td>
<td>207</td>
</tr>
<tr>
<td>407</td>
<td>286 (99% O$_2$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>205</td>
<td>114</td>
<td>104</td>
<td>206</td>
</tr>
<tr>
<td>15</td>
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<td>40</td>
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</tr>
<tr>
<td>157</td>
<td>70</td>
<td>0</td>
<td>70</td>
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<td>68 (converter dust, leach plant residue, gypsum)</td>
<td>40 solid matte</td>
<td>22</td>
<td>47 sludges &amp; residues</td>
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<tr>
<td>77 purchased scrap</td>
<td>83 copper residue</td>
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<td>288 FC slag</td>
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<td>48</td>
<td>80</td>
<td>75-85</td>
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<td>27-33</td>
<td>34</td>
<td>11.2</td>
<td>30.6</td>
</tr>
<tr>
<td>1770 (65.5% Cu)</td>
<td>1240 (63% Cu)</td>
<td>693 (62.5% Cu)</td>
<td>1344 (71% Cu)</td>
</tr>
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<td>1386</td>
<td>1212 (1.3% Cu)</td>
<td>609 (2% Cu)</td>
<td>2025 (1.8)</td>
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<td>0.85</td>
<td>0.89</td>
<td>0.7</td>
<td>0.64</td>
</tr>
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<td>electric furnace</td>
<td>electric fume with coal</td>
<td>electric furnace</td>
<td>slag flotation</td>
</tr>
<tr>
<td>solidify/flostation</td>
<td>solidify/flostation</td>
<td>same electric furnace</td>
<td>recycle to smelting</td>
</tr>
<tr>
<td>29-35</td>
<td>36.6</td>
<td>24</td>
<td>41</td>
</tr>
<tr>
<td>52-58 (calculated)</td>
<td>32.5</td>
<td>35</td>
<td>45</td>
</tr>
<tr>
<td>205</td>
<td>boiler 64, esp 64</td>
<td>104</td>
<td>boiler 125, esp 63</td>
</tr>
<tr>
<td>1258/1266/1266°C</td>
<td>1233/1241/1370°C</td>
<td>1220/1300/1330°C</td>
<td>1290/1330/1350°C</td>
</tr>
<tr>
<td>1900-2100 kg/hour</td>
<td>348 oil,</td>
<td>occasionally</td>
<td>none</td>
</tr>
<tr>
<td>fine coal with feed</td>
<td>100 pulverized coal</td>
<td>oil, 84 kg/h yearly avg</td>
<td>occasionally</td>
</tr>
<tr>
<td>none</td>
<td>none</td>
<td>670 bunker C oil</td>
<td>occasionally</td>
</tr>
</tbody>
</table>

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(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]) A 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 SO₂-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 SiO₂ content
(c) producing slag at specified temperature
(d) maintaining a protective coating of magnetite-rich slag on the furnace interior.
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 +/- 1.5% Cu and temperatures +/- 20°C are obtained.

5.4. 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 SO₂ 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:

\[
\frac{O_2 \text{- in - blast input rate}}{\text{concentrate feed rate}}
\]
	heratio 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 SiO₂ to form liquid slag. The amount of SiO₂ 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 SiO₂/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 N₂ '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 SiO₂ 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 electrorefining (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).

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

*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 electrowinning.

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 SO$_2$ capture and an SO$_2$-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


www.outokumpu.com

References


CHAPTER 6

Inco Flash Smelting

Inco flash smelting blows industrial oxygen, dried Cu-Fe-S concentrate, SiO₂ flux and recycle materials horizontally into a hot (~1250°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% SO₂.

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 ~45% Ni+Cu+Co matte and ~1% Ni+Cu+Co slag.

6.1 Furnace Details

The Inco flash furnace is made of high-quality MgO and MgO-Cr₂O₃ 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.

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

- **Blast temperature, °C**
  - Ambient

### Production details

<table>
<thead>
<tr>
<th></th>
<th>Matte, Tonnes/day</th>
<th>Matte Grade, %Cu</th>
<th>Matte Temperature, °C</th>
<th>Slag, Tonnes/day</th>
<th>Slag % Cu</th>
<th>Slag Temperature, °C</th>
<th>Cu Recovery, Flash Slag</th>
<th>Cu Recovery, Converter Slag</th>
<th>Offgas, Thousand Nm³/hour</th>
<th>Volume% SO₂ in Offgas</th>
<th>Offgas Temperature, °C</th>
<th>Dust Production, Tonnes/day</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>850</td>
<td>58</td>
<td>1190</td>
<td>1100</td>
<td>0.9</td>
<td>1250</td>
<td>Discard</td>
<td>Recycle Molten to Flash Furnace</td>
<td>21</td>
<td>75</td>
<td>1270</td>
<td>135 in Sludges</td>
</tr>
<tr>
<td></td>
<td>1020</td>
<td>58</td>
<td>1220</td>
<td>1160</td>
<td>1.3</td>
<td>1230</td>
<td>Discard</td>
<td>Recycle Molten to Flash Furnace</td>
<td>18-20</td>
<td>50-60</td>
<td>1300</td>
<td>100 Dry Tonnes</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>24%Cu + 21%Ni</td>
<td>1100</td>
<td>1230</td>
<td>0.6 Cu, 0.5 Ni</td>
<td>1280</td>
<td>Discard</td>
<td>Flotation, Chapter 11</td>
<td>18-20</td>
<td>50-60</td>
<td>1300</td>
<td>100 Dry Tonnes</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>850</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### Fuel inputs

<table>
<thead>
<tr>
<th></th>
<th>Natural Gas</th>
<th>Coke</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Occasionally (through burners above concentrate burners)</td>
<td>Petroleum Coke (~1 mm) Occasionally added with Crushed Reverts</td>
<td>For Downtimes longer than 0.5 hour, Added through Slag Return Launder or Revert Feeder</td>
</tr>
<tr>
<td></td>
<td>For Downtimes longer than 0.5 hour</td>
<td>For Downtimes longer than 0.5 hour, Added through Slag Return Launder or Revert Feeder</td>
<td>Minimal, Only as Fine Tuning</td>
</tr>
<tr>
<td></td>
<td>1-2 Tonnes/hr</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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 ~1230°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% SO₂) is pulled through the equipment by fans, which push the gas onwards to a sulfuric acid plant for SO₂ capture.

Solids from the cooler and dust removal equipment contain ~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 ~60% Cu
(c) produce slag of specified composition and temperature ~34% SiO₂, 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 dry 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 ~1250°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 ± 3% Cu while keeping slag temperature at its set point ± 20°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 SiO₂ 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

References


CHAPTER 7

Noranda and Teniente Smelting

Noranda and Teniente smelting use large, ~5 m diameter \( \times \) 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. \( \text{O}_2 \) 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\% H\(_2\)O) 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\% SO\(_2\).

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:

\[
\text{CuFeS}_2 + \text{O}_2 \rightarrow \text{Cu-Fe-S} + \text{FeO} + \text{SO}_2 + \text{heat} \quad \text{(7.1)}
\]
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% $\text{O}_2$, 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.

![Noranda smelting furnace diagram](image)

**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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Port Kembla, Aust.</th>
<th>Noranda, Québec</th>
<th>Altonorte, Chile</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Startup date</strong></td>
<td>1991</td>
<td>1973</td>
<td>2002 (design data)</td>
</tr>
<tr>
<td><strong>Furnace details</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>length × diameter, m</td>
<td>19 × 4.5</td>
<td>21.3 × 5.1</td>
<td>26.4 × 5.3</td>
</tr>
<tr>
<td>slag layer thickness</td>
<td>0.2-0.5</td>
<td>0.3-0.6</td>
<td>0.4</td>
</tr>
<tr>
<td>matte layer thickness</td>
<td>0.95-1.15</td>
<td>0.9-1.15</td>
<td>1.1-1.3</td>
</tr>
<tr>
<td>active slag tapholes</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>active matte tapholes</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>auxiliary burners</td>
<td>2</td>
<td>0</td>
<td>2</td>
</tr>
<tr>
<td><strong>Tuyere details</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tuyeres (total)</td>
<td>35</td>
<td>54</td>
<td>66</td>
</tr>
<tr>
<td>diameter, cm</td>
<td>5</td>
<td>5.4</td>
<td>6.35</td>
</tr>
<tr>
<td>active air blast tuyeres</td>
<td>20-22</td>
<td>54</td>
<td>47</td>
</tr>
<tr>
<td>concentrate injection</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>tuyeres</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Type of charge</strong></td>
<td>100% to top of bath</td>
<td>100% to top of bath</td>
<td>95% thru tuyeres, 5% to top of bath</td>
</tr>
<tr>
<td><strong>Feed, t/day (dry basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>new concentrate</td>
<td>1400-1500 (30% Cu)</td>
<td>2200-3000</td>
<td>2400 (35% Cu)</td>
</tr>
<tr>
<td>silica flux</td>
<td>190-210</td>
<td>200-250</td>
<td>170-200</td>
</tr>
<tr>
<td>slag concentrate</td>
<td>0</td>
<td>300-350</td>
<td>210-230</td>
</tr>
<tr>
<td>recycle dust</td>
<td>20 Noranda</td>
<td>50-75 Noranda + converter</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 converter</td>
<td>40-50 Noranda</td>
<td></td>
</tr>
<tr>
<td></td>
<td>20 baghouse</td>
<td></td>
<td></td>
</tr>
<tr>
<td>reverts</td>
<td>0</td>
<td>100-250</td>
<td>120-140</td>
</tr>
<tr>
<td>other</td>
<td>5 granulated converter slag</td>
<td>liquid converter slag</td>
<td></td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>19-23</td>
<td>20-22</td>
</tr>
<tr>
<td><strong>Tuyere blast details</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume% O₂</td>
<td>48</td>
<td>35-45</td>
<td>36-40</td>
</tr>
<tr>
<td>flowrate per tuyere, Nm³/minute</td>
<td>17</td>
<td>19-23</td>
<td>20-22</td>
</tr>
<tr>
<td><strong>Products, tonnes/day</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>matte, tonnes/day</td>
<td>600-700 (72% Cu)</td>
<td>800-1000 (70-72% Cu; 3-5% Fe)</td>
<td>1100-1150 (75% Cu)</td>
</tr>
<tr>
<td>slag, tonnes/day</td>
<td>800-900 (2-3% Cu)</td>
<td>1600-2200 (3-5% Cu)</td>
<td>1400-1500 (5-6% Cu)</td>
</tr>
<tr>
<td>mass% SiO₂/mass% Fe</td>
<td>0.69</td>
<td>0.6-0.7</td>
<td>0.59</td>
</tr>
<tr>
<td>Cu recovery, Noranda slag</td>
<td>electric furnace</td>
<td>solidification/flotation</td>
<td>solidification/flotation</td>
</tr>
<tr>
<td></td>
<td>molten to Noranda</td>
<td>molten to Noranda</td>
<td>molten to Noranda</td>
</tr>
<tr>
<td>Cu recovery, converter slag</td>
<td>furnace</td>
<td>furnace</td>
<td>furnace</td>
</tr>
<tr>
<td>offgas, thousand Nm³/hour</td>
<td>52</td>
<td>135-150</td>
<td>57-63</td>
</tr>
<tr>
<td>vol% SO₂, leaving furnace (wet)</td>
<td>16</td>
<td>15-20</td>
<td>25</td>
</tr>
<tr>
<td>dust production, t/day</td>
<td>20</td>
<td>50-75</td>
<td>40-50 (all recycled)</td>
</tr>
<tr>
<td>matte/slag/offgas T, °C</td>
<td>1190/1190/1200</td>
<td>1200/xx/xx</td>
<td>1215/1215/1243</td>
</tr>
<tr>
<td><strong>Consumptions, kg/tonne of concentrate</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydrocarbon fuel</td>
<td>26 kg coal</td>
<td>0-10 coal in solid charge</td>
<td>5-10 metallurgical coke in solid charge</td>
</tr>
<tr>
<td></td>
<td>9 Nm³ natural gas</td>
<td>charge</td>
<td></td>
</tr>
<tr>
<td>oxygen</td>
<td>130-150</td>
<td>170</td>
<td></td>
</tr>
</tbody>
</table>
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 CO$_2$/H$_2$O(s) 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$_2$O in the dried concentrate
(c) little H$_2$O 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>
<thead>
<tr>
<th>Element</th>
<th>% to matte</th>
<th>% to slag</th>
<th>% to offgas</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>8</td>
<td>12</td>
<td>80</td>
</tr>
<tr>
<td>Bi</td>
<td>9</td>
<td>12</td>
<td>79</td>
</tr>
<tr>
<td>Ni</td>
<td>77</td>
<td>22</td>
<td>1</td>
</tr>
<tr>
<td>Pb</td>
<td>13</td>
<td>13</td>
<td>74</td>
</tr>
<tr>
<td>Sb</td>
<td>15</td>
<td>31</td>
<td>54</td>
</tr>
<tr>
<td>Zn</td>
<td>6</td>
<td>84</td>
<td>10</td>
</tr>
</tbody>
</table>

### 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 CO₂ and H₂O(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 O₂-in-blast injection rate. This gives constant rate SO₂ delivery to the sulfuric acid plant.

Matte/slagger temperature (~1200°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.
Noranda and Teniente Smelting

\[ \frac{\text{hydrocarbon combustion rate}}{\text{solid feed mixture input rate}}. \]

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 \( \frac{N_2}{O_2} \) 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 \( \frac{SiO_2}{Fe} \) ratio is \( \sim 0.65 \).

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 \( O_2 \) 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 \( O_2 \) 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 \( O_2 \)-enrichment of the tuyere blast. Oxygen enrichment increases the rate at which \( O_2 \) 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/slack 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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>CODELCO Caletones, Chile</th>
<th>Mexicana de Cobre, Mexico</th>
<th>ZCCM, Nkana Zambia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Startup date</td>
<td>1989</td>
<td>1997</td>
<td>1994</td>
</tr>
<tr>
<td><strong>Furnace details, inside brick</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>length × diameter, m</td>
<td>21 × 4.2</td>
<td>20.8 × 4.5</td>
<td>18.2 × 4.5</td>
</tr>
<tr>
<td>slag layer thickness</td>
<td>0.9</td>
<td>0.4</td>
<td>0.3-0.5</td>
</tr>
<tr>
<td>matte layer thickness</td>
<td>1</td>
<td>1.1</td>
<td>1</td>
</tr>
<tr>
<td>active slag tapholes</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>active matte tapholes</td>
<td>2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>auxiliary burners</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td><strong>Tuyere details</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tuyeres (total)</td>
<td>47</td>
<td>44</td>
<td>40</td>
</tr>
<tr>
<td>diameter, cm</td>
<td>6.35</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>active air blast tuyeres</td>
<td>42</td>
<td>44</td>
<td>36</td>
</tr>
<tr>
<td>concentrate injection tuyeres</td>
<td>4</td>
<td>3</td>
<td>starting 2001</td>
</tr>
<tr>
<td><strong>Feed, tonnes/day (dry basis)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>dry concentrate through tuyeres</td>
<td>1850 (31.8% Cu)</td>
<td>1084 (28% Cu)</td>
<td>starting 2001</td>
</tr>
<tr>
<td>moist concentrate onto bath surface</td>
<td>0</td>
<td>216 (8% H₂O)</td>
<td>300 (32% Cu)</td>
</tr>
<tr>
<td>molten matte</td>
<td>0-100</td>
<td></td>
<td>920-1035</td>
</tr>
<tr>
<td>silica flux</td>
<td>200 (95% SiO₂)</td>
<td>121 (90% SiO₂)</td>
<td>70-100 (90%)</td>
</tr>
<tr>
<td>other</td>
<td>120 molten slags</td>
<td>200 solid reverts</td>
<td></td>
</tr>
<tr>
<td><strong>Tuyere blast details</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume% O₂</td>
<td>35</td>
<td>29</td>
<td>32</td>
</tr>
<tr>
<td>flowrate per tuyere, Nm³/minute</td>
<td>20</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td><strong>Products, tonnes/day</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>matte, tonnes/day</td>
<td>775 (74.3% Cu)</td>
<td>439 (72% Cu)</td>
<td>625 (74-75%)</td>
</tr>
<tr>
<td>slag, tonnes/day</td>
<td>1500 (6-8% Cu)</td>
<td>740 (5% Cu)</td>
<td>460 (4-6% Cu)</td>
</tr>
<tr>
<td>mass% SiO₂/mass% Fe</td>
<td>0.67</td>
<td>0.6</td>
<td>0.6-0.8</td>
</tr>
<tr>
<td>Cu recovery, Teniente slag</td>
<td>Teniente slag</td>
<td>electric furnace</td>
<td>recycle to rever-</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>beratory</td>
</tr>
</tbody>
</table>
| Cu recovery, converter slag  | recycle to smelting furnace | electric furnace      | recycle to rever-
|                             |                          |                           | beratory         |
| offgas, thousand Nm³/hour    | 60                       | 135                       | 25                |
| volume% SO₂, 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               |
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(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 (~1240°C) is controlled by adjusting revert feed rates and blast oxygen enrichment level (i.e. N₂ 'coolant' input rate). It is typically controlled within about ±10°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$_3$O$_4$ content of 20±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 \( \sim \frac{1}{2} \) 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).

<table>
<thead>
<tr>
<th>Element</th>
<th>% to matte</th>
<th>% to slag</th>
<th>% to offgas</th>
</tr>
</thead>
<tbody>
<tr>
<td>As</td>
<td>6</td>
<td>7</td>
<td>87</td>
</tr>
<tr>
<td>Bi</td>
<td>23</td>
<td>40</td>
<td>37</td>
</tr>
<tr>
<td>Ni</td>
<td>80</td>
<td>19</td>
<td>1</td>
</tr>
<tr>
<td>Pb</td>
<td>22</td>
<td>25</td>
<td>53</td>
</tr>
<tr>
<td>Sb</td>
<td>19</td>
<td>30</td>
<td>51</td>
</tr>
<tr>
<td>Se*</td>
<td>58</td>
<td>39</td>
<td>1</td>
</tr>
<tr>
<td>Zn</td>
<td>11</td>
<td>85</td>
<td>4</td>
</tr>
</tbody>
</table>

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


References


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.

![Diagram of Isasmelt furnace](image)

**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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Mt. Isa Mines Mt. Isa, Australia</th>
<th>Sterlite Copper Tuticorin, India</th>
<th>Phelps Dodge Miami, AZ, USA</th>
<th>Zhong Tiao Shan Houma, P.R. China</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Furnace type</strong></td>
<td>Isasmelt</td>
<td>Isasmelt</td>
<td>Isasmelt</td>
<td>Ausmelt</td>
</tr>
<tr>
<td><strong>Startup date</strong></td>
<td>1992</td>
<td>1996</td>
<td>1992</td>
<td>1999</td>
</tr>
<tr>
<td><strong>Furnace details</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diameter, m</td>
<td>3.75</td>
<td>2.85</td>
<td>3.5</td>
<td>4.4</td>
</tr>
<tr>
<td>height, m</td>
<td></td>
<td>11</td>
<td>13</td>
<td>11.9</td>
</tr>
<tr>
<td>bath depth, m</td>
<td>1-2</td>
<td>0.6-2</td>
<td>1-2</td>
<td>1.2</td>
</tr>
<tr>
<td>number of tapholes</td>
<td>1</td>
<td>2 (1 in use)</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>description of taphole</td>
<td>hole in water-cooled Cu block</td>
<td>410 mm diameter hole in water-cooled Cu block</td>
<td>hole in refractory-lined Cu block</td>
<td></td>
</tr>
<tr>
<td>auxiliary burners</td>
<td>4 m long pipe furnace oil/air burner</td>
<td></td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>furnace cooling system</td>
<td>internal water-cooling jackets (tapping block and below) and shell water curtain</td>
<td>water-cooled Cu blocks</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Lance details</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>inside fuel line pipe diameter</td>
<td>mild steel</td>
<td>mild steel</td>
<td>mild steel</td>
<td></td>
</tr>
<tr>
<td>construction material</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>lance pipe diameter, mm</td>
<td>500 mm</td>
<td>250 &amp; 300 mm</td>
<td>500 mm</td>
<td></td>
</tr>
<tr>
<td>construction material</td>
<td>stainless steel</td>
<td>316L stainless steel</td>
<td>stainless steel</td>
<td></td>
</tr>
<tr>
<td>tip penetration into bath</td>
<td>0.3 m</td>
<td>0.3 m</td>
<td>0.45 m</td>
<td>0.35 m</td>
</tr>
<tr>
<td>overall lance length</td>
<td>15.5 m</td>
<td>17 m</td>
<td>15.6 m</td>
<td></td>
</tr>
<tr>
<td>swirler description</td>
<td>6 vanes, ~235 mm long, positioned ~600 mm from lance tip</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 8.2. Operational details of three Isasmelt furnaces and one Ausmelt furnace.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Mt. Isa Mines Australia</th>
<th>Sterlite Copper Tuticorin, India</th>
<th>Phelps Dodge Tuticorin, India</th>
<th>Zhong Tiao Shan P.R. China</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace Type</td>
<td>Isasmelt</td>
<td>Isasmelt</td>
<td>Isasmelt</td>
<td>Ausmelt</td>
</tr>
<tr>
<td>Feed details, tonnes per day</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>type of charge</td>
<td>moist, pelletized</td>
<td>moist, non-pelletized</td>
<td>moist, non-pelletized</td>
<td></td>
</tr>
<tr>
<td>% moisture in charge</td>
<td>10</td>
<td>6-8</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>new concentrate</td>
<td>2850 (25-27% Cu)</td>
<td>1500-1600 (27-31% Cu)</td>
<td>2200 (28% Cu)</td>
<td>625 (17-22% Cu)</td>
</tr>
<tr>
<td>silica flux</td>
<td>75</td>
<td>260</td>
<td>340</td>
<td></td>
</tr>
<tr>
<td>lime flux</td>
<td>0</td>
<td>40</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>reverts</td>
<td>100</td>
<td>100-150</td>
<td>240</td>
<td></td>
</tr>
<tr>
<td>other</td>
<td>50</td>
<td>20 tonnes esp dust plus sludges</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>coal</td>
<td>10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lance inputs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>blast flowrate, Nm³/minute</td>
<td>750</td>
<td>300</td>
<td>481</td>
<td>333</td>
</tr>
<tr>
<td>volume% O₂ in blast</td>
<td>60</td>
<td>63</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>hydrocarbon fuel</td>
<td>natural gas</td>
<td>furnace oil</td>
<td>natural gas</td>
<td>coal</td>
</tr>
<tr>
<td>/tonne concentrate</td>
<td>23 kg</td>
<td>34 Nm³</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂, kg/tonne of concentrate</td>
<td>~290 (author estimate)</td>
<td>228 (~180 (author estimate))</td>
<td>~295 (~285 (author estimate))</td>
<td></td>
</tr>
<tr>
<td>Products,</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>matte/slag mixture</td>
<td>rotary holding furnace</td>
<td>rotary holding furnace</td>
<td>electric furnace</td>
<td>holding furnace</td>
</tr>
<tr>
<td>destination</td>
<td>acid plant via waste heat boiler</td>
<td>acid plant via waste evaporation gas cooler</td>
<td>acid plant via waste heat boiler</td>
<td>acid plant</td>
</tr>
<tr>
<td>offgas destination</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>offgas flowrate</td>
<td>70 000 Nm³/hr</td>
<td>54 000 Nm³/hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume% SO₂</td>
<td>27</td>
<td>22-25</td>
<td>20-25</td>
<td>11-13</td>
</tr>
<tr>
<td>dust production, tonnes/day</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>6</td>
</tr>
<tr>
<td>liquids/offgas</td>
<td>1220/1220</td>
<td>(1150-1180)/1150</td>
<td>1170/1050</td>
<td>(1200-1300)/x</td>
</tr>
<tr>
<td>temperatures, °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid products after settling</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>matte, tonnes/day</td>
<td>1300</td>
<td>700</td>
<td>1100</td>
<td>160</td>
</tr>
<tr>
<td>62% Cu</td>
<td>61-63% Cu</td>
<td>58% Cu</td>
<td>60% Cu</td>
<td></td>
</tr>
<tr>
<td>slag, tonnes/day</td>
<td>1270</td>
<td></td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>%Cu</td>
<td>0.75-0.8</td>
<td>0.7</td>
<td>0.7</td>
<td>~0.6</td>
</tr>
<tr>
<td>%SiO₂/%Fe</td>
<td>0.7</td>
<td>0.75</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>destination</td>
<td>mill/ granulation</td>
<td>discard</td>
<td>granulation</td>
<td>discard</td>
</tr>
<tr>
<td>concentrator</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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:

\[
\text{CuFeS}_2 \rightarrow \frac{1}{2}\text{Cu}_2\text{S} + \text{FeS} + \frac{1}{4}\text{S}_2(g) \quad (8.1)
\]

\[
\text{FeO} + \frac{1}{4}\text{O}_2(g) \rightarrow \text{FeO}_{1.5} \quad (8.2)
\]

\[
\text{FeS} + 6\text{FeO}_{1.5} \rightarrow 7\text{FeO} + \text{SO}_2(g) \quad (8.3)
\]

\[
\text{S}_2(g) + 2\text{O}_2(g) \rightarrow 2\text{SO}_2(g) \quad (8.4)
\]

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 O₂/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)
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/sludge 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 Cu₂S (white metal) followed by tapping slag. It is finished by oxidizing the Cu₂S to copper and SO₂. 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 SO₂ 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


References


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:

\[
\text{Cu-Fe-S} + \text{O}_2 + \text{SiO}_2 \rightarrow \text{Cu}^{\circ} + \left\{ \frac{2\text{FeO} : \text{SiO}_2}{\text{Fe}_3\text{O}_4} \right\} + \text{SO}_2
\]

molten in air and molten slag with
matte oxygen some solid Fe₃O₄

(9.1)
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 (‘Gar’ 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, Fe$_3$O$_4$ and SO$_2$ by reactions like:

\[
\text{FeS} + \frac{3}{2} \text{O}_2 \rightarrow \text{FeO} + \text{SO}_2 \quad (9.2)
\]

\[
3\text{FeS} + 5\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 + 3\text{SO}_2 \quad (9.3)
\]

The melting points of FeO and Fe$_3$O$_4$ are 1385°C and 1597°C so silica flux is added to form a liquid slag with FeO and Fe$_3$O$_4$. 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$_2$S,
‘white metal’, ~1200°C.

(b) the coppermaking stage when the sulfur in Cu$_2$S 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$_2$S) 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$_2$S ‘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$_2$S-
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:

\[
\text{Cu}_2\text{S} + \frac{3}{2} \text{O}_2 \rightarrow \text{Cu}_2\text{O} + \text{SO}_2 \quad (9.4)
\]

\[
\text{Cu}_2\text{S} + 2\text{Cu}_2\text{O} \rightarrow 6\text{Cu}_\ell^\circ + \text{SO}_2 \quad (9.5)
\]

though some copper may be made directly by:

\[
\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu}_\ell^\circ + \text{SO}_2 \quad (9.6).
\]

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 Cu$_2$S-Cu-Cu$_2$O-gas foam/emulsion from which metallic copper 'c' descends and SO$_2$ and N$_2$ ascend. The immiscibility of copper and Cu$_2$S is due to their different structures – copper is metallic while Cu$_2$S is a semiconductor.
(a) The first blowing of air and oxygen into the Cu₂S removes S as SO₂ to give S-deficient 'white metal', but no metallic copper. The reaction for this step is:

\[ \text{Cu}_2\text{S} + x\text{O}_2 \rightarrow \text{Cu}_2\text{S}_{1-x} + x\text{SO}_2 \]  

(9.7).

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 Cu₂S 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 Cu₂O. This care is necessary because Cu₂S is no longer available to reduce Cu₂O 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.

<table>
<thead>
<tr>
<th>Element</th>
<th>54% Cu matte feed distribution %</th>
<th>70% Cu matte feed distribution %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>to blister copper</td>
<td>to converter slag</td>
</tr>
<tr>
<td>As</td>
<td>28</td>
<td>13</td>
</tr>
<tr>
<td>Bi</td>
<td>13</td>
<td>17</td>
</tr>
<tr>
<td>Pb</td>
<td>4</td>
<td>48</td>
</tr>
<tr>
<td>Sb</td>
<td>29</td>
<td>7</td>
</tr>
<tr>
<td>Se</td>
<td>72</td>
<td>6</td>
</tr>
<tr>
<td>Zn</td>
<td>11</td>
<td>86</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Norddeutsche Affinerie Hamburg, Germany</th>
<th>Onahama Smelting and Refining Onahama, Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Converter type</td>
<td>Peirce-Smith</td>
<td>Peirce-Smith</td>
</tr>
<tr>
<td>Number of converters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>total</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>hot</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>blowing at one time</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Converter details</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diameter × length, inside shell, m</td>
<td>4.6 × 12.2</td>
<td>four: 3.96 × 9.15</td>
</tr>
<tr>
<td>number of tuyeres</td>
<td></td>
<td>one: 3.96 × 11.0</td>
</tr>
<tr>
<td>total</td>
<td>62</td>
<td>48</td>
</tr>
<tr>
<td>active</td>
<td>60</td>
<td>44</td>
</tr>
<tr>
<td>tuyere diameter, cm</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>usual blast rate per converter</td>
<td></td>
<td></td>
</tr>
<tr>
<td>slag blow, Nm$^3$/minute</td>
<td>700</td>
<td>520</td>
</tr>
<tr>
<td>copper blow, Nm$^3$/minute</td>
<td>700-800</td>
<td>500</td>
</tr>
<tr>
<td>usual volume% O$_2$ in blast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>slag blow</td>
<td>23</td>
<td>21, then 60 minutes at 29</td>
</tr>
<tr>
<td>copper blow</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>SO$_2$ in offgas, volume%</td>
<td>8-13</td>
<td>9</td>
</tr>
<tr>
<td>Production details (per converter)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inputs (tonnes/cycle)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>molten matte</td>
<td>270 (64% Cu)</td>
<td>140 (43% Cu)</td>
</tr>
<tr>
<td>source</td>
<td>Outokumpu flash</td>
<td>Reverberatory</td>
</tr>
<tr>
<td>Other inputs (tonnes)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>slag blow</td>
<td>15t ladle skulls</td>
<td>90t concentrate</td>
</tr>
<tr>
<td>+ 10t secondaries</td>
<td></td>
<td>+2.5t reverts</td>
</tr>
<tr>
<td>copper blow</td>
<td>75t Cu scrap</td>
<td>50t Cu scrap etc.</td>
</tr>
<tr>
<td>Outputs, (tonnes/cycle)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>blister copper</td>
<td>120</td>
<td></td>
</tr>
<tr>
<td>slag</td>
<td>150</td>
<td></td>
</tr>
<tr>
<td>average mass %Cu</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>mass%SiO$_2$/mass%Fe</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>Cycle time</td>
<td></td>
<td></td>
</tr>
<tr>
<td>usual converter cycle time, hours</td>
<td></td>
<td></td>
</tr>
<tr>
<td>slag blow, hours</td>
<td>9</td>
<td>13</td>
</tr>
<tr>
<td>copper blow, hours</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>Campaign details</td>
<td></td>
<td></td>
</tr>
<tr>
<td>time between tuyere line repairs, days</td>
<td>60</td>
<td>100</td>
</tr>
<tr>
<td>copper produced between tuyere line repairs, tonnes</td>
<td>50 000</td>
<td>21 600</td>
</tr>
<tr>
<td>time between complete converter re-lines, years</td>
<td>5</td>
<td>-</td>
</tr>
<tr>
<td>refractory consumption, kg/tonne of Cu</td>
<td>1.93</td>
<td>-</td>
</tr>
</tbody>
</table>
## Batch Converting of Cu Matte

Peirce-Smith and Hoboken converters.

<table>
<thead>
<tr>
<th>Mexicana de Cobre Nacazari, Mexico</th>
<th>Caraiba Metals Bahia, Brazil</th>
<th>CODELCO Caletones, Chile</th>
<th>Sumitomo Toyo, Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peirce-Smith</td>
<td>Hoboken</td>
<td>Peirce-Smith</td>
<td>Peirce-Smith</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>1 or 2</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

| 4.57 x 10.67                  | 4.16 x 11.4                 | 4.0 x 10.6               | 4.2 x 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% O2 |
| 23.26                         | 25                          | 21                       | 21                  |
| 7.5                           | 12                          | 15                       | 11                  |

| Outokumpu flash furnace       | Outokumpu flash furnace     | Teniente & slag cleaning furnaces | Outokumpu flash furnace |
| 211 (66.5% Cu)+73 WM          | 180 (62% Cu)                | none                                | 230 (63% Cu)           |
| + Teniente furnace            | 200 (74.3% Cu)              | 5t mostly reverts                  |                      |
| 15t mostly reverts            | 5.8 tonnes of 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.

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Fe</th>
<th>S</th>
<th>O</th>
<th>As</th>
<th>Bi</th>
<th>Pb</th>
<th>Sb</th>
<th>Zn</th>
<th>Au</th>
<th>Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matte</td>
<td>45-75</td>
<td>3-30</td>
<td>20-23</td>
<td>1-3</td>
<td>0-0.5</td>
<td>0-0.1</td>
<td>0-1</td>
<td>0-0.5</td>
<td>0-1</td>
<td>0-0.003</td>
<td>0-0.3</td>
</tr>
<tr>
<td>White metal(Cu₂S)</td>
<td>79</td>
<td>~1</td>
<td>~20</td>
<td>&lt;1</td>
<td>0-0.03</td>
<td>0-0.5</td>
<td>0-0.1</td>
<td>0</td>
<td>0-0.004</td>
<td>0-0.5</td>
<td></td>
</tr>
<tr>
<td>Blister copper</td>
<td>~99</td>
<td>0.001-0.3</td>
<td>0.001-0.3</td>
<td>0.1-0.8</td>
<td>0-0.2</td>
<td>0-0.03</td>
<td>0-0.5</td>
<td>0-0.1</td>
<td>0</td>
<td>0-0.004</td>
<td>0-0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Cu</th>
<th>Total Fe</th>
<th>SiO₂</th>
<th>Fe₃O₄ (ℓ+δ)</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Zn</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux</td>
<td>4-8</td>
<td>35-50</td>
<td>15-30</td>
<td>20-25</td>
<td>0-5</td>
<td>0-5</td>
<td>0-1</td>
<td>0-5</td>
<td>1-5</td>
</tr>
<tr>
<td>Converter slag</td>
<td>4-8</td>
<td>35-50</td>
<td>15-30</td>
<td>20-25</td>
<td>0-5</td>
<td>0-5</td>
<td>0-1</td>
<td>0-5</td>
<td>0</td>
</tr>
</tbody>
</table>
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:

\[
\text{FeS} + \frac{3}{2} \text{O}_2 \rightarrow \text{FeO} + \text{SO}_2 + \text{heat} \quad (9.2)
\]

\[
\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu} \uparrow + \text{SO}_2 + \text{heat} \quad (9.6)
\]

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).

<table>
<thead>
<tr>
<th>Input</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Input matte</td>
<td>1200°C</td>
</tr>
<tr>
<td>Skimmed slag</td>
<td>1220°C</td>
</tr>
<tr>
<td>Final blister copper</td>
<td>1200°C</td>
</tr>
</tbody>
</table>

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 Fe$_3$O$_4$ so they can be poured from the converter. SiO$_2$-bearing flux (e.g. quartz, quartzite, sand) is added for this purpose.

A common indicator of slag composition is the ratio:

$$\frac{\text{mass} \% \text{SiO}_2 \text{ in slag}}{\text{mass} \% \text{Fe in slag}}$$

Enough SiO$_2$-in-flux is added to give SiO$_2$/Fe ratio of ~0.5. Acceptable Fe$_3$O$_4$ 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 electrorefinery 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 O$_2$, 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).
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% O₂ 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% O\textsubscript{2} 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% O\textsubscript{2}) 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 SO\textsubscript{2}-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 SO\textsubscript{2} 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


References


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 SO₂-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, ~1220°C. They also contain highly oxidized slag with considerable Cu, Fe³⁺ and sometimes solid Fe₃O₄ (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:

\[
\begin{align*}
\text{a molten copper layer} & \quad \sim 1 \text{ m thick} \\
\text{a molten slag layer} & \quad \sim 0.15 \text{ m thick.}
\end{align*}
\]

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 Cu₂S layer (~1% S, Fig. 9.2a).

10.2.2 Reaction mechanism

The Mitsubishi converter's molten matte feed, O₂ and flux by the reactions:

\[
\begin{align*}
3\text{FeS} & + 5\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 + 3\text{SO}_2 \\
\text{in molten} & \quad \text{in lance} \\
\text{matte} & \quad \text{blast}
\end{align*}
\]

and:

\[
\begin{align*}
\text{CaO} & + \text{Fe}_3\text{O}_4 \rightarrow \text{molten calcium ferrite slag} \\
\text{in molten} & \quad \text{molten} \\
\text{matte} & \quad \text{copper}
\end{align*}
\]

then:

\[
\begin{align*}
\text{Cu}_2\text{S} & + \text{O}_2 \rightarrow 2\text{Cu}^\circ + \text{SO}_2 \\
\text{in molten} & \quad \text{in lance} \\
\text{matte} & \quad \text{blast} \\
\end{align*}
\]

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 Cu₂O – 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, CaCO₃ 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>
<thead>
<tr>
<th>Smelter</th>
<th>Port Kembla Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mitsubishi converter startup date</td>
<td>2000</td>
</tr>
</tbody>
</table>

**Converting furnace details**

- shape: circular
- diameter x height inside, m: 8.05 x 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)
- CaCO₃ flux: 20-35
- copper anode scrap: 60-80
- reverts: 40-45

**Blast**

- volume% O₂: 32-40
- input rate, thousand Nm³/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 Nm³/hour: 13-15
  - volume% SO₂ in offgas: 28
  - temperature, °C: 1200
- dust production, tonnes/day: 25-40

**Fuel inputs**

0 (autothermal)
Continuous Converting

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 revert 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 Fe³⁺)
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 minimize 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:

(a) tapping molten 70% Cu matte from a smelting furnace
(b) granulating the molten matte to ~0.5 mm granules in a water torrent
(c) crushing the matte granules to 50 μm followed by drying
(d) continuously feeding the dry crushed matte to the flash converter with 80 volume% O₂ blast and CaO flux, Fig. 10.2

![Flash smelting and converting diagram](image)

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:

\[
\text{Cu-Fe-S solidified matte} + \text{O}_2 \text{ in oxygen-air blast} \rightarrow \text{Cu}^0 \text{ in molten calcium ferrite slag} + \text{Fe}_3\text{O}_4 + \text{SO}_2
\]

Exactly enough \( \text{O}_2 \) is supplied to make metallic copper rather than \( \text{Cu}_2\text{S} \) or \( \text{Cu}_2\text{O} \).

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% \( \text{SO}_2 \) 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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Kennecott Utah Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Flash converter startup date</strong></td>
<td>1995</td>
</tr>
<tr>
<td><strong>Size, inside brick, m</strong></td>
<td></td>
</tr>
<tr>
<td>hearth: (w \times 1 \times h)</td>
<td>(6.5 \times 18.75 \times 3)</td>
</tr>
<tr>
<td>reaction shaft diameter</td>
<td>4.25</td>
</tr>
<tr>
<td>height above settler roof</td>
<td>6.5</td>
</tr>
<tr>
<td>gas uptake diameter</td>
<td>3</td>
</tr>
<tr>
<td>height above settler roof</td>
<td>8.7</td>
</tr>
<tr>
<td>slag layer thickness, m</td>
<td>0.3</td>
</tr>
<tr>
<td>copper layer thickness, m</td>
<td>0.46</td>
</tr>
<tr>
<td>active copper tapholes</td>
<td>6 tapholes + 2 drain holes</td>
</tr>
<tr>
<td>active slag tapholes</td>
<td>3</td>
</tr>
<tr>
<td>particulate matte burners</td>
<td>1</td>
</tr>
<tr>
<td><strong>Feeds, tonnes/day</strong></td>
<td></td>
</tr>
<tr>
<td>granulated/crushed matte</td>
<td>1344 (70% Cu)</td>
</tr>
<tr>
<td>matte particle size, (\mu m)</td>
<td>50</td>
</tr>
<tr>
<td>CaO flux</td>
<td>90</td>
</tr>
<tr>
<td>recycle flash converter dust</td>
<td></td>
</tr>
<tr>
<td><strong>Blast</strong></td>
<td></td>
</tr>
<tr>
<td>blast temperature, °C</td>
<td>ambient</td>
</tr>
<tr>
<td>volume% (O_2)</td>
<td>75-85</td>
</tr>
<tr>
<td>input rate, thousand Nm³/hour</td>
<td>307</td>
</tr>
<tr>
<td>oxygen input rate, tonnes/day</td>
<td></td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td></td>
</tr>
<tr>
<td>copper, tonnes/day</td>
<td>900</td>
</tr>
<tr>
<td>%S in copper</td>
<td>0.2</td>
</tr>
<tr>
<td>%O in copper</td>
<td>0.3</td>
</tr>
<tr>
<td>slag, tonnes/day</td>
<td>290</td>
</tr>
<tr>
<td>%Cu in slag</td>
<td>20</td>
</tr>
<tr>
<td>%CaO/%Fe</td>
<td>0.35</td>
</tr>
<tr>
<td>Cu-from-slag recovery method</td>
<td>granulate and recycle</td>
</tr>
<tr>
<td>to smelting furnace</td>
<td></td>
</tr>
<tr>
<td>offgas, thousand Nm³/hour</td>
<td>26</td>
</tr>
<tr>
<td>volume% (SO_2) in offgas</td>
<td>35-40</td>
</tr>
<tr>
<td>dust production, tonnes/day</td>
<td>130</td>
</tr>
<tr>
<td>copper/slag/offgas temperatures, °C</td>
<td>1220/1250/1290</td>
</tr>
<tr>
<td><strong>Fuel inputs</strong></td>
<td></td>
</tr>
<tr>
<td>hydrocarbon fuel burnt in reaction shaft</td>
<td>125 Nm³/hour natural gas</td>
</tr>
<tr>
<td>hydrocarbon fuel into settler burners</td>
<td>0</td>
</tr>
</tbody>
</table>
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 Cu$_2$S matte. The layer is avoided by keeping the converter's:

\[
\frac{O_2 \text{ input rate}}{\text{matte feed rate}}
\]

slightly towards Cu$_2$O formation rather than Cu$_2$S formation.

The matte layer is avoided to minimize the possibility of SO$_2$ formation (and slag foaming) by the reactions:

\[
\begin{align*}
2\text{Cu}_2\text{O} &+ \text{Cu}_2\text{S} \rightarrow 6\text{Cu}^° + \text{SO}_2 \\
2\text{CuO} &+ \text{Cu}_2\text{S} \rightarrow 4\text{Cu}^° + \text{SO}_2 \\
2\text{Fe}_3\text{O}_4 &+ \text{Cu}_2\text{S} \rightarrow 2\text{Cu}^° + 6\text{FeO} + \text{SO}_2
\end{align*}
\]

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$_2$S) and molten slag. It blows oxygen-enriched air continuously through its tuyeres and continuously collects ~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.](image-url)
Table 10.3. Physical and operating details of Noranda continuous submerged tuyere converting, 2001.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Noranda (Horne)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noranda converter startup date</td>
<td>1997</td>
</tr>
<tr>
<td><strong>Noranda converter details</strong></td>
<td>horizontal rotating cylinder</td>
</tr>
<tr>
<td>shape</td>
<td>horizontal rotating cylinder</td>
</tr>
<tr>
<td>diameter $\times$ length, inside, m</td>
<td>4.5 $\times$ 19.8</td>
</tr>
<tr>
<td>tuyeres</td>
<td>44</td>
</tr>
<tr>
<td>diameter, cm</td>
<td>6.35</td>
</tr>
<tr>
<td>slag layer thickness, m</td>
<td>$-0.4$</td>
</tr>
<tr>
<td>matte layer thickness, m</td>
<td>$-0.9$</td>
</tr>
<tr>
<td>copper layer thickness, m</td>
<td>$-0.4$</td>
</tr>
<tr>
<td>copper tapholes</td>
<td>2 on bottom</td>
</tr>
<tr>
<td>slag tapholes</td>
<td>1 on end opposite feed port</td>
</tr>
<tr>
<td>number of auxiliary burners</td>
<td>0</td>
</tr>
</tbody>
</table>

**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/sludge/offgas temperatures, °C: 1210 / 1190 / 1175
10.4.2 Chemical reactions

Noranda converting controls its matte and $O_2$ input rates to always have matte (mainly $Cu_2S$) in the furnace. It is this matte phase that is continuously oxidized by tuyere-injected $O_2$.

The constant presence of this matte is confirmed by the high $S$ content, $\sim$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 $\sim$70% Cu matte ($5$ to $10\%$ Fe, $\sim$$22\%$ S) is poured into the furnace – it joins the molten matte layer between copper and slag.

(b) this matte is oxidized by $O_2$ in the tuyere blast by the reactions:

$$3FeS + 5O_2 \rightarrow Fe_3O_4 + 3SO_2$$

in molten matte 'blast' in tuyere blast

(10.8)

$$3Fe_3O_4 + FeS \rightarrow 10FeO + SO_2$$

(10.9)

$$2FeO + SiO_2 \rightarrow 2FeO \cdot SiO_2$$

flux molten slag

(10.10)

then (Prevost et al., 1999, page 277):

$$Cu_2S + O_2 \rightarrow 2Cu_\ell^0 + SO_2$$

in molten matte in tuyere 'blast'

(10.11).

(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 $\text{SiO}_2$ slag rather than the Mitsubishi and Outokumpu continuous converting's $\text{CaO}$ slag. This is because:

(a) Noranda's $\text{Cu}_2\text{S}$ layer tends to reduce magnetite by Reaction (10.7) so that magnetite solubility (in CaO-base slag) is not critical

(b) $\text{SiO}_2$ 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:

\[
\frac{\text{total } O_2 \text{ input rate}}{\text{matte feed rate}}.
\]

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:

\[
\frac{O_2 \text{ input rate}}{\text{concentrate feed rate}}
\]

(a) is set high enough to produce metallic copper rather than Cu$_2$S
(b) this setting inadvertently produces some Cu$_2$O in slag.

Noranda's slag is lowest in Cu$_2$O. This is because the Noranda furnace always contains a Cu$_2$S layer which partially reduces Cu$_2$O to metallic copper, Reaction (10.5).

Flash converting's Cu$_2$O-in-slag is highest because it deliberately avoids a Cu$_2$S layer to avoid slag foaming.

Mitsubishi converting's Cu$_2$O-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**


**References**


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\(_2\)O), or with S\(^2-\) ions (Cu\(_2\)S). Cu\(_2\)O becomes the dominant form of dissolved Cu at matte grades above 70\% Cu\(_2\)S (Nagamori, 1974; Barnett, 1979), due to the increased activity of Cu\(_2\)S in the matte. Higher Cu\(_2\)S activity pushes the reaction:

\[
\text{Cu}_2\text{S} + \text{FeO} \rightarrow \text{Cu}_2\text{O} + \text{FeS}
\]

(11.1)

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\(_2\)O.

Conversely, the dissolved Cu in smelting furnace slags is present mostly as Cu\(_2\)S. 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.:

\[
V = \frac{1}{18} g \frac{\rho_{\text{drop}} - \rho_{\text{slag}}}{\mu_{\text{slag}}} (\phi_{\text{drop}})^2
\]

(11.2)

In this expression \(V\) is the settling rate of the matte droplets (m/s), \(g\) the gravitational constant (9.8 m/s\(^2\)), \(\rho_{\text{drop}}\) matte density (3900–5200 kg/m\(^3\)), \(\rho_{\text{slag}}\) slag density (3300–3700 kg/m\(^3\)), \(\mu_{\text{slag}}\) slag viscosity (~0.1 kg/m·s) and \(\phi_{\text{drop}}\), 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 ~1 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 Fe\(_3\)O\(_4\) 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.

<table>
<thead>
<tr>
<th>Drop diameter (mm)</th>
<th>Settling velocity (m/s)</th>
<th>Time to settle through one meter of slag (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.55</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>0.049</td>
<td>20</td>
</tr>
<tr>
<td>1</td>
<td>0.0055</td>
<td>183</td>
</tr>
<tr>
<td>0.3</td>
<td>0.00049</td>
<td>2039 (0.57 hr)</td>
</tr>
<tr>
<td>0.1</td>
<td>0.000055</td>
<td>18349 (5.1 hr)</td>
</tr>
</tbody>
</table>

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):

\[
3\text{Fe}_3\text{O}_4 + \text{FeS} \rightarrow 10\text{FeO} + \text{SO}_2
\]

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; Imrīš 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$_2$O 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 Fe$_3$O$_4$(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 Fe$_3$O$_4$(s) to 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):

\[
C + \text{Cu}_2\text{O} \rightarrow \text{CO} + 2\text{Cu}^0 \tag{11.4}
\]
\[
C + \text{Cu}_2\text{O} + \text{FeS}_2 \rightarrow \text{Cu}_2\text{S} + \text{FeS} + \text{CO} \tag{11.5}
\]

Carbon additions also reduce solid magnetite in the slag to liquid FeO:

\[
C + \text{Fe}_3\text{O}_4(s) \rightarrow \text{CO} + 3\text{FeO} \tag{11.6}
\]

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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Caraiba Metais</th>
<th>Norddeutsche Affinerie</th>
<th>Nippon Mining</th>
<th>Sumitomo Toyo</th>
<th>LG Nikko</th>
<th>Mexicana de Cobre Mexico Furnace 1</th>
<th>Mexicana de Cobre Mexico Furnace 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Dias d'Avila</td>
<td>Hamburg</td>
<td>Saganoseki</td>
<td>Japan</td>
<td>Japan</td>
<td>Korea</td>
<td>Mexico</td>
</tr>
<tr>
<td></td>
<td>Brazil</td>
<td></td>
<td>Japan</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Slag details, tonnes/day smelting furnace slag</th>
<th>880 OK flash furnace</th>
<th>1600 OK flash furnace</th>
<th>1386 OK flash furnace</th>
<th>1212 OK flash furnace</th>
<th>609 OK flash furnace</th>
<th>900 OK flash furnace</th>
<th>740 Teniente furnace</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Cu converter slag</td>
<td>1.7</td>
<td>1-1.5</td>
<td>1-1.2</td>
<td>1.3</td>
<td>2</td>
<td>1.5 to 2.5</td>
<td>5</td>
</tr>
<tr>
<td>% Cu</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>260</td>
<td>113</td>
<td>184</td>
</tr>
<tr>
<td>Products</td>
<td>0.7</td>
<td>0.6-0.8</td>
<td>0.8</td>
<td>0.7</td>
<td>0.8</td>
<td>1.26</td>
<td>1.3</td>
</tr>
<tr>
<td>slag, % Cu</td>
<td>65-70</td>
<td>65-70</td>
<td>65.5</td>
<td>63</td>
<td>68-72</td>
<td>70.3</td>
<td>70.5</td>
</tr>
<tr>
<td>matte, % Cu</td>
<td>11</td>
<td>10.2</td>
<td>9</td>
<td>5.1 x 13</td>
<td>8.1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Furnace details</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>shape</td>
<td>circular</td>
<td>circular</td>
<td>circular</td>
<td>ellipse</td>
<td>circular</td>
<td>circular</td>
<td>circular</td>
</tr>
<tr>
<td>diameter, m</td>
<td>11</td>
<td>10.2</td>
<td>9</td>
<td>5.1 x 13</td>
<td>8.1</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>power rating, MW</td>
<td>2-4</td>
<td>2-3</td>
<td>0.7-1.1</td>
<td>1.85</td>
<td>2-3</td>
<td>1.5-4.5</td>
<td>1.5-4.5</td>
</tr>
<tr>
<td>electrodes</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>material</td>
<td>self baking</td>
<td>self baking</td>
<td>self baking</td>
<td>self baking</td>
<td>self baking</td>
<td>self baking</td>
<td>self baking</td>
</tr>
<tr>
<td>diameter, m</td>
<td>1</td>
<td>1</td>
<td>0.68</td>
<td>3 x 0.72; 2 x 0.55</td>
<td>0.8</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Operating details</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>slag residence time, hours</td>
<td>2-3</td>
<td>5</td>
<td>1.5-3.0</td>
<td>2</td>
<td>2-5</td>
<td>0.25-1</td>
<td>0.25-1</td>
</tr>
<tr>
<td>energy use, kWh/tonne of slag</td>
<td>70</td>
<td>40-50</td>
<td>15</td>
<td>16</td>
<td>50</td>
<td>57</td>
<td>69</td>
</tr>
<tr>
<td>reductant, kg/tonne of slag</td>
<td>coke, 8.3</td>
<td>coke, 4-5</td>
<td>coke, 15</td>
<td>coal, 2</td>
<td>12.5 coke</td>
<td>7.17 coke</td>
<td>7.32 coke</td>
</tr>
<tr>
<td>slag layer thickness, m</td>
<td>0.97-1.4</td>
<td>1.5-1.8</td>
<td>0.5-0.9</td>
<td>0.6</td>
<td>1-1.3</td>
<td>0.8-1.5</td>
<td>0.8-1.5</td>
</tr>
<tr>
<td>matte layer thickness, m</td>
<td>0-0.45</td>
<td>0-0.4</td>
<td>0.4-0.8</td>
<td>0.8</td>
<td>0-0.3</td>
<td>0-0.2</td>
<td>0-0.2</td>
</tr>
</tbody>
</table>
Table 11.3. Details of Teniente rotary hydrocarbon-fired slag settling furnace at Caletones, Chile, 2001.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Caletones, Chile</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Slag details</strong></td>
<td></td>
</tr>
<tr>
<td>smelting furnace slag, tonnes/day</td>
<td>3000</td>
</tr>
<tr>
<td>% Cu</td>
<td>6 to 8</td>
</tr>
<tr>
<td>converting furnace slag, tonnes/day</td>
<td>0</td>
</tr>
<tr>
<td>% Cu</td>
<td></td>
</tr>
<tr>
<td><strong>Products</strong></td>
<td></td>
</tr>
<tr>
<td>slag, % Cu</td>
<td>1</td>
</tr>
<tr>
<td>matte, % Cu</td>
<td>72</td>
</tr>
<tr>
<td>matte destination</td>
<td></td>
</tr>
<tr>
<td>Peirce-Smith converters</td>
<td></td>
</tr>
<tr>
<td>Teniente smelting furnace</td>
<td></td>
</tr>
<tr>
<td>% Cu recovery</td>
<td>85%</td>
</tr>
<tr>
<td><strong>Furnace details</strong></td>
<td></td>
</tr>
<tr>
<td>number of slag cleaning furnaces</td>
<td>4</td>
</tr>
<tr>
<td>shape</td>
<td>horizontal cylinder</td>
</tr>
<tr>
<td>diameter inside refractory, m</td>
<td>4.6</td>
</tr>
<tr>
<td>length inside refractory, m</td>
<td>$3 \times 10.7; 1 \times 12.7$</td>
</tr>
<tr>
<td>number of reducing tuyeres</td>
<td>4</td>
</tr>
<tr>
<td>tuyere diameter, cm</td>
<td>6.35</td>
</tr>
<tr>
<td><strong>Operating details</strong></td>
<td></td>
</tr>
<tr>
<td>slag residence time, hours</td>
<td>2</td>
</tr>
<tr>
<td>reductant</td>
<td></td>
</tr>
<tr>
<td>kg per tonne of slag</td>
<td>6</td>
</tr>
<tr>
<td>slag layer thickness, m</td>
<td>1.4</td>
</tr>
<tr>
<td>matte layer thickness, m</td>
<td>0.4</td>
</tr>
<tr>
<td>fuel</td>
<td></td>
</tr>
<tr>
<td>bunker C fuel oil</td>
<td></td>
</tr>
<tr>
<td>kg per tonne of slag</td>
<td>8.8</td>
</tr>
</tbody>
</table>

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):

$$\text{Cu}_2\text{O} + 3\text{FeO} \rightarrow 2\text{Cu}^\circ(\ell) + \text{Fe}_3\text{O}_4$$

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$^\circ$. The entrained droplets are recovered by settling in a slag-cleaning furnace, usually electric. The dissolved Cu$^\circ$ 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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Noranda, Quebec</th>
<th>Saganoseki, Japan</th>
<th>Toyo, Japan</th>
<th>PASAR, Philippines</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slag inputs, tonnes/day</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>smelting furnace slag</td>
<td>1700</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>%Cu</td>
<td>6 (average)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>converter slag</td>
<td>300</td>
<td>450</td>
<td>450</td>
<td>370</td>
</tr>
<tr>
<td>%Cu</td>
<td>8.33</td>
<td>6.5</td>
<td>0.5-0.6</td>
<td>10-15*</td>
</tr>
<tr>
<td>Products</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>slag concentrate, %Cu</td>
<td>42</td>
<td>21.8</td>
<td>28</td>
<td>29-33</td>
</tr>
<tr>
<td>slag tailings, %Cu</td>
<td>0.65</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu recovery, %</td>
<td>90-95</td>
<td>95</td>
<td>95</td>
<td>97-98</td>
</tr>
<tr>
<td>Operating details</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>solidification method</td>
<td>ladle cooling with or without water sprays</td>
<td>~150 kg ingots on moving slag conveyor</td>
<td>~150 kg ingots on moving slag conveyor</td>
<td></td>
</tr>
<tr>
<td>cooling description</td>
<td>cooled on slag conveyor</td>
<td>1 hour in air then immersion in H₂O</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crushing/grinding equipment</td>
<td>80% semi autogenous grinding, jaw crusher; cone crusher (twice); ball mill (twice)</td>
<td>gyratory crusher; cone crusher (twice); ball mill 90%-44 μm</td>
<td>jaw crusher; cone crusher; ball mills (primary and regrind)</td>
<td></td>
</tr>
<tr>
<td>particle size after grinding</td>
<td>78%-44 μm</td>
<td>40%-50%-44 μm</td>
<td>90%-44 μm</td>
<td>65%-75%-45 μm</td>
</tr>
<tr>
<td>Flotation machinery</td>
<td>mechanically agitated cells</td>
<td>mechanically agitated cells</td>
<td>mechanically agitated cells</td>
<td>mechanical agitator Agitair 48, Jameson cell (Fig. 3.12)**</td>
</tr>
<tr>
<td>flotation residence time</td>
<td>60 minutes</td>
<td></td>
<td>30 minutes (rougher+scavenger)</td>
<td></td>
</tr>
<tr>
<td>Flotation reagents</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>promoter</td>
<td>thionocarbamate,</td>
<td>Na isopropyl xanthate, UZ200</td>
<td>thionocarbamate,</td>
<td>a) Danafloat 245, Penfloat TM3</td>
</tr>
<tr>
<td>collector</td>
<td>SIPX</td>
<td></td>
<td>PAX</td>
<td>b) K amyl xanthate</td>
</tr>
<tr>
<td>frother</td>
<td>propylene glycol</td>
<td>pine oil, MF550</td>
<td>pine oil</td>
<td></td>
</tr>
<tr>
<td>CaO?</td>
<td>no</td>
<td>no</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH</td>
<td>8.9</td>
<td>7.8</td>
<td>7.8</td>
<td></td>
</tr>
<tr>
<td>Energy use kWh/tonne slag</td>
<td>32.5</td>
<td>58.4</td>
<td>64</td>
<td>8.5-9.5</td>
</tr>
</tbody>
</table>

*Non-magnetic 'white metal' (Cu,S) 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 reverts 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**


**References**


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 SO₂ 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 (Cu₂S) and bornite (Cu₅FeS₄) 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 (Czernicki 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:
Direct-To-Copper Flash Smelting

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:

\[
\begin{align*}
\text{Cu}_2\text{S}, \text{Cu}_5\text{FeS}_4 + \text{O}_2 + \text{SiO}_2 & \rightarrow \text{Cu}_\beta^\circ + \text{FeO}, \text{Fe}_3\text{O}_4, \text{SiO}_2 + \text{SO}_2 \\
\text{concentrate in oxygen flux} & \text{molten slag in offgas}
\end{align*}
\]

(12.1).

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:

\[
2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu}_\beta^\circ + \text{SO}_2
\]

(12.2)

\[
2\text{Fe}_3\text{O}_4 + \text{Cu}_2\text{S} \rightarrow 2\text{Cu}_\beta^\circ + 6\text{FeO} + \text{SO}_2
\]

(12.3)

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:

**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% SO₂, 1350°C.
ratio based on these measured Cu-in-slag and S-in-copper values.

An increasing % Cu-in-slag is reversed by decreasing the \( \frac{O_2 \text{- in - blast input rate}}{\text{concentrate input rate}} \) 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:

\[
\frac{O_2 \text{- in - blast input rate}}{\text{concentrate input rate}}
\]

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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>WMC Resources Olympic Dam, Australia</th>
<th>KGHM Polska Miedz Glogow Poland</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Startup date</strong></td>
<td>1999</td>
<td>1978</td>
</tr>
<tr>
<td><strong>Size, inside brick, m</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hearth: w x l x h</td>
<td>6.3 x 19.2 x 1.9</td>
<td>9.2 x 26.4 x 3.0</td>
</tr>
<tr>
<td>reaction shaft</td>
<td></td>
<td></td>
</tr>
<tr>
<td>diameter</td>
<td>4.8</td>
<td>7.4</td>
</tr>
<tr>
<td>height, above settler roof</td>
<td>5.8</td>
<td>8.3</td>
</tr>
<tr>
<td>gas uptake</td>
<td>3.7</td>
<td>6.7</td>
</tr>
<tr>
<td>height above settler roof</td>
<td>7.5</td>
<td>12.3</td>
</tr>
<tr>
<td>slag layer thickness, m</td>
<td>0-0.65</td>
<td>0.5</td>
</tr>
<tr>
<td>copper layer thickness, m</td>
<td>0.5-0.85</td>
<td>0.7</td>
</tr>
<tr>
<td>active slag tapholes</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>active copper tapholes</td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>concentrate burners</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>settler burners</td>
<td>2</td>
<td>normally none</td>
</tr>
<tr>
<td><strong>Feed details, tonnes/day</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>new concentrate (dry)</td>
<td>1200-1600: 41-56% Cu</td>
<td>2000 (28% Cu)</td>
</tr>
<tr>
<td>oxygen</td>
<td>90-450</td>
<td></td>
</tr>
<tr>
<td>silica flux</td>
<td>12-120 (95% SiO₂)</td>
<td>self-fluxing</td>
</tr>
<tr>
<td>recycle flash furnace dust</td>
<td>0-144</td>
<td>270</td>
</tr>
<tr>
<td>other</td>
<td>100 desulfurizing dust</td>
<td></td>
</tr>
<tr>
<td><strong>Blast details</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>blast temperature, °C</td>
<td>ambient</td>
<td>140</td>
</tr>
<tr>
<td>volume% O₂</td>
<td>50-90</td>
<td>75</td>
</tr>
<tr>
<td>flowrate, thousand Nm³/hour</td>
<td>22</td>
<td>32</td>
</tr>
<tr>
<td><strong>Production details</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copper production, tonnes/day</td>
<td>390-680</td>
<td>392</td>
</tr>
<tr>
<td>composition</td>
<td>99% Cu, 0.7 to 0.85% S, 0.04% S, 0.45% O, 0.007% Fe, 0.25% Pb</td>
<td></td>
</tr>
<tr>
<td>temperature, °C</td>
<td>1280</td>
<td>1280</td>
</tr>
<tr>
<td>slag production, tonnes/day</td>
<td>620-883</td>
<td>1050</td>
</tr>
<tr>
<td>mass% Cu</td>
<td>24</td>
<td>14</td>
</tr>
<tr>
<td>mass% SiO₂/mass%Fe</td>
<td>0.5</td>
<td>5.7*</td>
</tr>
<tr>
<td>temperature, °C</td>
<td>1320</td>
<td>1290</td>
</tr>
<tr>
<td>Cu-from-slag recovery method</td>
<td>electric furnace</td>
<td>electric furnace</td>
</tr>
<tr>
<td>offgas, thousand Nm³/hour</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>volume% SO₂, leaving furnace</td>
<td>19</td>
<td>15</td>
</tr>
<tr>
<td>temperature, °C</td>
<td>1320-1400</td>
<td>1320</td>
</tr>
<tr>
<td>dust production, tonnes/day</td>
<td>boiler 65, ESP 55</td>
<td>260</td>
</tr>
<tr>
<td><strong>Hydrocarbon fuel inputs, kg/hour</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>burnt in reaction shaft</td>
<td>oil, 0-200</td>
<td>oil, 300</td>
</tr>
<tr>
<td>burnt in settler burners</td>
<td>oil, 900-1200</td>
<td>0</td>
</tr>
</tbody>
</table>

*32% SiO₂; 5.6% Fe; 10% Al₂O₃; 13.4% CaO; 6.9% MgO; 13.7% Cu; 3% Pb
The temperatures of the products are controlled by adjusting the oxygen-enrichment level of the blast (as represented by the \( \frac{N_2/O_2}{\text{ratio}} \)) 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 \( O_2/\text{concentrate} \) 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:

\[
2Cu_2O + Cu_2S \rightarrow 6Cu^\circ + SO_2 \quad \text{(12.2)}
\]

\[
2CuO + Cu_2S \rightarrow 4Cu^\circ + SO_2 \quad \text{(12.4)}
\]

\[
2Fe_3O_4 + Cu_2S \rightarrow 2Cu^\circ + 6FeO + SO_2 \quad \text{(12.3)}
\]

all of which can produce \( SO_2 \) beneath the slag layer.

Foaming is particularly favored if the input \( O_2/\text{concentrate} \) 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 \( O_2/\text{concentrate} \) 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 Cu₂O. It arises because there is no permanent layer of Cu₂S in the furnace to reduce Cu₂O 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 (Czerniecki et al., 1999b). This coke reduces the oxidized Cu from the slag by reactions like:

\[ \text{Cu}_2\text{O} + \text{C} \rightarrow 2\text{Cu}^\circ + \text{CO} \quad (12.5) \]

\[ \text{CuO} + \text{C} \rightarrow \text{Cu}^\circ + \text{CO} \quad (12.6). \]

Magnetite (molten and solid) is also reduced:

\[ \text{Fe}_3\text{O}_4 + \text{C} \rightarrow 3\text{FeO} + \text{CO} \quad (12.7) \]

and some FeO is inadvertently reduced to Fe by the reaction:
FeO + C → Fe + CO \hspace{1cm} (12.8).

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/floatation 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$_2$S, Cu$_5$FeS$_4$ 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>
<thead>
<tr>
<th>Impurity</th>
<th>Olympic Dam ppm in copper</th>
<th>Glogow II ppm in copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>200-300</td>
<td>1500-3500</td>
</tr>
<tr>
<td>As</td>
<td>250-350</td>
<td>500-800</td>
</tr>
<tr>
<td>Au</td>
<td>10-20</td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td>100-150</td>
<td>10-30</td>
</tr>
<tr>
<td>Fe</td>
<td>20-200</td>
<td>200-400</td>
</tr>
<tr>
<td>Ni</td>
<td>20-40</td>
<td>500-1000</td>
</tr>
<tr>
<td>Pb</td>
<td>10-50</td>
<td>2000-3000</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>20-30</td>
</tr>
<tr>
<td>Sb</td>
<td>5-15</td>
<td>50-200</td>
</tr>
<tr>
<td>Se</td>
<td>150-350</td>
<td>100</td>
</tr>
<tr>
<td>Te</td>
<td>30-50</td>
<td></td>
</tr>
</tbody>
</table>

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:

\[
\frac{O_2 \text{- in - blast input rate}}{\text{concentrate input rate}}
\]

at the point where all the Fe and S in the input concentrate are oxidized. The ratio must be controlled precisely, otherwise Cu$_2$S or Cu$_2$O will also be produced. Avoidance of forming a molten Cu$_2$S layer in the furnace is particularly important. Reactions between Cu$_2$S 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**


**References**


CHAPTER 13

Mitsubishi Continuous Smelting/Converting

Chapter 12 indicates that single furnace coppermaking:

(a) successfully restricts SO₂ 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 (Cu₂S) and bornite (Cu₃FeS₄) concentrates rather than chalcopyrite (CuFeS₂) 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 CuFeS₂ concentrates
(b) elimination of Peirce-Smith converting with its SO₂ collection and air infiltration difficulties
(c) continuous production of high SO₂-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.
Air, oxygen, dry concentrates, flux, converter slag 'granules' and reverts

Recycle to smelting and/or converting furnaces

SO₂ offgas

Matte, Electrodes

Granulated electric furnace slag for sale

Granulated converter slag

Recycle to smelting and/or converting furnaces

Hazelett caster

Anodes

Electrorefinery

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, SiO₂ 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, CaCO₃ 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 SO₂. It produces two continuous strong SO₂ streams, which are combined to make excellent feed gas for sulfuric acid or liquid SO₂ 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% O₂) 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 (MgO-Cr₂O₃). 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% $SO_2$) 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 $SO_2$ 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% $O_2$), CaCO$_3$ flux and converter slag granules onto the surface of the matte. It also receives considerable copper scrap including scrap anodes.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Mitsubishi Materials Corp. Naoshima, Japan</th>
<th>PT Smelting Co. Gresik, Indonesia</th>
<th>LG Nikko Smelter Co. Onsan, Korea</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Furnace commissioning date</strong></td>
<td>1991</td>
<td>1998</td>
<td>1998</td>
</tr>
<tr>
<td><strong>Copper production rate, tonnes/day</strong></td>
<td>900 to 1000</td>
<td>~750</td>
<td>800</td>
</tr>
<tr>
<td><strong>Smelting furnace</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>shape</td>
<td>circular</td>
<td>circular</td>
<td>circular</td>
</tr>
<tr>
<td>diameter x height (inside brick), m</td>
<td>10 x 4</td>
<td>10.1 x 4</td>
<td>10 x 4</td>
</tr>
<tr>
<td>number of lances</td>
<td>9</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>outside pipe diameter, cm</td>
<td>8 x 10 cm, 2 x 9 cm</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>inside pipe diameter, cm</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>lance rotations per minute</td>
<td>7.7</td>
<td>6.5</td>
<td>7.8</td>
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<tr>
<td>slag layer thickness, m</td>
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<td>0.1</td>
<td>0.1</td>
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<td>liquids, offgas temperature, °C</td>
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<td>1240, 1240</td>
<td>1240, 1250</td>
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<td><strong>Electric slag cleaning furnace</strong></td>
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<td></td>
</tr>
<tr>
<td>power rating, kW</td>
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<td>2100 (No.1); 1500 (No.2)</td>
<td>3600</td>
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<td>elliptical</td>
<td>elliptical</td>
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<tr>
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<td>5.9 x 12.5 x 2.0</td>
<td>6.0 x 12.5 x 2.0</td>
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<td>electrodes</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>material</td>
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<tr>
<td>number</td>
<td>6</td>
<td>6</td>
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</tr>
<tr>
<td>diameter, m</td>
<td>0.4</td>
<td>0.4</td>
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</tr>
<tr>
<td>immersion in slag, m</td>
<td>0.5</td>
<td>0.2 to 0.3</td>
<td>0.5 to 0.6</td>
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<tr>
<td>voltage between electrodes, V</td>
<td>90 to 120</td>
<td>90 to 120</td>
<td>80 to 100</td>
</tr>
<tr>
<td>current between electrodes, kA</td>
<td>10.5 to 12.0</td>
<td>6.5 (No.1); 5.5 (No.2)</td>
<td>5.5 to 7.0</td>
</tr>
<tr>
<td>applied power, kW</td>
<td>2400</td>
<td>3000</td>
<td>1700</td>
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<td>slag layer thickness, m</td>
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<td>0.60</td>
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<td>matte layer thickness, m</td>
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<td>0.65</td>
<td>0.45</td>
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<tr>
<td>matte, slag, offgas temperatures, °C</td>
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<td>1 to 2</td>
<td>1 to 2</td>
</tr>
<tr>
<td>estimated slag residence time, hours</td>
<td>~1</td>
<td>1 to 2</td>
<td>1 to 2</td>
</tr>
<tr>
<td><strong>Converting furnace</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>shape</td>
<td>circular</td>
<td>circular</td>
<td>circular</td>
</tr>
<tr>
<td>diameter x height, m</td>
<td>8.0 x 3.6</td>
<td>9.0 x 3.7</td>
<td>8.1 x 3.6</td>
</tr>
<tr>
<td>number of lances</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>outside pipe diameter, cm</td>
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<td>10.9</td>
<td>8 x 10 cm, 2 x 8.2 cm</td>
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<td>5</td>
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<td>5</td>
</tr>
<tr>
<td>lance rotations per minute</td>
<td>7.7</td>
<td>6.5</td>
<td>7.8</td>
</tr>
<tr>
<td>slag layer thickness, m</td>
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<td>0.15</td>
<td>0.13</td>
</tr>
<tr>
<td>copper layer thickness, m</td>
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<td>1.1</td>
<td>0.96</td>
</tr>
<tr>
<td>copper, slag, offgas temperature, °C</td>
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<td>1220, 1240, 1230, 1250</td>
<td>1220, 1240, 1230, 1250</td>
</tr>
</tbody>
</table>
Table 13.2. Operating data for three Mitsubishi coppermaking systems, 2001.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Naoshima, Japan</th>
<th>Gresik, Indonesia</th>
<th>Onsan, Korea</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Smelting furnace</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Inputs, tonnes/day</strong></td>
<td>2300 (34% Cu)</td>
<td>2000 to 2300 (31.7% Cu)</td>
<td>2109 (33.2% Cu)</td>
</tr>
<tr>
<td>concentrate</td>
<td>340</td>
<td>300 to 400</td>
<td>386 (82% SiO₂)</td>
</tr>
<tr>
<td>silica flux</td>
<td>42</td>
<td>35</td>
<td>52</td>
</tr>
<tr>
<td>limestone flux</td>
<td>240</td>
<td>160 to 180</td>
<td>96</td>
</tr>
<tr>
<td>granulated converting furnace slag</td>
<td>67</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>smelting furnace dust</td>
<td>61</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>converting furnace dust</td>
<td>5 compressed</td>
<td>40 sludge from</td>
<td>14 reverts</td>
</tr>
<tr>
<td>other:</td>
<td>copper scrap</td>
<td>wastewater</td>
<td></td>
</tr>
<tr>
<td><strong>Blast</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume% O₂</td>
<td>56</td>
<td>50 to 55</td>
<td>45 to 55</td>
</tr>
<tr>
<td>input rate, Nm³/minute</td>
<td>540</td>
<td>600 to 650</td>
<td>600</td>
</tr>
<tr>
<td>oxygen, tonnes/day</td>
<td>500</td>
<td></td>
<td>450 (99% O₂)</td>
</tr>
<tr>
<td><strong>Hydrocarbon Fuel</strong> (coal, tonnes/day)</td>
<td>63</td>
<td>90</td>
<td>140</td>
</tr>
<tr>
<td><strong>Output offgas</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume% SO₂ (entering boiler)</td>
<td>34</td>
<td>30</td>
<td>31</td>
</tr>
<tr>
<td>flowrate, Nm³/minute</td>
<td>560</td>
<td>600 to 650</td>
<td>570</td>
</tr>
<tr>
<td>dust tonnes/day</td>
<td>67</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td><strong>Electric Slag Cleaning Furnace</strong></td>
<td>matte and slag from smelting furnace</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Inputs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>matte, tonnes/day</td>
<td>1400</td>
<td>1270</td>
<td>1018</td>
</tr>
<tr>
<td>matte %Cu</td>
<td>68</td>
<td>68</td>
<td>68.8</td>
</tr>
<tr>
<td>slag, tonnes/day</td>
<td>1300</td>
<td>1450</td>
<td>1331</td>
</tr>
<tr>
<td>slag %Cu</td>
<td>0.7</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>slag %SiO₂/%Fe</td>
<td>0.9</td>
<td>0.8</td>
<td>0.9</td>
</tr>
<tr>
<td>offgas, Nm³/minute (ppm SO₂)</td>
<td>500 (&lt;150 ppm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>kWh consumption/tonne of slag</td>
<td>42</td>
<td>55</td>
<td>30</td>
</tr>
<tr>
<td><strong>Converting Furnace (autothermal)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Inputs, tonnes/day</strong></td>
<td>1400</td>
<td>1270</td>
<td>1018</td>
</tr>
<tr>
<td>matte from electric furnace</td>
<td>50</td>
<td>30</td>
<td>69</td>
</tr>
<tr>
<td>limestone flux</td>
<td>360</td>
<td>160 to 180</td>
<td>246</td>
</tr>
<tr>
<td>granulated converting furnace slag</td>
<td>120</td>
<td>95 to 100</td>
<td>78</td>
</tr>
<tr>
<td>anode scrap copper</td>
<td>34</td>
<td>0</td>
<td>44</td>
</tr>
<tr>
<td>purchased scrap copper</td>
<td>490</td>
<td>460 to 470</td>
<td>430</td>
</tr>
<tr>
<td><strong>Blast</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>volume% O₂</td>
<td>35</td>
<td>25 to 28</td>
<td>32 to 35</td>
</tr>
<tr>
<td>input rate, Nm³/minute</td>
<td>490</td>
<td>460 to 470</td>
<td>430</td>
</tr>
<tr>
<td>oxygen, tonnes/day</td>
<td>180</td>
<td></td>
<td>133 (99% O₂)</td>
</tr>
<tr>
<td><strong>Outputs</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>copper, tonnes/day</td>
<td>900 to 1000</td>
<td>850 to 900</td>
<td>820</td>
</tr>
<tr>
<td>copper, %Cu</td>
<td>98.4</td>
<td>98.5</td>
<td>98.5</td>
</tr>
<tr>
<td>copper, %O</td>
<td>0.3</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>copper, %S</td>
<td>0.7</td>
<td>0.7</td>
<td>0.9</td>
</tr>
<tr>
<td>slag, tonnes/day</td>
<td>600</td>
<td>160 to 180</td>
<td>360</td>
</tr>
<tr>
<td>slag, %Cu</td>
<td>14</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>slag, mass% CaO/mass% Fe</td>
<td>0.4</td>
<td>0.4</td>
<td>0.34</td>
</tr>
<tr>
<td>offgas, Nm³/minute</td>
<td>480</td>
<td>450</td>
<td>410</td>
</tr>
<tr>
<td>volume% SO₂</td>
<td>31</td>
<td>25</td>
<td>24</td>
</tr>
<tr>
<td>dust, tonnes/day</td>
<td>61</td>
<td>60</td>
<td>60</td>
</tr>
</tbody>
</table>
It produces:

(a) molten copper, \( \sim 0.7\% \) S
(b) molten slag, 14% Cu
(c) \( \text{SO}_2 \) bearing offgas, 25-30 volume% \( \text{SO}_2 \).

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 \( \text{SO}_2 \) 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 \( \text{SiO}_2 \) based) slag (Yazawa et al., 1981; Goto and Hayashi, 1998). Early in the development of the process, it was found that blowing strong \( \text{O}_2 \) 'blast' onto the surface of \( \text{SiO}_2 \)-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 \( \text{O}_2 \) to form a liquid CaO-Cu\(_2\text{O}\)-Fe\(_0\) slag, Fig. 13.3. The slag typically contains:

- 12-16% Cu (\( \sim 60\% \) as \( \text{Cu}_2\text{O} \), balance Cu)
- 40-55% Fe (\( \sim 70\% \) as \( \text{Fe}^{+++} \), balance \( \text{Fe}^{++} \))
- 15-20% CaO.

Its viscosity is \( \sim 10^{-1} \) kg/m·s (Wright et al., 2000).

### 13.4.2 Converting furnace copper

Mitsubishi copper contains more S than Peirce-Smith converter copper, \( \sim 0.7\% \) vs. \( \sim 0.02\% \). 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 \( \text{O}_2 \), 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-FeOₙ 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:

(a) increased oxygen enrichment of the smelting and converting furnace blasts
(b) improvements in furnace refractories and water-cooling, which have enhanced reliability and extended furnace campaign life (Majumdar et al., 1997)
(c) better measurements of temperature and lance tip position plus improved computer control
(d) 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:

(a) increasing the lance diameter to reduce gas/solids velocity
(b) 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 $\sim 50^\circ$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, $SO_2$ 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, CaCO₃ flux and recycle converter slag granules through ten roof lances. The velocity of the gas/solid mix is typically 120 m/second. O₂ 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 O₂ 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 Cu₂S 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 O₂ under the lances to make FeO and molten copper by the reactions:

\[
\text{FeS} + \frac{3}{2}\text{O}_2 \rightarrow \text{FeO} + \text{SO}_2 \quad \text{in slag} \quad (13.1)
\]

\[
\text{Cu}_2\text{S} + \text{O}_2 \rightarrow 2\text{Cu}^\circ + \text{SO}_2 \quad (13.2).
\]

(c) the above mentioned excess O₂ leads to over-oxidation of Cu and FeO by the reactions:

\[
3\text{FeO} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4 \quad \text{in slag} \quad (13.3)
\]

\[
2\text{Cu} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cu}_2\text{O} \quad \text{in slag} \quad (13.4).
\]
(d) \( \text{Cu}_2\text{O}, \text{FeO} \) and \( \text{Fe}_3\text{O}_4 \) are slagged by the reactions:

\[
\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \\
\text{from lance}
\]

\[
\text{CaO} + \text{Cu}_2\text{O} + \text{FeO} + \text{Fe}_3\text{O}_4 \rightarrow \text{molten slag} \\
(\sim 15\% \text{CaO}, 15\% \text{Cu}, \ 15\% \text{Fe}^{++}, 35\% \text{Fe}^{+++})
\] (13.6)

This slag probably reacts with matte by reactions like:

\[
3\text{Fe}_3\text{O}_4 + \text{FeS} \rightarrow \text{10FeO} + \text{SO}_2 \\
in \text{slag} \quad \text{in matte} \quad (13.7)
\]

\[
2\text{Fe}_3\text{O}_4 + \text{Cu}_2\text{S} \rightarrow 2\text{Cu}^\circ + 6\text{FeO} + \text{SO}_2 \\
in \text{slag} \quad \text{in matte} \quad (13.8)
\]

\[
2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6\text{Cu}^\circ + \text{SO}_2 \\
in \text{slag} \quad \text{in matte} \quad (13.9)
\]

The relative importance of direct oxidation (by \( \text{O}_2 \)) 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:

(a) the amount of Cu lost in the discard slag from the electric furnace, Fig. 4.6
(b) the amount of granulated high-Cu slag which must be recycled back from the converting furnace to the smelting furnace
(c) 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.

<table>
<thead>
<tr>
<th>Process</th>
<th>% of impurity-in-feed reporting to anode copper</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>As</td>
</tr>
<tr>
<td>Naoshima Mitsubishi smelting/converting with complete dust recycle</td>
<td>21</td>
</tr>
<tr>
<td>Naoshima Mitsubishi smelting/converting, electrostatic precipitator dust not recycled</td>
<td>4</td>
</tr>
<tr>
<td>Timmins Mitsubishi smelting/converting, electrostatic precipitator dust sent to Zn plant</td>
<td>11</td>
</tr>
</tbody>
</table>

### 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$_3$O$_4$ and/or SiO$_2$.

Precipitation of Fe$_3$O$_4$ 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.

<table>
<thead>
<tr>
<th></th>
<th>minimum (°C)</th>
<th>maximum (°C)</th>
<th>optimum (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelting furnace – matte/slag outlet</td>
<td>1200</td>
<td>1240</td>
<td>1220</td>
</tr>
<tr>
<td>Electric slag cleaning furnace – slag outlet</td>
<td>1220</td>
<td>1260</td>
<td>1240</td>
</tr>
<tr>
<td>Converting furnace – slag outlet</td>
<td>1210</td>
<td>1250</td>
<td>1230</td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Information</th>
<th>Adjustable or Result</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Smelting furnace</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt temperature</td>
<td>Result</td>
<td>Continuous measurement by submerged K-type thermocouple at smelting furnace melt outlet.</td>
</tr>
<tr>
<td>Feedrate</td>
<td>Adjustable</td>
<td>Continuous monitoring of blended concentrate, silica, CaCO₃, coal, converter slag granules, Cu scrap and dust input rates.</td>
</tr>
<tr>
<td>Blowing rate</td>
<td>Adjustable</td>
<td>Continuous monitoring of oxygen and air input rates.</td>
</tr>
<tr>
<td>Matte composition</td>
<td>Result</td>
<td>Hourly analysis by X-ray fluorescence analyzer (Cu and Pb). Samples are taken at electric slag cleaning furnace outlet.</td>
</tr>
<tr>
<td>Slag composition</td>
<td>Result</td>
<td>Hourly analysis by X-ray fluorescence analyzer (Cu, Fe, SiO₂, CaO and Al₂O₃). Samples are taken at electric slag cleaning furnace outlet.</td>
</tr>
<tr>
<td><strong>Converting furnace</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slag temperature</td>
<td>Result</td>
<td>Hourly manual measurement by disposable K-type thermocouples.</td>
</tr>
<tr>
<td>Copper temperature</td>
<td>Result</td>
<td>Automatic measurement by submerged glass fiber optical pyrometer – every 15 minutes.</td>
</tr>
<tr>
<td>Feedrate</td>
<td>Adjustable</td>
<td>Continuous monitoring of CaCO₃, recycled converter slag granules and Cu scrap input rates.</td>
</tr>
<tr>
<td>Matte flowrate</td>
<td>Result</td>
<td>Continuous measurement by infrared scanner at electric slag cleaning furnace matte siphon.</td>
</tr>
<tr>
<td>Blowing rate</td>
<td>Adjustable</td>
<td>Continuous measurement of oxygen and air input rates.</td>
</tr>
<tr>
<td>Slag composition</td>
<td>Result</td>
<td>Hourly sample and analysis (Cu, SiO₂, CaO, S and Pb) by X-ray fluorescence analyzer.</td>
</tr>
</tbody>
</table>

Table 13.6. Qualitative process parameters in Mitsubishi smelting/converting.

<table>
<thead>
<tr>
<th>Information</th>
<th>Adjustable or Result</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Smelting furnace</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Melt flowrate and melt surface condition</td>
<td>Result</td>
<td>Visual inspection by remote camera and at the furnace.</td>
</tr>
<tr>
<td><strong>Converting furnace</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Slag flowrate and slag surface condition</td>
<td>Result</td>
<td>Visual inspection by remote camera and at the furnace.</td>
</tr>
<tr>
<td>Matte inflow rate</td>
<td>Result</td>
<td>Visual inspection by remote camera and at the furnace.</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Operation parameter</th>
<th>Corrective action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smelting furnace melt temperature</td>
<td>decrease/increase recycle converter slag granule feedrate</td>
</tr>
<tr>
<td>Converting furnace slag temperature</td>
<td>decrease/increase recycle converter slag granule feedrate</td>
</tr>
<tr>
<td>Smelting furnace matte grade</td>
<td>decrease/increase concentrate feedrate</td>
</tr>
<tr>
<td></td>
<td>decrease/increase coal feedrate</td>
</tr>
<tr>
<td></td>
<td>increase/decrease oxygen feedrate</td>
</tr>
<tr>
<td></td>
<td>increase/decrease air flowrate</td>
</tr>
<tr>
<td>%SiO₂ in electric slag cleaning</td>
<td>increase/decrease SiO₂ feedrate to smelting furnace</td>
</tr>
<tr>
<td>furnace slag</td>
<td></td>
</tr>
<tr>
<td>%CaO in electric slag cleaning</td>
<td>increase/decrease CaCO₃ feedrate to smelting and</td>
</tr>
<tr>
<td>furnace slag</td>
<td>converting furnace</td>
</tr>
<tr>
<td>%Cu in converting furnace slag</td>
<td>increase/decrease oxygen flowrate</td>
</tr>
<tr>
<td></td>
<td>increase/decrease air flowrate</td>
</tr>
<tr>
<td></td>
<td>decrease/increase concentrate feedrate</td>
</tr>
<tr>
<td>%CaO in converting furnace slag</td>
<td>increase/decrease CaCO₃ feedrate</td>
</tr>
</tbody>
</table>

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


**References**


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 \( \text{SO}_2 \) gas from smelting and converting.

\( \text{SO}_2 \) is harmful to fauna and flora. It must be prevented from reaching the environment. Regulations for ground level \( \text{SO}_2 \) concentrations around copper smelters are presented in Table 14.1. Other regulations such as maximum total \( \text{SO}_2 \) emission (tonnes per year), percent \( \text{SO}_2 \) capture and \( \text{SO}_2 \)-in-gas concentration at point-of-emission also apply in certain locations.

In the past, \( \text{SO}_2 \) 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 \( \text{SO}_2 \). It is almost always made into sulfuric acid, occasionally liquid \( \text{SO}_2 \) 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. \( \text{SO}_2 \) strengths in smelting furnace gases vary from about 70 volume% in Inco flash furnace gases to 1 volume% in reverberatory furnace gases. The \( \text{SO}_2 \) 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.

<table>
<thead>
<tr>
<th>Country</th>
<th>Time period</th>
<th>Maximum SO₂ + SO₃ concentration (parts per million)</th>
</tr>
</thead>
<tbody>
<tr>
<td>U.S.A. (EPA, 2001)</td>
<td>Yearly mean</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>daily mean</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>3-hour mean</td>
<td>0.5</td>
</tr>
<tr>
<td>Ontario, Canada</td>
<td>Yearly mean</td>
<td>0.02</td>
</tr>
<tr>
<td>(St. Eloi et al., 1989)</td>
<td>daily mean</td>
<td>0.10 recommendation</td>
</tr>
<tr>
<td></td>
<td>1-hour mean</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>0.5 hour average</td>
<td>0.3 (regulation)</td>
</tr>
<tr>
<td>Japan (Inami et al., 1990)</td>
<td>Daily average</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>hourly average</td>
<td>0.1</td>
</tr>
</tbody>
</table>

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 offgases. 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.

<table>
<thead>
<tr>
<th>Furnace</th>
<th>SO$_2$ concentration (volume%)</th>
<th>Temperature (°C)</th>
<th>Dust loading (kg/Nm$^3$)</th>
<th>Destination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inco flash furnace</td>
<td>50-75</td>
<td>1270-1300</td>
<td>0.2-0.25</td>
<td>H$_2$SO$_4$ occasionally liquid SO$_2$ plant</td>
</tr>
<tr>
<td>Outokumpu flash furnace</td>
<td>25-50</td>
<td>1270-1350</td>
<td>0.1-0.25</td>
<td>H$_2$SO$_4$ plant, occasionally liquid SO$_2$ plant</td>
</tr>
<tr>
<td>Outokumpu flash converter</td>
<td>35-40</td>
<td>1290</td>
<td>0.2</td>
<td>H$_2$SO$_4$ plant</td>
</tr>
<tr>
<td>Outokumpu direct-to-copper</td>
<td>43</td>
<td>1320-1400</td>
<td>0.2</td>
<td>H$_2$SO$_4$ plant</td>
</tr>
<tr>
<td>Mitsubishi smelting furnace</td>
<td>30-35</td>
<td>1240-1250</td>
<td>0.07</td>
<td>H$_2$SO$_4$, occasionally liquid SO$_2$ plant</td>
</tr>
<tr>
<td>Mitsubishi converting furnace</td>
<td>25-30</td>
<td>1230-1250</td>
<td>0.1</td>
<td>H$_2$SO$_4$, occasionally liquid SO$_2$ plant</td>
</tr>
<tr>
<td>Noranda process</td>
<td>15-25</td>
<td>1200-1240</td>
<td>0.015-0.02</td>
<td>H$_2$SO$_4$ plant</td>
</tr>
<tr>
<td>Teniente furnace</td>
<td>12-25</td>
<td>1220-1250</td>
<td></td>
<td>H$_2$SO$_4$ plant</td>
</tr>
<tr>
<td>Isasmelt furnace</td>
<td>20-25</td>
<td>1150-1220</td>
<td>~0.01</td>
<td>H$_2$SO$_4$ plant</td>
</tr>
<tr>
<td>Electric furnace</td>
<td>2-5</td>
<td>400-800</td>
<td>~0.03</td>
<td>H$_2$SO$_4$ or liquid SO$_2$ plant or vented to atmosphere</td>
</tr>
<tr>
<td>Reverberatory furnace</td>
<td>1</td>
<td>1250</td>
<td>~0.03</td>
<td>Vented to atmosphere (made into gypsum in one plant, scrubbed with flotation tailings in another)</td>
</tr>
<tr>
<td>Peirce-Smith converter</td>
<td>8-15</td>
<td>1200</td>
<td></td>
<td>H$_2$SO$_4$ plant or vented to atmosphere</td>
</tr>
<tr>
<td>Hoboken converter</td>
<td>12</td>
<td>1200</td>
<td></td>
<td>H$_2$SO$_4$ plant</td>
</tr>
<tr>
<td>Electric slag cleaning furnaces</td>
<td>0.1</td>
<td>800</td>
<td></td>
<td>Vented to atmosphere (occasionally scrubbed with basic solution)</td>
</tr>
<tr>
<td>Anode furnaces</td>
<td>&lt;0.1</td>
<td>1000</td>
<td></td>
<td>Vented to atmosphere (occasionally scrubbed with basic solution)</td>
</tr>
<tr>
<td>Gas collection hoods around the smelter</td>
<td>&lt;0.1</td>
<td>50</td>
<td></td>
<td>Vented to atmosphere (occasionally scrubbed with basic solution)</td>
</tr>
</tbody>
</table>
Table 14.3. Distribution of sulfur in four copper smelters.

<table>
<thead>
<tr>
<th></th>
<th>Toyo, Japan (Inami et al., 1990)</th>
<th>Timmins, Canada (Newman et al., 1993)</th>
<th>Tamano, Japan (Shibata and Oda, 1990)</th>
<th>Norddeutsche, Germany (Willbrandt, 1993)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outokumpu flash furnace/smelting/ converting</td>
<td>Peirce-Smith converters</td>
<td>Mitsubishi converters</td>
<td>Outokumpu flash furnace</td>
<td>Outokumpu flash furnace</td>
</tr>
<tr>
<td><strong>Percent of incoming S in:</strong></td>
<td><strong>96.6</strong></td>
<td><strong>95</strong></td>
<td><strong>96</strong></td>
<td><strong>96.2</strong></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gypsum</td>
<td>2.7</td>
<td></td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Slag</td>
<td>1.2</td>
<td>1.4</td>
<td>1.2</td>
<td>1.2</td>
</tr>
<tr>
<td>Dust</td>
<td>0.2</td>
<td>2.0</td>
<td>(to Zn plant)</td>
<td></td>
</tr>
<tr>
<td>Other</td>
<td></td>
<td></td>
<td></td>
<td>1.0</td>
</tr>
<tr>
<td>Neutralized liquid effluent</td>
<td>0.3</td>
<td>0.6</td>
<td>1.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Gaseous emissions</td>
<td>0.2 (0.6*; 0.4')</td>
<td>1.0</td>
<td>0.1</td>
<td>0.8</td>
</tr>
</tbody>
</table>

* 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.
Capture and Fixation of Sulfur

Cool gases to 300°C for entry into electrostatic precipitators. Recover heat in waste heat boilers. Drop out dust.

Clean gas, recover dust.

Absorb Cl₂, F₂ and SO₃. Remove dust. Precipitate and absorb vapors, e.g. As₂S₃. Condense water vapor.

Remove acid mist and final traces of dust.

Remove moisture to avoid H₂SO₄ condensation and corrosion in downstream equipment.

Prepare for SO₃ absorption

Create H₂SO₄ by absorbing SO₃ into ~98% H₂SO₄·2%H₂O solution

Tail gas (~80°C) to stack or scrubbing with basic solution

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
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/Nm$^3$ of gas) to avoid fouling of downstream acid plant catalyst
(b) absorbs Cl$_2$, F$_2$, SO$_3$ and vapor impurities (e.g. As$_2$S$_3$).
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 SO₃ 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 H₂SO₄ content of the cooling water below about 10% - to avoid corrosion. The quantity of bleed depends on the amount of SO₃ in the offgas as it enters the water-quench system.

Several smelters have found that SO₃ formation is inhibited by recycling some cooled offgas to the entrance of the waste heat boiler. This has the effect of slowing SO₂ → SO₃ 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 H₂O(g) removal (drying). It is done to prevent unintentional H₂SO₄ formation and corrosion in downstream ducts, heat exchangers and catalyst beds.

The H₂O is removed by contacting it with 93% H₂SO₄-7% H₂O (occasionally 96 or 98%) acid. H₂O reacts strongly with H₂SO₄ molecules to form hydrated acid molecules.
Capture and Fixation of Sulfur

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:

<table>
<thead>
<tr>
<th>Item</th>
<th>Concentration, kg/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂SO₄</td>
<td>80 - 150</td>
</tr>
<tr>
<td>Cu</td>
<td>0.5 - 1</td>
</tr>
<tr>
<td>As</td>
<td>2 - 5</td>
</tr>
<tr>
<td>Zn</td>
<td>0.5 - 2</td>
</tr>
<tr>
<td>Cl</td>
<td>1 - 5</td>
</tr>
</tbody>
</table>

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.
Slightly diluted 93% H₂SO₄ to strong acid circuit and/or market

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 $\text{SO}_2$ to $\text{SO}_3$

The $\text{SO}_2$ in the offgas is oxidized to $\text{SO}_3$ in preparation for absorption in the water component of 98% $\text{H}_2\text{SO}_4$-2%H$_2$O acid. The oxidation reaction is:

$$\text{SO}_2 (g) + \frac{1}{2} \text{O}_2 (g) \rightarrow \text{SO}_3 (g) \quad (14.1)$$

This reaction is very slow without a catalyst so the offgas is always passed through $\text{V}_2\text{O}_5$-$\text{K}_2\text{SO}_4$ catalyst 'beds'. The volumetric $\text{O}_2$/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 $\text{V}_2\text{O}_5$-$\text{K}_2\text{SO}_4$ based catalyst contains the following (mass%):

- 5 - 10% $\text{V}_2\text{O}_5$
- 10 - 20% $\text{K}_2\text{SO}_4$
- 1 - 5% $\text{Na}_2\text{SO}_4$
- 55 - 70% $\text{SiO}_2$

It may also contain 5-15% cesium sulfate ($\text{Cs}_2\text{SO}_4$) substituted for $\text{K}_2\text{SO}_4$.

The active components of the catalyst are $\text{V}_2\text{O}_5$, $\text{K}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4$ and $\text{Cs}_2\text{SO}_4$ (if present). The inactive material is $\text{SiO}_2$, which acts as a support for the active components.

$\text{V}_2\text{O}_5$-$\text{K}_2\text{SO}_4$ catalyst is supported liquid phase catalyst (Livbjerg, et al., 1978). At the catalyst operation temperature, ~400°C, the active catalyst components ($\text{V}_2\text{O}_5$, $\text{K}_2\text{SO}_4$, $\text{Na}_2\text{SO}_4$, $\text{Cs}_2\text{SO}_4$) exist as a film of molten salt solution on the solid inactive $\text{SiO}_2$ 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 $\text{V}^{5+}$ to $\text{V}^{4+}$ and
formation of SO$_3$ from SO$_2$ and O$^{2-}$ ions, i.e.:

$$\text{SO}_2 + 2V^{5+} + O^{2-} \rightarrow \text{SO}_3 + 2V^{4+} \quad (14.2)$$

and:

(b) absorption of oxygen, re-oxidation of the vanadium ions and formation of O$^{2-}$ ions

$$\frac{1}{2}O_2 + 2V^{4+} \rightarrow 2V^{5+} + O^{2-} \quad (14.3).$$

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$_2$O$_5$-K$_2$SO$_4$ catalysts*

Catalyst is manufactured by mixing together the active components and substrate to form a paste which is extruded and baked at ~530°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 SO$_2$ → SO$_3$ conversion reaction begins with V$_2$O$_5$-K$_2$SO$_4$ catalyst is ~360°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 SO$_2$ → 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$_2$O$_5$-K$_2$SO$_4$ 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$_2$ → SO$_3$ conversion rate.

**Cs-promoted catalyst**

Substituting Cs$_2$SO$_4$ for K$_2$SO$_4$ 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$_2$ → 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% $\text{SO}_2$, 12 volume% $\text{O}_2$ and 76 volume% $\text{N}_2$ at a total pressure of 1.2 atmospheres. The curve shows that higher $\text{SO}_2$ conversions are possible at lower temperatures.

14.5.2 Absorption of $\text{SO}_3$ into $\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ solution

The $\text{SO}_3$ formed by the above-described catalytic oxidation of $\text{SO}_2$ is absorbed into 98% $\text{H}_2\text{SO}_4$-2% $\text{H}_2\text{O}$ acid. The process occurs in a packed tower of similar design to a drying tower, Fig. 14.4. In absorption, $\text{SO}_3$ laden gas and sulfuric acid flow counter currently. The overall absorption reaction is:

\[
\text{SO}_3 (g) + \text{H}_2\text{O} (\ell) \rightarrow \text{H}_2\text{SO}_4 (\ell)
\]

(14.4)

It is not possible to manufacture sulfuric acid by absorbing sulfur trioxide directly into water. Sulfur trioxide reacts with water vapor to form $\text{H}_2\text{SO}_4$ 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% $\text{H}_2\text{SO}_4$ is low ($< 2 \times 10^{-5}$ atmospheres at 80°C), avoiding this water vapor problem. The most likely absorption reactions are:

\[
\text{SO}_3 (g) + \text{H}_2\text{SO}_4 (\ell) \rightarrow \text{H}_2\text{S}_2\text{O}_7 (\ell)
\]

(14.5)

followed by:
\[
\text{H}_2\text{O}(\ell) + \text{H}_2\text{S}_2\text{O}_7(\ell) \rightarrow 2\text{H}_2\text{SO}_4(\ell) \tag{14.6}
\]

Some \( \text{SO}_3 \) is undoubtedly absorbed directly by water according to Equation 14.4. Because of the preponderance of \( \text{H}_2\text{SO}_4 \) molecules in the absorbent, however, absorption by Equations 14.5 and 14.6 probably predominates. \( \text{SO}_3 \) 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% \( \text{H}_2\text{SO}_4 \). This is the composition at which the sum of the equilibrium partial pressures of \( \text{H}_2\text{O} \), \( \text{SO}_3 \) and \( \text{H}_2\text{SO}_4 \) over sulfuric acid is at its minimum.

Below this optimum, \( \text{H}_2\text{O} \) vapor pressure increases and sulfuric acid mist may form by the reaction of \( \text{H}_2\text{O}(g) \) and \( \text{SO}_3 \). This mist is difficult to coalesce so it tends to escape the acid plant into the environment. Above this optimum, \( \text{SO}_3 \) and \( \text{H}_2\text{SO}_4 \) 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 \( \text{SO}_3 \) 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 \( \text{SO}_3 \) 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 \( \text{SO}_3 \) absorbed into 98% \( \text{H}_2\text{SO}_4 \)-2% \( \text{H}_2\text{O} \) 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 \( \text{SO}_2 \) entering the acid plant. Single absorption acid plants convert \( \text{SO}_2 \) to \( \text{SO}_3 \) in three or four catalyst beds followed by single absorption of \( \text{SO}_3 \), Table 14.5. Their conversion of \( \text{SO}_2 \) to \( \text{SO}_3 \) 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.

![Catalyst bed showing steel support, catalyst and silica rock.](image)

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 \( \text{SO}_2 \) to \( \text{SO}_3 \) conversion reaction paths

Figs. 14.8 and 14.9 show the schematic steady state %\( \text{SO}_2 \) conversion/temperature reaction path for a 12 volume% \( \text{SO}_2 \), 12 volume% \( \text{O}_2 \) 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. \( \text{SO}_2 \) is oxidized to \( \text{SO}_3 \) in the bed – heating the gas to about 630°C. About 64% of the input \( \text{SO}_2 \) is converted to \( \text{SO}_3 \).

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

<table>
<thead>
<tr>
<th>Smelter</th>
<th>WMC, Olympic Dam, Australia</th>
<th>Norddeutsche Affinerie, Hamburg (lines 1 and 2)</th>
<th>Norddeutsche Affinerie, Hamburg (line 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Startup date</td>
<td>1998</td>
<td>1972</td>
<td>1991</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Lurgi wet gas/Monsanto</td>
<td>Lurgi</td>
<td>Lurgi</td>
</tr>
<tr>
<td>Gas source</td>
<td>Strong acid Direct-to-copper flash furnace and anode furnace oxidation gases</td>
<td>Outokumpu flash furnace and Peirce-Smith converters</td>
<td>Outokumpu flash furnace and Peirce-Smith converters</td>
</tr>
<tr>
<td>Single or double absorption number of catalyst beds</td>
<td>double</td>
<td>double</td>
<td>double</td>
</tr>
<tr>
<td>intermediate SO₃ absorption after bed</td>
<td>4</td>
<td>4</td>
<td>5</td>
</tr>
<tr>
<td>Converter diameter, m</td>
<td>10</td>
<td>8</td>
<td>8.5</td>
</tr>
<tr>
<td>Thickness of catalyst beds, m</td>
<td>0.76</td>
<td>0.99</td>
<td>0.8</td>
</tr>
<tr>
<td>bed 1</td>
<td>0.81</td>
<td>0.94</td>
<td>0.87</td>
</tr>
<tr>
<td>bed 2</td>
<td>0.99</td>
<td>0.94</td>
<td>0.91</td>
</tr>
<tr>
<td>bed 3</td>
<td>1.12</td>
<td>0.94</td>
<td>0.87</td>
</tr>
<tr>
<td>bed 4</td>
<td></td>
<td></td>
<td>1.02</td>
</tr>
<tr>
<td>bed 5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Catalyst</td>
<td>Monsanto LP 120</td>
<td>BASF+0.19 m Cs ring type catalysts</td>
<td>BASF+0.19 m Cs ring type catalysts</td>
</tr>
<tr>
<td>bed 1</td>
<td></td>
<td>BASF ring type</td>
<td>BASF ring type</td>
</tr>
<tr>
<td>bed 2</td>
<td></td>
<td>BASF ring type</td>
<td>BASF ring type</td>
</tr>
<tr>
<td>bed 3</td>
<td></td>
<td>BASF ring type</td>
<td>BASF ring type</td>
</tr>
<tr>
<td>bed 4</td>
<td></td>
<td>BASF Cs ring type</td>
<td>BASF ring type</td>
</tr>
<tr>
<td>bed 5</td>
<td></td>
<td>BASF ring type</td>
<td></td>
</tr>
<tr>
<td>Gas into converter</td>
<td>2166</td>
<td>1830 (maximum)</td>
<td></td>
</tr>
<tr>
<td>flowrate, Nm³/minute</td>
<td>volume% SO₂</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>volume% O₂</td>
<td>&gt;12</td>
<td></td>
<td>&gt;12.1</td>
</tr>
<tr>
<td>H₂SO₄ production rate</td>
<td>900-1400</td>
<td>2500</td>
<td></td>
</tr>
<tr>
<td>tonnes 100% H₂SO₄ day</td>
<td>98.5</td>
<td>94, 96, 98 and 20% SO₃ oleum</td>
<td></td>
</tr>
<tr>
<td>Products, mass% H₂SO₄</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Capture and Fixation of Sulfur

acid manufacturing plants, 2001. Smelting and continuous con-
air through filters just before the acid plant’s drying tower.

<table>
<thead>
<tr>
<th>PT Smelting Co.</th>
<th>Sumitomo Mining Co.</th>
<th>Mexicana de Cobre, Nacozeri</th>
<th>Mexicana de Cobre, Nacozeri</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gresik, Indonesia</td>
<td>Toyo, Japan</td>
<td>Mexico (Plant 1)</td>
<td>Mexico (Plant 2)</td>
</tr>
<tr>
<td>Lurgi</td>
<td>Sumitomo Chemical Engineering</td>
<td>Monsanto</td>
<td>Monsanto</td>
</tr>
<tr>
<td>Mitsubishi process and anode furnace (oxidation stage only)</td>
<td>Outokumpu flash furnace &amp; Peirce-Smith converters</td>
<td>Outokumpu flash + Teniente furnaces + Peirce-Smith converters</td>
<td>Outokumpu flash + Teniente furnaces + Peirce-Smith converters</td>
</tr>
<tr>
<td>double</td>
<td>double</td>
<td>double</td>
<td>double</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>4</td>
<td>3rd</td>
</tr>
<tr>
<td>12</td>
<td>12.5</td>
<td>12.5</td>
<td>12.3</td>
</tr>
<tr>
<td>0.715</td>
<td>0.35</td>
<td>0.824</td>
<td>0.715</td>
</tr>
<tr>
<td>0.67</td>
<td>0.23</td>
<td>0.938</td>
<td>0.757</td>
</tr>
<tr>
<td>0.75</td>
<td>0.67</td>
<td>0.946</td>
<td>0.799</td>
</tr>
<tr>
<td>1.185</td>
<td>1.04</td>
<td>0.946</td>
<td>0.952</td>
</tr>
</tbody>
</table>

VK38&59 daisy type catalyst
Nihonshokubai 7S
split: Cs-K-V₂O₅ input side, K-V₂O₅ output side

VK38 daisy type
Monsanto T-516
K-V₂O₅

VK48 daisy type
Topsoe VK38
split: Cs-K-V₂O₅ input side, K-V₂O₅ output side
K-V₂O₅

VK38 daisy type
Nihonshokubai R10
split: Cs-K-V₂O₅ input side, K-V₂O₅ output side

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>
<thead>
<tr>
<th>Smelter</th>
<th>Mt. Isa, Queensland Australia</th>
<th>Altonorte, Chile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start-up date</td>
<td>1999</td>
<td>2003 (design data)</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>Lurgi</td>
<td>Lurgi</td>
</tr>
<tr>
<td>Gas source</td>
<td>Isasmelt, 4 Peirce-Smith converters and sulfur burner</td>
<td>Noranda smelting furnace</td>
</tr>
<tr>
<td>Single or double absorption</td>
<td>single</td>
<td>single</td>
</tr>
<tr>
<td>number of catalyst beds</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>intermediate SO$_3$ absorption</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>after ? bed</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Converter diameter, m</td>
<td>15</td>
<td>11.7 with 4 m diameter internal heat exchanger</td>
</tr>
<tr>
<td>First pass</td>
<td>15</td>
<td>same</td>
</tr>
<tr>
<td>Others</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>Thickness of catalyst beds, m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bed 1</td>
<td>0.68</td>
<td>0.67</td>
</tr>
<tr>
<td>bed 2</td>
<td>0.8</td>
<td>0.87</td>
</tr>
<tr>
<td>bed 3</td>
<td>0.95</td>
<td>0.98</td>
</tr>
<tr>
<td>bed 4</td>
<td>no</td>
<td>1.42</td>
</tr>
<tr>
<td>Catalyst type</td>
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<td>BASF 04-110 Low ignition</td>
</tr>
<tr>
<td>bed 1</td>
<td>K-V$_2$O$_5$</td>
<td>BASF 04-111 V$_2$O$_5$</td>
</tr>
<tr>
<td>bed 2</td>
<td>K-V$_2$O$_5$</td>
<td>BASF 04-111 V$_2$O$_5$</td>
</tr>
<tr>
<td>bed 3</td>
<td>Cs-K-V$_2$O$_5$</td>
<td>BASF 04-111 V$_2$O$_5$</td>
</tr>
<tr>
<td>bed 4</td>
<td></td>
<td>BASF 04-111 V$_2$O$_5$</td>
</tr>
<tr>
<td>Gas into converter</td>
<td>6333</td>
<td>2917</td>
</tr>
<tr>
<td>flowrate, Nm$^3$/minute</td>
<td>11.2 maximum</td>
<td>12</td>
</tr>
<tr>
<td>volume% SO$_2$</td>
<td>10.6 normal operating</td>
<td>not measured</td>
</tr>
<tr>
<td>volume% O$_2$</td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>H$_2$SO$_4$ production rate</td>
<td>3300</td>
<td>2290 (capacity)</td>
</tr>
<tr>
<td>tonnes 100% H$_2$SO$_4$/day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Products, mass% H$_2$SO$_4$</td>
<td>98.5</td>
<td>96 to 98.5</td>
</tr>
</tbody>
</table>
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 ~200°C and sent to the intermediate absorption tower where virtually all (99.99%) of its SO$_3$ is absorbed into 98% H$_2$SO$_4$-H$_2$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 ~200°C and sent to the final SO$_3$ absorption tower.

Overall conversion of SO$_2$ is approximately:

$$\frac{[12\%\text{SO}_2\text{ (in initial gas)} - 0.025\%\text{SO}_2\text{ (in final gas)}]}{12\%\text{SO}_2\text{ (in initial gas)}} \times 100 = 99.8\%.$$
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.

(a) Conversion to $\text{SO}_3$ is maximized by a low conversion temperature, consistent with meeting the minimum continuous operating temperature requirement of the catalyst.

(b) 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 $\text{SO}_2$ concentration in the gas because $\text{SO}_2 \rightarrow \text{SO}_3$ conversion energy release has to heat less $\text{N}_2$. Cs catalyst is expensive, so it is only used when low temperature catalysis is clearly advantageous.

(c) Conversion of $\text{SO}_2$ to $\text{SO}_3$ after intermediate absorption is very efficient, Fig. 14.9. This is because (i) the gas entering the catalyst contains no $\text{SO}_3$ (driving Reaction (14.1) to the right) and because (ii) the temperature of the gas rises only slightly due to the small amount of $\text{SO}_2$ being oxidized to $\text{SO}_3$.

(d) Maximum cooling of the gases is required for the gases being sent to $\text{SO}_3$
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 SO₃ twice: after partial \( \text{SO}_2 \to \text{SO}_3 \) 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% H₂SO₄-2% H₂O acid into which rising SO₃ 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% H₂SO₄ 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% H₂SO₄ 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).

<table>
<thead>
<tr>
<th>Tower</th>
<th>Sulfuric acid irrigation rate (m³/tonne of 100%H₂SO₄ produced)</th>
<th>Sulfuric acid irrigation density (m³/min per m² of tower cross section)</th>
<th>Sulfuric acid temperature (°C) inlet / outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying tower</td>
<td>0.005</td>
<td>0.2 - 0.4</td>
<td>45 / 60</td>
</tr>
<tr>
<td>Intermediate absorption tower</td>
<td>0.01</td>
<td>0.6 - 0.8</td>
<td>80 / 110</td>
</tr>
<tr>
<td>Final absorption tower</td>
<td>0.005</td>
<td>0.4</td>
<td>80 / 95</td>
</tr>
</tbody>
</table>

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 SO₂ concentrations can be processed. This is especially significant for smelters treating offgases generated by batch type Peirce-Smith converters.
The hot acid from SO$_3$ 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% H$_2$SO$_4$ according to market demand. The principal product in cold climates is 93% H$_2$SO$_4$ because of its low freezing point, -35°C (DuPont, 1988).

Oleum, H$_2$SO$_4$ into which SO$_3$ is absorbed, is also sold by several smelters. It is produced by diverting a stream of SO$_3$-bearing gas and contacting it with 98+ H$_2$SO$_4$ in a small absorption tower.

14.7 Recent and Future Developments in Sulfuric Acid Manufacture

14.7.1 Maximizing feed gas SO$_2$ 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 SO$_2$ strength in the gases that enter smelter sulfuric acid plants.

SO$_2$ offgases entering their drying tower now average 6 to 18 volume% SO$_2$. 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 SO$_2$ gases contain little N$_2$. They heat up more than conventional smelter gas during passage through SO$_2$ $\rightarrow$ SO$_3$ catalyst beds. This can lead to overheating and degradation of the V$_2$O$_5$-K$_2$SO$_4$ 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 $\sim$13 volume% SO$_2$ (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$370°C, i.e. about 40°C cooler than conventional catalysts. This allows a larger temperature rise (i.e. more SO$_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 SO$_2$ $\rightarrow$ 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 SO$_2$ $\rightarrow$ 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% H$_2$SO$_4$-H$_2$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 SO$_2$ → 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 SO$_2$ → 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


References


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 \( \sim 0.01\% \) S and \( \sim 0.5\% \) 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 \( \text{SO}_2 \) 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 cm\(^3\) of \( \text{SO}_2 \) (1083°C) per cm\(^3\) of copper.

Fire refining removes sulfur and oxygen from liquid blister copper by:

(a) air-oxidation removal of sulfur as \( \text{SO}_2 \) to \( \sim 0.002\% \) S
then:

(b) hydrocarbon-reduction removal of oxygen as CO and \( \text{H}_2\text{O(g)} \) to \( \sim 0.15\% \) 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
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.

<table>
<thead>
<tr>
<th>Stage of process</th>
<th>mass% S</th>
<th>mass% O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blister copper*</td>
<td>0.01-0.03</td>
<td>0.1-0.8</td>
</tr>
<tr>
<td>(Lehner et al., 1994)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After oxidation</td>
<td>0.002-0.005</td>
<td>0.6-1</td>
</tr>
<tr>
<td>(Reygadas et al., 1987)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>After reduction ('poling')</td>
<td>0.002-0.005</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Cast anodes</td>
<td>0.002-0.005</td>
<td>0.1-0.2</td>
</tr>
<tr>
<td>(Davenport et al., 1999)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*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 $3 \times 10^6$ 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 Nm$^3$/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:

(a) molten copper is delivered by crane and ladle from converters to the anode furnace until 200 or 300 tonnes are accumulated

(b) the accumulated charge is then desulfurized by blowing air into the molten copper until its S-in-copper is lowered to ~0.002%

(c) 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

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Caraiba Metais S/A, Dias d'Avila, Brazil</th>
<th>Norddeutsche Affinerie, Hamburg</th>
<th>PT Smelting Co. Gresik, Indonesia</th>
<th>Anode production tonnes/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of anode furnaces</td>
<td></td>
<td></td>
<td></td>
<td>257 000</td>
</tr>
<tr>
<td>total</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>active</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Furnace dimensions, m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diameter × length</td>
<td>4.19 × 9.92</td>
<td>4.25 × 10</td>
<td>3.12 × 12.5 (ID)</td>
<td></td>
</tr>
<tr>
<td>Tuyeres</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diameter, cm</td>
<td>4.8</td>
<td>0.8, 1, 1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>number per furnace</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>used during oxidation</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>used during reduction</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>reductant</td>
<td>natural gas</td>
<td>natural gas</td>
<td>diesel oil</td>
<td></td>
</tr>
<tr>
<td>Production details</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tap-to-tap duration, hours</td>
<td>9.91</td>
<td>9</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>anode production</td>
<td>150-200</td>
<td>270</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>tonnes/cycle</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>oxidation duration, hours</td>
<td>1.28</td>
<td>0.5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>air flowrate, Nm³/minute</td>
<td>18.33</td>
<td>6-7</td>
<td>50 air; 5 oxygen</td>
<td></td>
</tr>
<tr>
<td>reduction duration, hours</td>
<td>1.71</td>
<td>3</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>reducing gas flowrate</td>
<td>14 total</td>
<td>10</td>
<td>15 liters per minute</td>
<td></td>
</tr>
<tr>
<td>Nm³/minute per tuyere</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>scrap addition, tonnes/cycle</td>
<td>0</td>
<td>0-10</td>
<td>0-30</td>
<td></td>
</tr>
<tr>
<td>Anode casting</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>method</td>
<td>mold on wheel</td>
<td>mold on wheel</td>
<td>Contilanod</td>
<td></td>
</tr>
<tr>
<td>number of wheels, m</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>diameter of wheels, m</td>
<td>12.8</td>
<td>24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>number of molds per wheel</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>casting rate, tonnes/hour</td>
<td>60</td>
<td>75-80</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Automatic weighing</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>anode mass, kg</td>
<td>360</td>
<td>400</td>
<td>370</td>
<td></td>
</tr>
<tr>
<td>variation, kg</td>
<td>±4</td>
<td>±4</td>
<td>±7</td>
<td></td>
</tr>
</tbody>
</table>
Hazelett continuous anode casting is described in Table 15.3.

<table>
<thead>
<tr>
<th>Onahama Smelting &amp; Refining, Japan</th>
<th>Sumitomo Mining Co. Toyo, Japan</th>
<th>Mexicanana de Cobre, Nacozari, Mexico</th>
<th>Palabora Mining Company, South Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td>160 000</td>
<td>4.2 x 14.2</td>
<td>4.6 x 10.7</td>
<td>3.96 x 9.14</td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>3 or 2</td>
<td>2</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>two 3.96 x 9.15</td>
<td>4.4</td>
<td>5</td>
<td>1.9</td>
</tr>
<tr>
<td>one 4.40 x 10.0</td>
<td>2</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>recovered oil</td>
<td>LP gas</td>
<td>LP gas</td>
<td>80% ethanol/20% propanol mixture</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>9</td>
<td>24</td>
</tr>
<tr>
<td>300</td>
<td>400-500</td>
<td>380</td>
<td>240</td>
</tr>
<tr>
<td>1</td>
<td>-0.5</td>
<td>0.6</td>
<td>1 to 3</td>
</tr>
<tr>
<td>40</td>
<td>8</td>
<td>15</td>
<td>2.5 to 5</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>2.5</td>
<td>2.5 to 3.5</td>
</tr>
<tr>
<td>40</td>
<td>8</td>
<td>10.5 kg/min (total)</td>
<td>20 liters per minute for 90 minutes; 17 liters per minute for next 30 minutes; then 14 liters per minute</td>
</tr>
<tr>
<td>0-8</td>
<td>0-5</td>
<td>40-50</td>
<td>0</td>
</tr>
<tr>
<td>mold on wheel and Hazelett</td>
<td>mold on wheel</td>
<td>mold on wheel</td>
<td>mold on wheel</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>13</td>
<td>10</td>
<td>14.44/11.5</td>
<td>22</td>
</tr>
<tr>
<td>24</td>
<td>18</td>
<td>28/20</td>
<td>35</td>
</tr>
<tr>
<td>50</td>
<td>100</td>
<td>55</td>
<td>310</td>
</tr>
<tr>
<td>yes</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>365</td>
<td>384</td>
<td>342</td>
<td>310</td>
</tr>
<tr>
<td>±5</td>
<td>±3</td>
<td>±2</td>
<td>±20</td>
</tr>
</tbody>
</table>
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:

\[
\text{S}_{\text{in molten copper}} + O_2(g) \rightarrow SO_2(g) \tag{15.1}
\]

while oxygen dissolves in the copper by the reaction:

\[
O_2(g) \rightarrow 2O_{\text{in molten copper}} \tag{15.2}.
\]

The equilibrium relationship between gaseous oxygen entering the bath and S in the bath is, from Eqn. (15.1):

\[
K = \frac{pSO_2}{[\text{mass}\% \text{ S}] \times pO_2} \tag{15.3}
\]

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 \sim 0.002; pO_2 \sim 0.21 atmospheres), SO_2 formation is strongly favored (i.e. $pSO_2 > 1$ 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 Cu₂O 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:

\[
\begin{align*}
C(s) + [O] & \rightarrow CO(g) \\
CO(g) + [O] & \rightarrow CO_2(g) \\
H_2(g) + [O] & \rightarrow H_2O(g)
\end{align*}
\]

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 H₂O. 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 Contilanod 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).
Steel upper band

Molten copper

Water sprays

Water sprays

Steel lower band

Cast copper ready for shearing into anodes

(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 Hazelett continuous anode casting plants at Gresik, Indonesia and Onahama, Japan, 2001. The Gresik support lugs are ~half thickness.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>PT Smelting Co.</th>
<th>Onahama Smelting &amp; Refining</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Gresik Indonesia</td>
<td>Japan</td>
</tr>
<tr>
<td><strong>Startup data</strong></td>
<td>1998</td>
<td>1972</td>
</tr>
<tr>
<td><strong>Anode production tonnes/year</strong></td>
<td>257 000</td>
<td>160 000</td>
</tr>
<tr>
<td><strong>Casting machine size, m</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>length between molten copper entrance and solid copper exit</td>
<td>3.81</td>
<td>2.3</td>
</tr>
<tr>
<td>band width (total)</td>
<td>1.65</td>
<td>1.24</td>
</tr>
<tr>
<td>width of cast copper strip</td>
<td>0.93</td>
<td>1.07</td>
</tr>
<tr>
<td>(between edge dams)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>length of lug</td>
<td>0.18</td>
<td>0.175</td>
</tr>
<tr>
<td>thickness of cast strip</td>
<td>0.045</td>
<td>0.0158</td>
</tr>
<tr>
<td>thickness of lug</td>
<td>0.027</td>
<td>0.0158</td>
</tr>
<tr>
<td><strong>Band details</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>material</td>
<td>ASTM A607</td>
<td>low carbon cold rolled steel</td>
</tr>
<tr>
<td></td>
<td>Grade 45 steel</td>
<td></td>
</tr>
<tr>
<td>life, tonnes of cast copper</td>
<td>1200</td>
<td>600</td>
</tr>
<tr>
<td>lubrication</td>
<td>silicone oil</td>
<td>silicone fluid</td>
</tr>
<tr>
<td><strong>Edge block details</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>material</td>
<td>hardened bronze</td>
<td>high chromium stainless steel</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>life, years</td>
<td>~3 years (~0.5 years for anode lug blocks)</td>
<td>~5 years</td>
</tr>
<tr>
<td><strong>Method of controlling copper level at caster entrance</strong></td>
<td>electromagnetic level indicator</td>
<td>manual</td>
</tr>
<tr>
<td><strong>Temperatures, °C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>molten copper</td>
<td>1120-1150</td>
<td>1120</td>
</tr>
<tr>
<td>cast anode (leaving caster)</td>
<td>880-930</td>
<td>800</td>
</tr>
<tr>
<td><strong>Casting details</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>casting rate, tonnes/hour</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>caster use, hours/day</td>
<td>9</td>
<td>6</td>
</tr>
<tr>
<td><strong>Method of cutting anodes from strip</strong></td>
<td>hydraulic shear</td>
<td>blanking press</td>
</tr>
<tr>
<td><strong>Anode details</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>mass, kg</td>
<td>370</td>
<td>143</td>
</tr>
<tr>
<td>acceptable deviation</td>
<td>±7 kg</td>
<td>±3 kg</td>
</tr>
<tr>
<td>% acceptable anodes</td>
<td>97</td>
<td>97</td>
</tr>
</tbody>
</table>
15.5.1 Contilanod 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 Contilanod 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 Contilanod 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$_2$CO$_3$) 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 (Czernecki 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


References


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.
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 CuSO₄-H₂SO₄-H₂O 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 CuSO₄-H₂SO₄-H₂O electrolyte causes the following.
Copper electrorefinery flow sheet. The process produces pure copper cathode 'plates' from impure copper anodes. CuSO$_4$-H$_2$SO$_4$-H$_2$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:

\[ \text{Cu}^{\circ}_{\text{anode}} \rightarrow \text{Cu}^{++} + 2e^{-} \quad E^o = -0.34 \text{ volt} \quad (16.1). \]

(b) The electrons produced by Reaction (16.1) are conducted towards the cathode through the external circuit and power supply.
Electrolytic Refining

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 electrorefining 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.:

$$\text{Cu}^{++} + 2e^- \rightarrow \text{Cu}_{\text{cathode}}^{\text{cathode}} \quad E^\circ = +0.34 \text{ volt} \quad (16.2).$$
Overall copper electrorefining is the sum of Reactions (16.1) and (16.2):

\[
Cu_{\text{impure}}^\circ \rightarrow Cu_{\text{pure}}^\circ
\]  

(16.3)

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. Cu₂Se, Ag₂Se, Ag₂Te (Campin, 2000).

**Pb and Sn**
Lead forms solid PbSO₄. Tin forms SnO₂. 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 CuSO₄·H₂SO₄·H₂O 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).

<table>
<thead>
<tr>
<th>Element</th>
<th>Anodes (range of %)</th>
<th>Cathodes (range of %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>98.4 - 99.8</td>
<td>99.99</td>
</tr>
<tr>
<td>O</td>
<td>0.1 - 0.25</td>
<td>not determined</td>
</tr>
<tr>
<td>Ag</td>
<td>0.01 - 0.60</td>
<td>0.0004 - 0.0016</td>
</tr>
<tr>
<td>S</td>
<td>0.001 - 0.008</td>
<td>0.0002 - 0.001</td>
</tr>
<tr>
<td>Sb</td>
<td>trace - 0.3</td>
<td>trace - 0.001</td>
</tr>
<tr>
<td>Pb</td>
<td>0.001 - 0.35</td>
<td>trace - 0.0005</td>
</tr>
<tr>
<td>Ni</td>
<td>0.003 - 0.6</td>
<td>trace - 0.0003</td>
</tr>
<tr>
<td>Fe</td>
<td>0.001 - 0.03</td>
<td>trace - 0.0003</td>
</tr>
<tr>
<td>As</td>
<td>trace - 0.25</td>
<td>trace - 0.0001</td>
</tr>
<tr>
<td>Se</td>
<td>0.001 - 0.12</td>
<td>trace - 0.0001</td>
</tr>
<tr>
<td>Te</td>
<td>0.001 - 0.05</td>
<td>trace - 0.0001</td>
</tr>
<tr>
<td>Bi</td>
<td>trace - 0.02</td>
<td>trace</td>
</tr>
<tr>
<td>Au</td>
<td>trace - 0.02</td>
<td>trace</td>
</tr>
</tbody>
</table>

**Table 16.2.** Fractions of anode elements entering 'slimes' and electrolyte. As, Bi and Sb are discussed by Larouche, 2001.

<table>
<thead>
<tr>
<th>Element</th>
<th>% into 'slimes'</th>
<th>% into electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>&lt;0.2</td>
<td>&gt;99.8</td>
</tr>
<tr>
<td>Au</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Ag</td>
<td>&gt;99</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Se</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Te</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Pb</td>
<td>98</td>
<td>2</td>
</tr>
<tr>
<td>Bi</td>
<td>60% with 0.1% Pb in anode</td>
<td>40</td>
</tr>
<tr>
<td>Sb</td>
<td>60% with 0.1% As, Bi, Pb and Sb (each) in anode</td>
<td>40</td>
</tr>
<tr>
<td>As</td>
<td>25% with 0.1% As in anode</td>
<td>75</td>
</tr>
<tr>
<td>S</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>Ni</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>Co</td>
<td>1</td>
<td>99</td>
</tr>
<tr>
<td>Fe</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>0</td>
<td>100</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Electrochemical reaction</th>
<th>Standard reduction potential (25°C), volts</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Au}^{3+} + 3\text{e}^- \rightarrow \text{Au}^0 )</td>
<td>1.5</td>
</tr>
<tr>
<td>( \text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}^0 )</td>
<td>0.80</td>
</tr>
<tr>
<td>( \text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}^0 )</td>
<td>0.34</td>
</tr>
<tr>
<td>( \text{BiO}^+ + 2\text{H}^+ + 3\text{e}^- \rightarrow \text{Bi}^0 + \text{H}_2\text{O} )</td>
<td>0.32</td>
</tr>
<tr>
<td>( \text{HAsO}_2^- + 3\text{H}^+ + 3\text{e}^- \rightarrow \text{As}^0 + 2\text{H}_2\text{O} )</td>
<td>0.25</td>
</tr>
<tr>
<td>( \text{SbO}^- + 2\text{H}^+ + 3\text{e}^- \rightarrow \text{Sb}^0 + \text{H}_2\text{O} )</td>
<td>0.21</td>
</tr>
<tr>
<td>( 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 )</td>
<td>0.0000 (pH = 0; ( p\text{H}_2 \text{O} = 1 \text{ atmosphere} ))</td>
</tr>
<tr>
<td>( \text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}^0 )</td>
<td>-0.13</td>
</tr>
<tr>
<td>( \text{Ni}^{2+} + 2\text{e}^- \rightarrow \text{Ni}^0 )</td>
<td>-0.26</td>
</tr>
<tr>
<td>( \text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}^0 )</td>
<td>-0.28</td>
</tr>
<tr>
<td>( \text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}^0 )</td>
<td>-0.45</td>
</tr>
</tbody>
</table>

16.3 Industrial Electrorefining (Table 16.4)

Industrial electrorefining is done with large (~1 m × 1 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 CuSO₄-H₂SO₄-H₂O 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.

<table>
<thead>
<tr>
<th>Refinery</th>
<th>Caraiba Metais Union Miniere Plirdop Bulgaria</th>
<th>Norddeutsche Affinerie</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Startup date</strong></td>
<td>1982</td>
<td>1958</td>
</tr>
<tr>
<td><strong>Cathode Cu, thousand tonnes/yr</strong></td>
<td>220</td>
<td>35 (1998)</td>
</tr>
<tr>
<td><strong>Electrolytic cells</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>number (total)</td>
<td>1150</td>
<td>492</td>
</tr>
<tr>
<td>construction material</td>
<td>1020 concrete changing to polymer concrete</td>
<td></td>
</tr>
<tr>
<td>lining material</td>
<td>1020 Pb</td>
<td></td>
</tr>
<tr>
<td>length x width x depth (inside), m</td>
<td>4.82x1.07x1.28</td>
<td>3 x 1 x 1.2</td>
</tr>
<tr>
<td>anodes/cathodes per cell</td>
<td>42/43</td>
<td>25/26</td>
</tr>
<tr>
<td><strong>Anodes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>type</td>
<td>mold on wheel</td>
<td>mold on wheel</td>
</tr>
<tr>
<td>% Cu</td>
<td>99.94</td>
<td>99.4</td>
</tr>
<tr>
<td>mass Cu</td>
<td>925 x 890 x 50</td>
<td>930 x 830 x 45</td>
</tr>
<tr>
<td>center-line spacing, cm</td>
<td>350</td>
<td>245</td>
</tr>
<tr>
<td>life, days</td>
<td>11.0</td>
<td>10.8</td>
</tr>
<tr>
<td>% scrap after refining</td>
<td>22</td>
<td>21</td>
</tr>
<tr>
<td>anode slimes kg/tonne anode</td>
<td>19</td>
<td>21</td>
</tr>
<tr>
<td><strong>Cathodes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>type</td>
<td>Cu starter sheet</td>
<td>Cu starter sheet</td>
</tr>
<tr>
<td>length x width x thickness mm</td>
<td>980 x 960 x 0.7</td>
<td>880 x 860 x 0.7</td>
</tr>
<tr>
<td>plating time, days</td>
<td>11</td>
<td>7</td>
</tr>
<tr>
<td>mass Cu plated (total), kg</td>
<td>150</td>
<td>65</td>
</tr>
<tr>
<td>ppm total impurities</td>
<td>25</td>
<td>&lt;25</td>
</tr>
<tr>
<td>ppm Ag</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td><strong>Electrolyte</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu kg/m³</td>
<td>43</td>
<td>185</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>65</td>
<td>63</td>
</tr>
<tr>
<td>inlet temperature, °C</td>
<td>63</td>
<td>59</td>
</tr>
<tr>
<td>outlet temperature, °C</td>
<td>0.026</td>
<td>0.016</td>
</tr>
<tr>
<td>inlet rate per cell, m³/minute</td>
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<td></td>
</tr>
<tr>
<td>addition agents, grams per tonne of cathode copper</td>
<td>bone glue</td>
<td>128</td>
</tr>
<tr>
<td></td>
<td>thionua</td>
<td>77</td>
</tr>
<tr>
<td></td>
<td>avitone</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Cl (as HCl or NaCl)</td>
<td>17 to 0.035 kg/m³</td>
</tr>
<tr>
<td>automatic control</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>electrolyte filtering</td>
<td>partial</td>
<td></td>
</tr>
<tr>
<td><strong>Power and energy</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>cathode current density, A/m²</td>
<td>281</td>
<td>257</td>
</tr>
<tr>
<td>cathode current efficiency, %</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>cell voltage, V</td>
<td>0.35</td>
<td>0.21-0.35</td>
</tr>
<tr>
<td>cell current, thousand amps</td>
<td>22.25</td>
<td>9.5</td>
</tr>
<tr>
<td>kWh/tonne of Cu shipped (plating only)</td>
<td>307</td>
<td>388</td>
</tr>
</tbody>
</table>
Davenport et al., 1999 give additional information.

<table>
<thead>
<tr>
<th>Gresik Indonesia</th>
<th>Sumitomo Toyo, Japan</th>
<th>Palabora Mining South Africa</th>
<th>Kennecott Utah Cu Magna Utah</th>
</tr>
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<tr>
<td>1999</td>
<td>1968</td>
<td>1995</td>
<td>220</td>
</tr>
<tr>
<td>220</td>
<td>123</td>
<td>90</td>
<td>280</td>
</tr>
<tr>
<td>654</td>
<td>488</td>
<td>960</td>
<td>1400</td>
</tr>
<tr>
<td>polymer concrete</td>
<td>precast &amp; polymer concrete</td>
<td>steel reinforced concrete</td>
<td>polymer concrete</td>
</tr>
<tr>
<td>none</td>
<td>FRP, PVC</td>
<td>6% Sb lead</td>
<td>none</td>
</tr>
<tr>
<td>6.3 x 1.2 x 1.4</td>
<td>5.6 x 1.25 x (1.4, 1.6)</td>
<td>3.8 x 1.07 x 1.14</td>
<td>4.81 x 1.19 x 1.52</td>
</tr>
<tr>
<td>59/58</td>
<td>51/50</td>
<td>32/33</td>
<td>47/46</td>
</tr>
<tr>
<td>Contelanod</td>
<td>mold on wheel</td>
<td>mold on wheel</td>
<td>mold on wheel</td>
</tr>
<tr>
<td>99.3-99.7</td>
<td>99.4</td>
<td>99.5</td>
<td>99.1</td>
</tr>
<tr>
<td>974 x 934 x 45</td>
<td>1015 x 1015 x 39</td>
<td>922 x 920 x 43</td>
<td>1038 x 938 x 39</td>
</tr>
<tr>
<td>370</td>
<td>384</td>
<td>318</td>
<td>330</td>
</tr>
<tr>
<td>10.35</td>
<td>10.5</td>
<td>11.2</td>
<td>9.8</td>
</tr>
<tr>
<td>21</td>
<td>20</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>13.7</td>
<td>13.8</td>
<td>17</td>
<td>17</td>
</tr>
<tr>
<td>1 to 3</td>
<td>4</td>
<td>1.19</td>
<td>9.7</td>
</tr>
<tr>
<td>Isa stainless steel</td>
<td>1050 x 1070 x 0.7</td>
<td>940 x 920 x 0.6</td>
<td>Kidd stainless steel</td>
</tr>
<tr>
<td>1000 x 1000 x (6-12)</td>
<td>1050 x 1070 x 0.7</td>
<td>940 x 920 x 0.6</td>
<td>990 x 990 x 3</td>
</tr>
<tr>
<td>7 &amp; 14</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>100 &amp; 200</td>
<td>169</td>
<td>127</td>
<td>135</td>
</tr>
<tr>
<td>&lt;17</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
<tr>
<td>7-10</td>
<td>10</td>
<td>5-8</td>
<td>10</td>
</tr>
<tr>
<td>Cu</td>
<td>H2SO4</td>
<td>Cu H2SO4</td>
<td>Cu H2SO4</td>
</tr>
<tr>
<td>52</td>
<td>49</td>
<td>195</td>
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</tr>
<tr>
<td>63</td>
<td>62</td>
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<td>63</td>
</tr>
<tr>
<td>0.035</td>
<td>0.025</td>
<td>0.018</td>
<td>0.020</td>
</tr>
<tr>
<td>52-53</td>
<td>100</td>
<td>76</td>
<td>80</td>
</tr>
<tr>
<td>72-76</td>
<td>70</td>
<td>41</td>
<td>100</td>
</tr>
<tr>
<td>0</td>
<td>20</td>
<td>25-30</td>
<td>0</td>
</tr>
<tr>
<td>40 (HCl)</td>
<td>30 (35% HCl)</td>
<td>21</td>
<td>NaCl to 40 ppm Cl</td>
</tr>
<tr>
<td>no</td>
<td>no</td>
<td>no</td>
<td>CollaMat for glue</td>
</tr>
<tr>
<td>yes</td>
<td>no</td>
<td>yes, Scheibler</td>
<td>yes, 15% of circulation</td>
</tr>
<tr>
<td>295</td>
<td>267</td>
<td>277</td>
<td>282</td>
</tr>
<tr>
<td>97</td>
<td>98</td>
<td>91-95</td>
<td>95</td>
</tr>
<tr>
<td>0.3-0.4</td>
<td>0.31</td>
<td>0.29</td>
<td>0.28</td>
</tr>
<tr>
<td>34.2</td>
<td>36</td>
<td>16</td>
<td>25.5</td>
</tr>
<tr>
<td>285</td>
<td>302</td>
<td>390</td>
<td>320</td>
</tr>
</tbody>
</table>
(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.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration, kg/m(^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>40-50</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>150-200</td>
</tr>
<tr>
<td>Cl</td>
<td>0.02-0.05</td>
</tr>
<tr>
<td>protein colloids (glue)</td>
<td>0.0001-0.001</td>
</tr>
<tr>
<td>thiourea</td>
<td>0.0001-0.0005</td>
</tr>
<tr>
<td>Upper limits</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>25</td>
</tr>
<tr>
<td>As</td>
<td>20</td>
</tr>
<tr>
<td>Fe</td>
<td>2</td>
</tr>
<tr>
<td>Sb</td>
<td>0.7</td>
</tr>
<tr>
<td>Bi</td>
<td>0.6</td>
</tr>
</tbody>
</table>

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\(_2\)O 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 CuSO₄ (Bravo, 1995).

The remaining concentrated acid (~1000 kg H₂SO₄/m³) 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 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/m³ 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 CuSO₄·5H₂O 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.:

\[
\text{Cu}^{\circ}_{\text{anode}} \rightarrow \text{Cu}^{++} + 2e^- \quad (16.1)
\]

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 x 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 electrowinning.

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/m\(^3\)) 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%
- stay current to ground 1%
- reoxidation of cathode copper by O₂ 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 electrorefinery, 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 electrorefinery – 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 electrorefining 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 electrowinning, 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 electrorefining 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


References


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 H₂SO₄-H₂O solution. Heap leaching is trickling the H₂SO₄-H₂O 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 H₂SO₄-H₂O 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.

<table>
<thead>
<tr>
<th>Type</th>
<th>Common minerals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbonates</td>
<td>Azurite 2CuCO₃·Cu(OH)₂</td>
</tr>
<tr>
<td>Malachite</td>
<td>CuCO₃·Cu(OH)₂</td>
</tr>
<tr>
<td>Hydroxy-chlorides</td>
<td>Atacamite Cu₂Cl(OH)₃</td>
</tr>
<tr>
<td>Hydroxy-silicates</td>
<td>Chrysocolla CuO·SiO₂·2H₂O</td>
</tr>
<tr>
<td>Native copper</td>
<td>Metal Cu⁺</td>
</tr>
<tr>
<td>Oxides</td>
<td>Cuprite Cu₂O</td>
</tr>
<tr>
<td>Tenorite</td>
<td>CuO</td>
</tr>
<tr>
<td>Sulfates</td>
<td>Antlerite CuSO₄·2Cu(OH)₂</td>
</tr>
<tr>
<td>Brochantite</td>
<td>CuSO₄·3Cu(OH)₂</td>
</tr>
<tr>
<td>Supergene sulfides</td>
<td>Chalcocite Cu₂S</td>
</tr>
<tr>
<td>Covellite</td>
<td>CuS</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Primary sulfide minerals**

| Hypogene sulfides  | Chalcopyrite CuFeS₂                     |
| Bornite            | Cu₄FeS₄                                  |
| Pyrite, source of Fe⁺⁺ | FeS₂                       |
| Fe⁺⁺⁺ and H₂SO₄    |                                          |

\[
\text{CuO + H}_2\text{SO}_4 \rightarrow \text{Cu}^{++} + \text{SO}_4^{-} + \text{H}_2\text{O} \quad \text{aqueous solution (17.1)}.
\]

Leaching of sulfide minerals, on the other hand, requires an oxidant as well as H₂SO₄. The oxidant is dissolved O₂ from air. A representative reaction is:

\[
\text{Cu}_2\text{S} + 2.5\text{O}_2 + \text{H}_2\text{SO}_4 \rightarrow 2\text{Cu}^{++} + 2\text{SO}_4^{-} + \text{H}_2\text{O} \quad \text{in aqueous solution (17.2).}
\]

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:
2FeS₂ + 7O₂ + 2H₂O → 2Fe⁺⁺ + 2SO₄⁻⁻ + 2H₂SO₄

pyrite in ore aqueous bacteria (17.3)

catalyst

0.5O₂ + 2Fe⁺⁺ + 2SO₄⁻⁻ + H₂SO₄ → 2Fe⁺⁺⁺ + 3SO₄⁻⁻ + H₂O

aqueous solution bacteria enzyme (17.4)
catalyst

and:

Cu₂S + 10Fe⁺⁺⁺ + 15SO₄⁻⁻ + 4H₂O → 2Cu⁺⁺⁺ + 10Fe⁺⁺ + 12SO₄⁻⁻ + 4H₂SO₄

bacteria enzyme catalyst (17.5).

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 m³ 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 × 2 μm 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 10¹² 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 ~30°C, often generated in leach heaps and dumps by exothermic sulfide oxidation reactions)
(c) an adequate \( \text{O}_2 \) 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 \( \text{NH}_4^+ \) and \( \text{PO}_4^{3-} \) 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 \( \text{O}_2 \) 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 \( \text{CuFeS}_2 \) before \( \text{Cu} \) – leaving behind a passive layer of metastable \( \text{CuS}_2 \)

(b) subsequent leaching of \( \text{Cu} \) from \( \text{CuS}_2 \) 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 \( 10^6 \) m\(^2\) in top area

(b) applying drops of \( \text{H}_2\text{SO}_4-\text{H}_2\text{O} \) 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 \( \text{Cu} \) minerals by Reactions (17.1) through (17.5)

(d) collecting the \( \text{Cu}^{++} \)-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\textsuperscript{2+}-depleted H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}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 (Lasillo 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\textsuperscript{2+} 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\(_2\)S) 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

<table>
<thead>
<tr>
<th>Operation</th>
<th>Cerro Colorado</th>
<th>El Abra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Startup date</td>
<td>1994</td>
<td>1996</td>
</tr>
<tr>
<td>Cathode production, tonnes/year</td>
<td>130 000</td>
<td>194 000</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$ consumption, tonnes/tonne of cathode Cu</td>
<td>1.25</td>
<td>5.04</td>
</tr>
<tr>
<td><strong>Ore information</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>leached mineral</td>
<td>chalcocite, 0.8%</td>
<td>chrysocolla</td>
</tr>
<tr>
<td>%Cu in ore</td>
<td>19</td>
<td>0.63</td>
</tr>
<tr>
<td>leachable</td>
<td>1.16</td>
<td>0.55</td>
</tr>
<tr>
<td>non-leachable</td>
<td>0.04% in covellite</td>
<td>0.08</td>
</tr>
<tr>
<td>location of ore's leachable minerals</td>
<td>oxides on fracture surfaces, sulfides disseminated</td>
<td>disseminated</td>
</tr>
<tr>
<td>% of total Cu in ore recovered in solution</td>
<td>80% of leachable Cu</td>
<td>78</td>
</tr>
<tr>
<td><strong>Heaps</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>permanent or on/off</td>
<td>on/off</td>
<td>on/off</td>
</tr>
<tr>
<td>building machines</td>
<td>dump truck</td>
<td>conveyor stacking</td>
</tr>
<tr>
<td>usual total area under leach, thousand m$^2$</td>
<td>1600</td>
<td>710</td>
</tr>
<tr>
<td>usual number of 'cells' under leach</td>
<td>27</td>
<td>55</td>
</tr>
<tr>
<td>typical lift height, m</td>
<td>6-9</td>
<td>7 (0.3 m 'ripping')</td>
</tr>
<tr>
<td>maximum total heap height, m</td>
<td>6-9</td>
<td>7</td>
</tr>
<tr>
<td>aeration pipes beneath heap, yes/no</td>
<td>no</td>
<td></td>
</tr>
<tr>
<td><strong>Heap base</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>liner material &amp; thickness, mm</td>
<td>HDPE 2 mm</td>
<td>HDPE 1.5 mm</td>
</tr>
<tr>
<td><strong>Ore preparation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>crush, yes/no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>agglomeration in rotation drum, yes/no</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>ore size on heap</td>
<td>90% &lt;12 mm</td>
<td>80% &lt;11.5-12.5 mm</td>
</tr>
<tr>
<td><strong>Acid cure, yes/no</strong></td>
<td>yes</td>
<td></td>
</tr>
<tr>
<td>on heap or during agglomeration</td>
<td>in rotating drum</td>
<td>in rotating drum, 45</td>
</tr>
<tr>
<td>$\text{kg/m}^3\text{H}_2\text{SO}_4$ in cure solution</td>
<td>concentrated</td>
<td>33 mass%</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4$, kg/tonne of ore</td>
<td>16-20</td>
<td></td>
</tr>
<tr>
<td>rest duration before leaching</td>
<td>20</td>
<td>3 to 4 days</td>
</tr>
<tr>
<td><strong>Lixiviant</strong></td>
<td>raffinate</td>
<td>$\text{H}_2\text{SO}_4$ fortified</td>
</tr>
<tr>
<td>$\text{kg H}_2\text{SO}_4$/m$^3$ of solution</td>
<td>11</td>
<td>12-14</td>
</tr>
<tr>
<td>$\text{kg Cu}^{+}$/m$^3$ of solution</td>
<td>0.4</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>temperature, °C</td>
<td>17-22</td>
<td>15-20</td>
</tr>
<tr>
<td>application rate, m$^3$/hour/m$^2$ of heap surface</td>
<td>0.006</td>
<td>0.01</td>
</tr>
<tr>
<td>drop emitters or sprinklers (wobblers)</td>
<td>emitters</td>
<td></td>
</tr>
<tr>
<td>distance apart</td>
<td></td>
<td></td>
</tr>
<tr>
<td>along header pipe, m</td>
<td>0.4</td>
<td>0.46</td>
</tr>
<tr>
<td>between header pipes, m</td>
<td>0.6</td>
<td>0.46</td>
</tr>
<tr>
<td><strong>Leach cycle sequence</strong></td>
<td>agglomerate in rotating drum with raffinate and $\text{H}_2\text{SO}_4$; heap; rest for 20 days; leach for 480 days</td>
<td>acid cure in rotating drum, build cured ore into heap, rest 3 or 4 days, leach for 55 days</td>
</tr>
<tr>
<td><strong>Pregnant solution</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{kg Cu}^{+}$/m$^3$ of solution</td>
<td>4.8</td>
<td>5 to 6</td>
</tr>
<tr>
<td>$\text{kg H}_2\text{SO}_4$/m$^3$ of solution</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>temperature, °C</td>
<td>18-23</td>
<td>15-20</td>
</tr>
<tr>
<td>collection system</td>
<td>HDPE-lined ponds</td>
<td>ditches</td>
</tr>
<tr>
<td>total flow from leach system, m$^3$/hour</td>
<td>4000</td>
<td>5000-7500</td>
</tr>
</tbody>
</table>
solvent extraction and electrowinning plants are given in Chapters 18 and 19.

<table>
<thead>
<tr>
<th>Zaldivar (heap leach)</th>
<th>Hellenic Copper</th>
<th>Morenci (mine for leach)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1995</td>
<td>1996</td>
<td>1987</td>
</tr>
<tr>
<td>145 000</td>
<td>8000</td>
<td>366 000</td>
</tr>
<tr>
<td>14</td>
<td>5</td>
<td>1</td>
</tr>
</tbody>
</table>

- chalcocite, bronchantite, chrysocolla
- 1% chalcocite disseminated, others on fracture surfaces
- 75 conveyor stacking
- 78% of leachable
- permanent on/off
- 1200 conveyor stacking
- 250 excavator stacking
- 78% of leachable
- conveyor stacking
- 2137 yes (10^3 m³ air/minute/m²)
- HDPE
- HDPE 1.5 mm
- yes
- belt curing
- 80% <12 mm no
- 50% <75 mm yes
- <12 mm (crushed), 300 mm ROM
- yes, for about 30% of material, in rotating drum
- concentrated
- 8 yes
- 200 kg/m³ H₂SO₄ onto heap for 3 days
- no
- H₂SO₄-fortified raffinate
- 8 yes
- 0.25 yes
- 29.7 yes
- 0.008 yes
- 0.5 no
- 0.5 no
- 0.6 no
- raffinate
- 4 yes
- 0.5 yes
- 22 yes
- 0.0075 yes
- 0.5 no
- 0.6 no
- 12 mine for leach, other 4-5
- 0.3 yes
- 32 yes
- 0.006 yes
- 0.9 yes
- both, principally emitters
- belt acid cure, leach with raffinate for 30 days, then leach with recycling pregnant solution for 270 days
- 3.5 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
- 1.8 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
- 1 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
- 20.7 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
- belt acid cure, leach with raffinate for 30 days, then leach with recycling pregnant solution for 270 days
- 4800 on-pad piping
- 520 (clay + HDPE)-lined ponds
- 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.

<table>
<thead>
<tr>
<th>Item</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Individual heap (module)</td>
<td>85 m \times 400 m horizontal dimensions (34 000 m²). Consists of 7 m lifts, eventually piled to a total of 60 m high.</td>
</tr>
<tr>
<td>Air supply rate</td>
<td>170 m³/minute (0.005 m³/min/m² of top surface). The design assumes 20% utilization of O₂ entering heap</td>
</tr>
<tr>
<td>Air header (400 m long)</td>
<td>0.45 m diameter HDPE pipe, corrugated outside for strength, smooth inside</td>
</tr>
<tr>
<td>Air distribution lines (85 m long)</td>
<td>5 cm HDPE pipes, 2 mm diameter hole every 1 m, rotated around the pipe. The pipes are spaced 2 m apart.</td>
</tr>
<tr>
<td>Fan</td>
<td>single stage axial fan, ~0.1 atmosphere gage delivery pressure</td>
</tr>
</tbody>
</table>

17.2.5 Pregnant solution collection

The product pregnant solution (1 to 6 kg Cu²⁺/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:

(a) placement of run-of-mine ore on the heap followed by trickling strong H₂SO₄-H₂O solution through the heap ('acid curing')
(b) 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 Cu²⁺ recovery.
'Acid curing' quickly dissolves Cu$^{2+}$ 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$^{2+}$ extraction rate and efficiency, Table 17.2.

**17.2.7 Crushing, agglomeration and acid curing**

Cu$^{2+}$ 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$^{2+}$ 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$_2$SO$_4$ 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$^{2+}$ 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$^{2+}$-depleted solution ('raffinate') returning from solvent extraction, Fig. 17.1. Its composition is typically 0.4 kg Cu and ~5 kg H$_2$SO$_4$/m$^3$ of solution as it leaves the solvent extraction circuit. Sulfuric acid is often added (to ~10 kg H$_2$SO$_4$/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 $10^{-2} \text{ m}^3$ 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$^{2+}$ 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°C, pH $\sim$2, 5-10 kg H$_2$SO$_4$/m$^3$ of lixiviant, no organics)

(c) uniform, lixiviant application ($\sim 10^{-2} \text{ m}^3$/hour/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 H$_2$SO$_4$-H$_2$O lixiviant uniformly through flat-surface heaps of crushed ore agglomerate or run-of-mine ore. 'Oxide' ores are leached quickly by H$_2$SO$_4$ without oxidation. Chalcocite (and to a much lesser extent bornite and covellite) are oxidized and leached by H$_2$SO$_4$-H$_2$O-O$_2$-Fe$^{+++}$ solutions.
Table 17.4. Description and status of chalcopyrite concentrate leach processes (McElroy and Young, 1999).

<table>
<thead>
<tr>
<th>Name of process</th>
<th>Description</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arbiter ammonia-O₂ pressure leach</td>
<td>agitation pressure leach, solvent extraction, electrowinning</td>
<td>100 tonnes copper per day plant started in 1974 but closed in 1977 due to technical difficulties and high costs</td>
</tr>
<tr>
<td>(Arbiter &amp; McNulty, 1999)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Escondida ammonia-air leach</td>
<td>Ammonia-air agitation leach of Cu₂S to CuS + Cu²⁺ followed by solvent extraction electrowinning recovery of metallic copper</td>
<td>80 000 tonnes of copper per year plant started in 1994 but closed due to its slow rate of copper production</td>
</tr>
<tr>
<td>(Duyvesteyn and Sabacky, 1993, 1995; Arbiter and McNulty, 1999)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Halide leach</td>
<td>Halide leach, electrowinning</td>
<td>Industrial scale attained. Interest seems to have waned due to impure products, environmental problems and adverse economics</td>
</tr>
<tr>
<td>(Cymet, CLEAR, Cuprex and Intec processes)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen sulfuric acid pressure leach</td>
<td>High (7 atmospheres) and moderate O₂ pressure leach with sulfuric acid, raffinate, electrolyte and various additives (Anderson, 2000; Collins et al., 2000; Fleming et al., 2000)</td>
<td>Development is continuing</td>
</tr>
</tbody>
</table>

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 Cu²⁺/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 Cu²⁺-depleted 'raffinate' from solvent extraction is recycled to leaching, usually fortified with H₂SO₄.

Cu²⁺ 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


References


Columbus Instruments (2002) Oxymax-F measures O₂/CO₂/CH₄ consumption and production www.colinst.com (Environmental Instruments, Respirometer for Fermentation)


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/m$^3$)

and:

(b) too impure (1-10 kg Fe/m$^3$)

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/m$^3$. 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.

(a) contacting pregnant aqueous leach solution (1-6 kg Cu⁺²/m³, 0.5 to 5 kg H₂SO₄/m³) with a Cu-specific liquid organic extractant—causing extraction of Cu⁺⁺ from the aqueous solution into the organic extractant

(b) separating by gravity the now-Cu-depleted aqueous leach solution (raffinate) from the now-Cu-loaded organic extractant

(c) sending the low-Cu raffinate back to leach

(d) sending the Cu-loaded organic extractant to contact with strong-H₂SO₄ electrowinning electrolyte (170-200 kg H₂SO₄/m³)—causing Cu to be stripped from the organic into the electrolyte

(e) separating by gravity the now-Cu-stripped organic extractant from the now-Cu⁺⁺-enriched aqueous electrolyte

(f) returning the stripped organic extractant to renewed contact with pregnant leach solution

(g) 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:

\[
2\text{RH} + \text{Cu}^{++} + \text{SO}_4^{--} \rightarrow \text{R}_2\text{Cu} + 2\text{H}^+ + \text{SO}_4^{--}
\]

(18.1)

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\(_2\)SO\(_4\) 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.:

\[
2\text{H}^+ + \text{SO}_4^{--} + \text{R}_2\text{Cu} \rightarrow 2\text{RH} + \text{Cu}^{++} + \text{SO}_4^{--}
\]

(18.2)

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:

(a) loaded with Cu from weak H\(_2\)SO\(_4\) pregnant leach solution
(b) separated from the pregnant leach solution
(c) contacted with strong H\(_2\)SO\(_4\) electrolyte and stripped of its Cu.

It is the different H\(_2\)SO\(_4\) 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 CuSO₄-H₂SO₄-H₂O 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):

(a) efficiently extract Cu from the project’s pregnant leach solution
(b) efficiently strip Cu into the project’s electrowinning electrolyte
(c) have economically rapid extraction and strip kinetics
(d) 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. Alodoximes: R = C₉H₁₉ or C₁₂H₂₅, A = H. Ketoxime: R = C₅H₁₀, A = CH₃ (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 (CH₃) 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.

<table>
<thead>
<tr>
<th>Property</th>
<th>Ketoxime</th>
<th>Aldoxime with modifier</th>
<th>Aldoxime-ketoxime mixtures, no modifiers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractive strength</td>
<td>moderate</td>
<td>strong</td>
<td>customized</td>
</tr>
<tr>
<td>Stripping ability</td>
<td>very good</td>
<td>good</td>
<td>customized</td>
</tr>
<tr>
<td>Cu/Fe selectivity</td>
<td>excellent</td>
<td>excellent</td>
<td>excellent</td>
</tr>
<tr>
<td>Cu extraction and stripping speed</td>
<td>fast</td>
<td>very fast</td>
<td>fast</td>
</tr>
<tr>
<td>Phase separation speed</td>
<td>very fast</td>
<td>very fast</td>
<td>very fast</td>
</tr>
<tr>
<td>Stability</td>
<td>very good</td>
<td>very good*</td>
<td>very good*</td>
</tr>
<tr>
<td>Crud generation**</td>
<td>low</td>
<td>variable</td>
<td>low</td>
</tr>
<tr>
<td>Examples</td>
<td>LIX 84-1</td>
<td>LIX 622 (tridecanol modified)</td>
<td>LIX 984N</td>
</tr>
<tr>
<td></td>
<td>Acorga M5640 (ester modified)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 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-setter. 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

<table>
<thead>
<tr>
<th>Operation</th>
<th>Cerro Colorado</th>
<th>El Abra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Startup date</td>
<td>1994</td>
<td>1996</td>
</tr>
<tr>
<td>Cathode production, tonnes/year</td>
<td>130 000</td>
<td>218 000</td>
</tr>
<tr>
<td><strong>Total pregnant solution input rate, m³/hour</strong></td>
<td><strong>4000</strong></td>
<td><strong>5000-7500</strong></td>
</tr>
<tr>
<td>SX plant details</td>
<td></td>
<td></td>
</tr>
<tr>
<td>plant type</td>
<td>series</td>
<td>2 series</td>
</tr>
<tr>
<td>number of SX 'trains'</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>extraction mixer-settlers per train</td>
<td>2</td>
<td>series 2; series-parallel 3</td>
</tr>
<tr>
<td>strip mixer-settlers per train</td>
<td>1</td>
<td>series 2; series-parallel 1</td>
</tr>
<tr>
<td><strong>Mixer-settler details</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixers</td>
<td></td>
<td></td>
</tr>
<tr>
<td>round or square</td>
<td>square</td>
<td>square</td>
</tr>
<tr>
<td>number of mixing compartments</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>compartment size: depth ( \times ) width ( \times ) length, m</td>
<td>Lightnin pump mixer 77030</td>
<td>suction mixer</td>
</tr>
<tr>
<td>mixer system</td>
<td></td>
<td>3.1 ( \times ) 3.7 ( \times ) 12.7</td>
</tr>
<tr>
<td>construction materials</td>
<td>316 stainless steel</td>
<td>polymer concrete</td>
</tr>
<tr>
<td>liquids residence time, minutes</td>
<td>3</td>
<td>2.4</td>
</tr>
<tr>
<td><strong>Settler</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>length ( \times ) width ( \times ) depth, m</td>
<td>22 ( \times ) 22 ( \times ) 0.9</td>
<td>28 ( \times ) 29 ( \times ) 1.1</td>
</tr>
<tr>
<td>flow distributor system</td>
<td>2 picket fences</td>
<td>2 picket fences</td>
</tr>
<tr>
<td>construction materials</td>
<td>HDPE-lined concrete</td>
<td>HDPE-lined concrete</td>
</tr>
<tr>
<td>organic depth, m</td>
<td>0.28-0.3</td>
<td>0.27</td>
</tr>
<tr>
<td>aqueous depth, m</td>
<td>0.45</td>
<td>0.63</td>
</tr>
<tr>
<td>estimated residence time, minutes</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>estimated phase separation time, minutes</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td><strong>Organic details</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>extractant</td>
<td>LIX 860-NIC/LIX 84-IC</td>
<td>PT5050-LIX 984NC</td>
</tr>
<tr>
<td>volume% in organic diluent</td>
<td>13</td>
<td>21.4%L1, 15.8% L2</td>
</tr>
<tr>
<td>diluent</td>
<td>Orfom SX-12</td>
<td>Conosol 170ES</td>
</tr>
<tr>
<td>organic washing?</td>
<td>no wash</td>
<td>water wash to pH 1.1</td>
</tr>
<tr>
<td>aqueous removal from organic</td>
<td>none</td>
<td>Wemco coalescers</td>
</tr>
<tr>
<td>crud removal system</td>
<td>pneumatic pump</td>
<td>pneumatic pump</td>
</tr>
<tr>
<td>crud treatment system</td>
<td>Chuquicamata mechanical breakage</td>
<td>centrifuge and pressure filter</td>
</tr>
<tr>
<td>organic cleaning system</td>
<td>clay treatment with Sparkle filter</td>
<td>zeolite treatment</td>
</tr>
<tr>
<td>organic removal from raffinate</td>
<td>Wemco coalescers</td>
<td></td>
</tr>
<tr>
<td><strong>Flowrates per train, m³/hour</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pregnant solution input rate</td>
<td>750</td>
<td>1400 series</td>
</tr>
<tr>
<td>organic flowrate, extraction to strip</td>
<td>1040</td>
<td>2400 series-parallel 1500-1650</td>
</tr>
<tr>
<td>depleted electrolyte input rate</td>
<td>180</td>
<td>450-500</td>
</tr>
<tr>
<td>% of electrolyte flow sent to SX</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td><strong>Solution details, kg/m³</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pregnant solution</td>
<td>Cu 4.8</td>
<td>Cu 4.94</td>
</tr>
<tr>
<td>raffinate</td>
<td>H₂SO₄ 5</td>
<td></td>
</tr>
<tr>
<td>barren organic</td>
<td>0.4</td>
<td>0.70</td>
</tr>
<tr>
<td>loaded organic</td>
<td>3</td>
<td>3.33</td>
</tr>
<tr>
<td>depleted electrolyte</td>
<td>5.6</td>
<td>7.40</td>
</tr>
<tr>
<td>enriched electrolyte</td>
<td>37</td>
<td>36.33</td>
</tr>
<tr>
<td>organic removal from electrolyte</td>
<td>52</td>
<td>40.29</td>
</tr>
<tr>
<td>electrolyte treatment before tankhouse</td>
<td>garnet/anthracite filtration</td>
<td>sand/garnet/anthracite filtration</td>
</tr>
</tbody>
</table>
equivalent leach and electrowinning plants are given in Chapters 17 and 19.

<table>
<thead>
<tr>
<th>Zaldivar</th>
<th>Hellenic Copper</th>
<th>Morenci (Stargo)</th>
</tr>
</thead>
<tbody>
<tr>
<td>145 000</td>
<td>8000</td>
<td>156 000</td>
</tr>
<tr>
<td>4800</td>
<td>520</td>
<td>4320</td>
</tr>
</tbody>
</table>

- 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
- Outokumpu Spirok and Dop pump mixers

- Ti & 316L stainless steel
- 316L stainless steel
- stainless steel

- 23.5 × 25 × 0.9
- 22 × 9 × 1
- 24 × 6 × 1.25
- 3 picket fences

- 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

- 15
- 15
- 0.375

- 0.5
- 0.7
- 12

- LIX 984 NC
- Acorga M5640
- LIX 984

- 14.3
- 14.0
- 21

- Orfom SX 12
- no wash
- 1 wash stage mixer-settler

- one wash mixer-settler
- aqueous entrainment pumps in loaded organic tank
- drain loaded organic tank

- 8 Disep garnet/anthracite filters
- diaphragm pump
- interface pumping and settler dumping

- clay treatment + centrifuge + clay filter
- filter press
- clay mixing and filter press

- floating absorption system
- pumping from pond
- skinned from organic recovery tanks

- 1200
- 520
- 4320

- 1100
- 350
- 21

<table>
<thead>
<tr>
<th>Cu</th>
<th>H$_2$SO$_4$</th>
<th>Cu</th>
<th>H$_2$SO$_4$</th>
<th>Cu</th>
<th>H$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8</td>
<td>0.55</td>
<td>1.8</td>
<td>1</td>
<td>3.00</td>
<td>3.50</td>
</tr>
<tr>
<td>0.28</td>
<td>6</td>
<td>0.2</td>
<td>4</td>
<td>0.30</td>
<td>7.00</td>
</tr>
<tr>
<td>3</td>
<td>1.3</td>
<td>3.8</td>
<td>9.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.2</td>
<td>3.8</td>
<td>30</td>
<td>180</td>
<td>38.0</td>
<td>200.0</td>
</tr>
<tr>
<td>41.5</td>
<td>165</td>
<td>30</td>
<td>160</td>
<td>50.0</td>
<td>185.0</td>
</tr>
<tr>
<td>55</td>
<td>151</td>
<td>38</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Cominco column flotation
- Disep sand/anthracite filters

- sand/anthracite filters and heat exchanging

- 6 anthracite garnet filters

- organic is floated from rich booster tank
(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-pregant-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/m³ per volume% LIX 984N in organic (Cognis, 1997) |
| Specified organic/aqueous ratio in extraction mixer-settlers (A/O) | 1/1 (m³ organic per hour/m³ aqueous per hour)* |
| Expected pregnant leach solution composition and input rate | 3 kg Cu/m³, 1,000 m³/hour |
| Specified composition of Cu depleted electrolyte from tankhouse | 35 kg Cu/m³ (sufficient to give high-purity cathode copper at electrowinning cell exits) |
| Specified composition of Cu-enriched electrolyte returning to tankhouse | 45 kg Cu/m³ |
| Stripping data from laboratory tests (Cognis, 1997) | 45 kg Cu/m³ in enriched electrolyte is at equilibrium with ~1.5 kg Cu/m³ 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:

\[
\frac{0.25 \text{ kg of Cu extracted}}{\text{per m}^3 \text{ of organic per volume% LIX 984 in the organic}} \times \frac{\text{volume% LIX 984 in the organic}}{\text{volumetric flowrate of organic, m}^3/\text{hour}} = \frac{\text{required Cu extraction from pregnant leach solution into organic, kg Cu/m}^3 \text{ of pregnant leach solution}}{\text{volumetric flowrate of pregnant leach solution, m}^3/\text{hour}}
\]

or:

\[
\text{required Cu extraction from pregnant leach solution into organic, kg Cu/m}^3 \text{ of pregnant leach solution} = \frac{0.25 \text{ kg of Cu extracted per m}^3 \text{ of organic per volume% LIX 984 in the organic}}{\text{volumetric flowrate of organic, m}^3/\text{hour}} \times \frac{\text{volume% LIX 984 in the organic}}{\text{volumetric flowrate of pregnant leach solution, m}^3/\text{hour}}
\]
Solvent Extraction Transfer of Copper

\[
\text{volume}\% \text{ LIX 984N in organic} = \frac{\text{required Cu extraction from pregnant leach solution}}{0.25} \times \text{A/O}. 
\]

(where A/O is the aqueous/organic volumetric ratio entering the extraction mixer-settler).

Extraction of Cu from a 3 kg Cu/m\(^3\) pregnant leach solution with the Table 18.3-prescribed A/O volume ratio of 1/1 requires, therefore:

\[
\text{volume}\% \text{ LIX 984N in organic} = \frac{3}{0.25} \times 1 = 12\%
\]

So each train of the solvent extraction plant requires pumping of 1000 m\(^3\)/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/m\(^3\) pregnant solution, the raffinate leaving the series of two extraction mixer-settlers will contain \(~0.3\) kg Cu/m\(^3\) 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:

\[
\text{Cu extraction rate} = \frac{\text{flow rate, m}^3/\text{hour}}{\text{Cu in pregnant leach solution}} \times \left[ \text{Cu in pregnant leach solution} - \text{Cu in raffinate} \right] \quad (18.4).
\]

In this case it is:

\[
\text{Cu extraction rate} = 1000 \text{ m}^3/\text{hour leach solution} \times \left[ \frac{3 \text{ kg Cu/m}^3 \text{ of pregnant leach solution}}{0.3 \text{ kg Cu/m}^3 \text{ of raffinate}} - \text{of raffinate} \right]
\]

\[= 2700 \text{ kg Cu/hour}.\]
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 (~185 kg H₂SO₄/m³ 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:

~1.5 kg Cu/m³ 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.:

\[
\text{electrowinning rate} = \frac{\text{electrolyte flowrate to and from solvent extraction, m}^3/\text{hour}}{\text{Cu in electrolyte leaving solvent extraction, kg Cu/m}^3} - \frac{\text{Cu in electrolyte entering solvent extraction, kg Cu/m}^3}{(45 - 35)} \]

from which the electrolyte flowrate in and out of the strip mixer-settler is:

\[
\text{electrolyte flowrate} = \frac{2700 \text{ kg Cu/hour}}{(45 - 35)} \times 270 \text{ m}^3 \text{ of electrolyte per hour}
\]

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 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-H\(_2\)SO\(_4\) 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/m\(^3\) H\(_2\)SO\(_4\)) of the pregnant leach solution. Stripping of Cu from the organic extractant is favored by the high acid concentration (170-200 kg/m\(^3\) H\(_2\)SO\(_4\)) 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


Jergensen, G.V. (1999) Copper Leaching, Solvent Extraction, and Electrowinning Technology, SME, Littleton, CO.


References


Chevron Phillips (2002) Orfom SX 12 Solvent Extraction Diluent www.cpchem.co (Mining chemicals, Orfom SX 12)


Lightnin (2002) Solvent extraction. www.lightnin-mixers.com (Your industry, Mining and minerals, Solvent extraction)


Electrowinning

(Written with Tim Robinson, CTI Ancor, Phoenix, AZ)

Chapters 17 and 18 show how leaching and solvent extraction produce CuSO₄-
H₂SO₄-H₂O electrolyte with ~45 kg/m³ 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 CuSO₄-
H₂SO₄-H₂O 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.:

$$\text{Cu}^{++} + 2e^- \rightarrow \text{Cu}^0 \quad E^o = +0.34 \text{ V} \quad (16.2).$$

The anode reaction is, however, completely different. It is formation of oxygen gas at the inert anode:

$$\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \quad E^o = -1.23 \text{ V} \quad (19.1).$$

The overall electrowinning reaction is the sum of Reactions (16.2) and (19.1) plus sulfate ions:

$$\text{Cu}^{++} + \text{SO}_4^{--} + \text{H}_2\text{O} \rightarrow \text{Cu}^0 + \frac{1}{2}\text{O}_2 + 2\text{H}^+ + \text{SO}_4^{--} \quad E^o = -0.89 \text{ V} \quad (19.2).$$

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.:

<table>
<thead>
<tr>
<th>Cells</th>
<th>Anodes</th>
<th>Cathodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>polymer concrete, 6.5 m long × 1.2 m wide × 1.5 m deep</td>
<td>rolled Pb-Sn-Ca alloy, 1.1 m long × 0.9 m wide × 0.006 m thick</td>
<td>stainless steel, 1.2 m long × 1.0 m wide × 0.003 m thick</td>
</tr>
</tbody>
</table>

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 electrowinnery 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.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Cerro Colorado</th>
<th>El Abra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operation Cerro Colorado</td>
<td>1994</td>
<td>1996</td>
</tr>
<tr>
<td>Cathode production, tonnes/year</td>
<td>130 000</td>
<td>218 000</td>
</tr>
<tr>
<td>Electrolytic cells</td>
<td></td>
<td></td>
</tr>
<tr>
<td>total number</td>
<td>420</td>
<td>680</td>
</tr>
<tr>
<td>construction material</td>
<td>polymer concrete</td>
<td>polymer concrete</td>
</tr>
<tr>
<td>lining material</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>length x width x depth (inside), m</td>
<td>6.39 x 1.27 x 1.42</td>
<td>6.57 x 1.2 x 1.4</td>
</tr>
<tr>
<td>anodes, cathodes per cell</td>
<td>63, 62</td>
<td>67, 66</td>
</tr>
<tr>
<td>spacers between anodes &amp; cathodes</td>
<td></td>
<td>2 'yo-yo' type</td>
</tr>
<tr>
<td>cell inspection system</td>
<td>OSI CP 1000</td>
<td>gaussmeter (once a day)</td>
</tr>
<tr>
<td>time between cell cleanouts, days</td>
<td>45</td>
<td>120</td>
</tr>
<tr>
<td>mist suppression system</td>
<td>BB's and ventilation</td>
<td>balls, FC 1100</td>
</tr>
<tr>
<td>electrolyte input arrangement</td>
<td>5.1 cm diameter bottom manifold with 120 six mm holes angled 45° up</td>
<td>PVC cell distributor with 7 mm holes 45° upward</td>
</tr>
</tbody>
</table>

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 x width x thickness                     | 1.077 x 0.94 x 0.006 m | 1.1 x 0.94 x 0.006 m |
| 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 x width x thickness                      | 1 x 1 x ?               | 1.05 x 1.3 x 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          | Epco/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/m²                   | 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, m³/minute      | 0.2                      | 0.22                    |

into cells

| Cu, kg/m³                                      | 41                       | 44                      |
| H₂SO₄, kg/m³                                  | 175                      | 170                     |
| temperature, °C                                | 50                       | 43                      |

out of cells

| Cu, kg/m³                                      | 38                       | 36                      |
| H₂SO₄, kg/m³                                  | 180                      | 183                     |
| temperature, °C                                | 51                       | 45                      |

other electrolyte components

| Fe⁺⁺⁺, kg/m³                                   | 0.4                      | 0.21                    |
| Fe⁺⁺⁺⁺, kg/m³                                  | 1.5                      | 1.5                     |
| Co⁺⁺, ppm                                     | 150                      | 150                     |
| Cl⁻, ppm                                      | 20                       | 35                      |
| Mn⁺⁺, ppm                                     | 38                       |                         |

addition rates, g per tonne of cathode

| guar gum                                       | 270                      | 300-350                 |
| other                                          | 430                      | 150 ppm                 |

electrolyte treatments before entering tankhouse

| gamet/thrombolite filtration, heat exchange    |                         |                         |

electrolyte bleed rate, m³/day

| Pb in cathodes                                 | 60                       | 240                     |
| Cl⁻ and Fe⁺⁺⁺                                  |                         |                         |

destination

| raffinate pond                                 |                         |                         |
| SX wash stage & other                          |                         |                         |
Electrowinning

Additional details are given in Jenkins et al., 1999.

<table>
<thead>
<tr>
<th>Zaldivar</th>
<th>Hellenic Copper</th>
<th>Morenci, Stargo</th>
</tr>
</thead>
<tbody>
<tr>
<td>145 000</td>
<td>5200</td>
<td>146 000</td>
</tr>
<tr>
<td>368</td>
<td>50</td>
<td>324</td>
</tr>
<tr>
<td>polymer concrete none</td>
<td>precast monolithic concrete paraliner</td>
<td>CTI polymer concrete none</td>
</tr>
<tr>
<td>6.7 × 1.2 × 1.5</td>
<td>3.48 × 1.25 × 1.5</td>
<td>6.98 × 1.18 × 1.37</td>
</tr>
<tr>
<td>64/63</td>
<td>31/30</td>
<td>66/65</td>
</tr>
<tr>
<td>two ‘butterflies’ on bottom corners</td>
<td>polymer cones on bottom corners</td>
<td>vinyl-ester cap blocks</td>
</tr>
<tr>
<td>IR camera, twice daily</td>
<td>gaussmeter</td>
<td>IR camera, hand held</td>
</tr>
<tr>
<td>60</td>
<td>365</td>
<td>90</td>
</tr>
<tr>
<td>19 mm balls, FC 1100, ventilation manifold with 120 six mm holes</td>
<td>plastic balls</td>
<td>cell bottom manifold</td>
</tr>
<tr>
<td>98.6 Pb, 1.3 Sn, 0.08 Ca</td>
<td>98.4 Pb, 1.5 Sn, 0.1 Ca</td>
<td>98.5 Pb, 1 Sn, 0.5 Ca</td>
</tr>
<tr>
<td>rolled</td>
<td>rolled</td>
<td>rolled</td>
</tr>
<tr>
<td>1.04 × 0.93 × 0.009</td>
<td>1.092 × 0.92 × 0.006</td>
<td>1.04 × 0.914 × 0.015</td>
</tr>
<tr>
<td>10.1</td>
<td>10</td>
<td>10.2</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>ISA 316L stainless steel 1.23 × 1.03 × 0.003</td>
<td>ISA 316L stainless steel 1.079 × 1.036 × 0.003</td>
<td>ISA 316L stainless steel 1.245 × 0.99 × 0.003</td>
</tr>
<tr>
<td>polypropylene wax</td>
<td>CPVC</td>
<td>single durometer CPCV</td>
</tr>
<tr>
<td>5</td>
<td>7-10</td>
<td>none</td>
</tr>
<tr>
<td>40</td>
<td>50-60</td>
<td>43.2</td>
</tr>
<tr>
<td>Wenmec/ISA machine Pb&lt;2, S&lt;4, Fe&lt;2</td>
<td>semi-automatic machine</td>
<td>Wenmec machine Pb&lt;3, S&lt;4</td>
</tr>
<tr>
<td>317-326</td>
<td>150-275</td>
<td>290</td>
</tr>
<tr>
<td>91</td>
<td>88-92</td>
<td>93</td>
</tr>
<tr>
<td>1.9</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>42</td>
<td>10-18</td>
<td>45</td>
</tr>
<tr>
<td>1840</td>
<td>2000</td>
<td>1900</td>
</tr>
<tr>
<td>0.36</td>
<td>0.11</td>
<td>0.19</td>
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<tr>
<td>44</td>
<td>44</td>
<td>44</td>
</tr>
<tr>
<td>148</td>
<td>150</td>
<td>196</td>
</tr>
<tr>
<td>50</td>
<td>42</td>
<td>47.2</td>
</tr>
<tr>
<td>43</td>
<td>37</td>
<td>38</td>
</tr>
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<td>165</td>
<td>165</td>
<td>199</td>
</tr>
<tr>
<td>50</td>
<td>42</td>
<td>48.2</td>
</tr>
<tr>
<td>0.17</td>
<td>0.5</td>
<td>0.28</td>
</tr>
<tr>
<td>1.5</td>
<td>1.5</td>
<td>1.25</td>
</tr>
<tr>
<td>140</td>
<td>100</td>
<td>130</td>
</tr>
<tr>
<td>&lt;5</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Mn 2</td>
<td>Mn 35, Pb 0.05</td>
<td></td>
</tr>
<tr>
<td>250 Co&quot; 800</td>
<td>Co&quot; to 100 ppm</td>
<td>250 Co&quot;</td>
</tr>
<tr>
<td>Cominco column flotation, Disep sand anthracite filters 300</td>
<td>dual media filter</td>
<td>anthracite/garnet filters, heat exchangers</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>CI, Fe</td>
<td>Fe and Mn</td>
</tr>
<tr>
<td>raffinate pond</td>
<td>pregnant leach solution</td>
<td>pregnant leach solution</td>
</tr>
</tbody>
</table>
19.2.4 Electrolyte

Electrowinning electrolyte typically contains 44 kg Cu\(^{++}\) and 170 kg H\(_2\)SO\(_4\) per m\(^3\) as it enters an electrowinning cell. It contains ~5 kg Cu\(^{++}\) less per m\(^3\) 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 O\(_2\) 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:

\[
2\text{Cl}^- + \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Cl}_2 + 2(\text{OH})^- \quad (19.3).
\]

This Cl\(_2\) '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 PbSO₄ 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.

$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ 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.

---

\textbf{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 Cu$^{++}$ 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 CuSO$_4$-H$_2$SO$_4$-H$_2$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 electorefined 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


References


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>
<thead>
<tr>
<th>Source of Scrap</th>
<th>Disposed</th>
<th>Collected</th>
<th>Landfilled</th>
<th>Percent Recycled</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power, Telecommunications, Railway Cables</td>
<td>197</td>
<td>197</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Electric Appliances, Machinery</td>
<td>142</td>
<td>29</td>
<td>113</td>
<td>20</td>
</tr>
<tr>
<td>Automotive</td>
<td>79</td>
<td>38</td>
<td>41</td>
<td>48</td>
</tr>
<tr>
<td>Industrial machines, ships, rail cars</td>
<td>62</td>
<td>51</td>
<td>11</td>
<td>82</td>
</tr>
<tr>
<td>Buildings</td>
<td>118</td>
<td>81</td>
<td>37</td>
<td>69</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>598</strong></td>
<td><strong>396</strong></td>
<td><strong>202</strong></td>
<td><strong>66</strong></td>
</tr>
</tbody>
</table>

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, revert, 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.
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.
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


References


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.:

$$C + \frac{1}{2}O_2 \rightarrow CO + \text{ heat}$$

O$_2$ 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.:

$$CO + Cu_2O \rightarrow CO_2 + 2Cu^\circ(\ell)$$

$$CO + ZnO \rightarrow CO_2 + Zn^\circ(g)$$

$$CO + PbO \rightarrow CO_2 + Pb^\circ(\ell,g)$$

$$CO + NiO \rightarrow CO_2 + Ni^\circ(\ell)$$

$$CO + SnO_2 \rightarrow CO_2 + SnO(\ell,g)$$

$$CO + SnO \rightarrow CO_2 + Sn^\circ(\ell)$$

Metallic iron in the scrap also performs some reduction, especially of easily reduced oxides like Cu$_2$O:

$$Fe + Cu_2O \rightarrow FeO(\ell) + 2Cu^\circ(\ell)$$

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, Al$_2$O$_3$, SiO$_2$ along with 0.6-1.0% Cu (as Cu$_2$O), 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, CO$_2$ and N$_2$ 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% $O_2$
(b) inclusion of scrap iron in the charge.

Oxygen enrichment:

(a) increases smelting rate by decreasing the amount of $N_2$ that must be blown up the furnace shaft
(b) decreases the coke requirement (per tonne of copper) by decreasing the amount of $N_2$ 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 (NeImes, 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)
rcverberatory 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).
Sludges and pulverized materials

Crushable non-metallic in-plant reverts

Concentrate feeding system

>6 mm

Low grade scrap

<6 mm

Regular metallic scrap

Screening

Chute

>50 mm

Smelting furnace

6 to 50 mm

Scrap pressing

Chute

>6 mm

Through lance

Converting furnace

<6 mm

Anode scrap

Through sidewall

Boat

Defective anodes, used anode molds etc.

Chute

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 electorefining. Electorefining 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


References


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 electorefining 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 electorefining 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.
Selenium and tellurium form Cu$_2$Se and Cu$_2$Te, 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 22.1. 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.)

<table>
<thead>
<tr>
<th>Element</th>
<th>ASTM B-115 Grade 1</th>
<th>BS EN 1978 Grade 1</th>
<th>IWCC High Grade</th>
<th>SCR (Southwire) Classification System</th>
</tr>
</thead>
<tbody>
<tr>
<td>% Cu+Ag</td>
<td>99.95</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Se (ppm)</td>
<td>2</td>
<td>10</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Te (ppm)</td>
<td>2</td>
<td>5</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>Bi (ppm)</td>
<td>1</td>
<td>3</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>Bi+Se+Te (ppm)</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Sb (ppm)</td>
<td>4</td>
<td>15</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>5</td>
<td>40</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>As (ppm)</td>
<td>5</td>
<td>15</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>10</td>
<td>25</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>10</td>
<td>20</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Sn (ppm)</td>
<td>5</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S (ppm)</td>
<td>15</td>
<td>25</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Ag (ppm)</td>
<td>25</td>
<td>70</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>Co (ppm)</td>
<td>3</td>
<td>5</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>Mn (ppm)</td>
<td>3</td>
<td>5</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>5</td>
<td>20</td>
<td></td>
<td>15</td>
</tr>
<tr>
<td>Total (ppm)</td>
<td>65</td>
<td>65</td>
<td>65</td>
<td></td>
</tr>
</tbody>
</table>
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.)

<table>
<thead>
<tr>
<th>Element</th>
<th>CDA Cu–ETP–1 (Grade 1)</th>
<th>CDA Cu–ETP–2 (Grade 2)</th>
<th>ASTM B216–97</th>
<th>BS 1038</th>
</tr>
</thead>
<tbody>
<tr>
<td>%Cu (min.)</td>
<td>99.95</td>
<td>99.90</td>
<td>99.88</td>
<td>99.85</td>
</tr>
<tr>
<td>Ag (ppm)</td>
<td>25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>As (ppm)</td>
<td>05</td>
<td>120</td>
<td>0200</td>
<td></td>
</tr>
<tr>
<td>Sb (ppm)</td>
<td>04</td>
<td>030</td>
<td>0050</td>
<td></td>
</tr>
<tr>
<td>Bi (ppm)</td>
<td>02</td>
<td>005</td>
<td>030</td>
<td>0030</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>10</td>
<td></td>
<td>0100</td>
<td></td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>05</td>
<td>050</td>
<td>040</td>
<td>0100</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td></td>
<td>500</td>
<td>0500</td>
<td></td>
</tr>
<tr>
<td>O (ppm)</td>
<td>60</td>
<td>060</td>
<td>550</td>
<td>1000</td>
</tr>
<tr>
<td>Se (ppm)</td>
<td>02</td>
<td>250</td>
<td>0300</td>
<td></td>
</tr>
<tr>
<td>S (ppm)</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te (ppm)</td>
<td>02</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn (ppm)</td>
<td></td>
<td></td>
<td>0100</td>
<td></td>
</tr>
<tr>
<td>Total (ppm)</td>
<td>65</td>
<td>300</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

removal of inadvertently absorbed hydrogen during melting by the reaction:

$$[O] + 2[H] \rightarrow H_2O(g)$$

(22.1).

This reduces the amount of porosity created by $H_2O(g)$ 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 Cu₂O 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 Cu₂O 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>
<thead>
<tr>
<th>Processing Facility</th>
<th>Copper processed in 1999, kilotonnes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire rod mills</td>
<td>2259.6</td>
</tr>
<tr>
<td>Brass mills</td>
<td>1878.2</td>
</tr>
<tr>
<td>Foundaries</td>
<td>167.3</td>
</tr>
<tr>
<td>Powder plants</td>
<td>18.1</td>
</tr>
<tr>
<td>Other</td>
<td>82.8</td>
</tr>
</tbody>
</table>

**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.

<table>
<thead>
<tr>
<th>Melting plant</th>
<th>Nexans Canada Montreal</th>
<th>Phelps Dodge Refinery El Paso, U.S.</th>
<th>Norddeutsche Affinerie Germany</th>
<th>Palabora Mining South Africa</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inputs</strong></td>
<td>cathodes and 'runaround' scrap rod</td>
<td>cathodes</td>
<td>cathodes</td>
<td>cathodes and recycled scrap</td>
</tr>
<tr>
<td><strong>Molten copper destination</strong></td>
<td>Hazelett caster &amp; rod mill</td>
<td>Hazelett caster &amp; rod mill</td>
<td>Southwire caster &amp; rod mill</td>
<td>Southwire caster &amp; rod mill</td>
</tr>
<tr>
<td><strong>Melting rate, tonnes of copper per hour</strong></td>
<td>48</td>
<td>75</td>
<td>45</td>
<td>35 capacity, 21 operating</td>
</tr>
<tr>
<td><strong>Feed system</strong></td>
<td>skip hoist</td>
<td>elevator with automatic trip</td>
<td>forklift truck &amp; skip hoist</td>
<td>forklift truck</td>
</tr>
<tr>
<td><strong>Furnace details, m</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>height, taphole to charge floor</td>
<td>13</td>
<td>12.2</td>
<td>10</td>
<td>7.9</td>
</tr>
<tr>
<td>inside diameter at charge floor</td>
<td>1.7</td>
<td>1.75</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>inside diameter at taphole</td>
<td>1.3</td>
<td>1.37</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td><strong>Burner details</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>number of burners</td>
<td>23</td>
<td>32</td>
<td>22</td>
<td>23</td>
</tr>
<tr>
<td>rows of burners</td>
<td>3</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>fuel</td>
<td>natural gas</td>
<td>natural gas</td>
<td>natural gas</td>
<td>propane</td>
</tr>
<tr>
<td>combustion rate, Nm³/hour</td>
<td>2400</td>
<td>1100</td>
<td>50 x 10⁶ kJ/h @21.5 t Cu/h</td>
<td></td>
</tr>
<tr>
<td>Nm³ of natural gas burnt per tonne of copper melted</td>
<td>1.9 giga-joules</td>
<td>1.8 giga-joules</td>
<td>26 (furnace only)</td>
<td>2.34 giga-joules</td>
</tr>
<tr>
<td><strong>Refractory life, tonnes of copper</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>above burners</td>
<td>500 000</td>
<td>500 000</td>
<td>3±0.5 years</td>
<td></td>
</tr>
<tr>
<td>below burners</td>
<td>250 000</td>
<td>300 000</td>
<td>3±0.5 years</td>
<td></td>
</tr>
</tbody>
</table>
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 (60–360 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.

![Continuous direct-chill casting machine for casting copper billet (Nussbaum, 1973). Reprinted with permission of TMS.](image-url)
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.

![Diagram of Southwire casting machine](image_url)

**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 Hazelett 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 Hazelett and Southwire continuous casting machines, 2001.

<table>
<thead>
<tr>
<th>Casting plant</th>
<th>Nexans Canada</th>
<th>Phelps Dodge Refinery</th>
<th>Norddeutsche Affinerie</th>
<th>Palabora Mining</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Casting machine</strong></td>
<td>Hazelett twin band</td>
<td>Hazelett twin band</td>
<td>Southwire wheel &amp; band</td>
<td>Southwire wheel &amp; band</td>
</tr>
<tr>
<td><strong>Bar size, cm x cm</strong></td>
<td>7 × 13</td>
<td>7 × 13.2</td>
<td>5.8 × 11.7</td>
<td>2.15 × 15</td>
</tr>
<tr>
<td><strong>Casting rate of this bar, tonnes/hour</strong></td>
<td>48</td>
<td>63</td>
<td>45</td>
<td>21.5</td>
</tr>
<tr>
<td><strong>Molten copper level control in caster</strong></td>
<td>electromagnetic pool level measurement</td>
<td>electromagnetic pool level measurement</td>
<td>X-ray</td>
<td>infrared scanner</td>
</tr>
<tr>
<td><strong>Casting temp., °C</strong></td>
<td>1125</td>
<td>1130</td>
<td>1110-1125</td>
<td>1100-1130</td>
</tr>
<tr>
<td><strong>Bar temperature leaving caster, °C</strong></td>
<td>~950</td>
<td>1015</td>
<td>900</td>
<td>890-930</td>
</tr>
<tr>
<td><strong>Target O in copper, ppm</strong></td>
<td>250</td>
<td>250</td>
<td>160-250</td>
<td>180-250</td>
</tr>
<tr>
<td><strong>control system</strong></td>
<td>Electro-nite cell in launder; Tempolab in holding furnace; Leco on rod manual</td>
<td>compressed air injection into molten Cu</td>
<td>protective gas, larger or smaller quantity</td>
<td>holding furnace CO and launder burner CO</td>
</tr>
<tr>
<td><strong>Wheel and band details</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>wheel diameter, m</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rotation speed, rpm</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rim materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>rim life, tonnes of cast copper</td>
<td>100 000</td>
<td></td>
<td>45 000</td>
<td></td>
</tr>
<tr>
<td>band material</td>
<td></td>
<td>cold rolled steel</td>
<td></td>
<td>steel low split C</td>
</tr>
<tr>
<td>band life</td>
<td></td>
<td>72 hours</td>
<td></td>
<td>1000-1800 t Cu per band</td>
</tr>
<tr>
<td>lubrication</td>
<td></td>
<td>Lubro 30 FM</td>
<td></td>
<td>Thermia B (Shell)</td>
</tr>
<tr>
<td><strong>Twin band details</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>caster length, m</td>
<td>3.7</td>
<td>3.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>band material</td>
<td>low carbon steel</td>
<td>titanium steel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>life</td>
<td>24 hours</td>
<td>1300 tonnes Cu</td>
<td></td>
<td></td>
</tr>
<tr>
<td>lubrication</td>
<td>oil</td>
<td>Union Carbide Lb-300x oil</td>
<td></td>
<td></td>
</tr>
<tr>
<td>dam block material</td>
<td>Si bronze</td>
<td></td>
<td>Cu with 1.7-2% Ni &amp; 0.5-0.9% Si</td>
<td></td>
</tr>
<tr>
<td>dam block life</td>
<td>100 000 tonnes cast copper</td>
<td>~300 hours</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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


References


Copper Development Association (2001) CDA’s annual data '00. www.copper.org


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:

\[
\frac{\text{Cost} \ (\text{year } A)}{\text{Cost} \ (\text{year } B)} = \frac{\text{Index} \ (\text{year } A)}{\text{Index} \ (\text{year } B)}
\]  

(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.
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 ±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 electorefined 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:

\[
\text{plant cost} = \frac{\text{investment cost per annual tonne of copper}}{\text{plant capacity, tonnes of copper per year}} \times \text{plant capacity, tonnes of copper per year} \quad (23.2).
\]

This equation shows, for example, that the investment in an electorefinery
which:

(a) costs $500 per annual tonne of copper
(b) produces 200 000 tonnes of copper per year

will be:

\[
\text{investment cost} = \frac{\$500 \text{ per annual tonne of copper}}{} \times \frac{200 000 \text{ tonnes of copper per year}}{}
\]

or:

\[\$100 \times 10^6.\]

Table 23.1 indicates that the fixed capital investment for a complex which produces electrorefined 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.

<table>
<thead>
<tr>
<th>Facility</th>
<th>Fixed investment cost (U.S. per annual tonne of Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mine (open pit)</td>
<td>3000</td>
</tr>
<tr>
<td>Concentrator</td>
<td>2500</td>
</tr>
<tr>
<td>Smelter (Outokumpu flash furnace smelting/converting), including sulfuric acid plant</td>
<td>2500</td>
</tr>
<tr>
<td>Electrolytic refinery (excluding precious metals refinery)</td>
<td>500</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>8500</strong></td>
</tr>
</tbody>
</table>
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/smelting/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.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Direct operating cost ($U.S. per kg of Cu)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Open pit mining, 0.75% Cu ore @ $1.6/tonne of ore</td>
<td>0.25</td>
</tr>
<tr>
<td>Beneficiation from 0.75% Cu ore to 30% Cu concentrate at shipping point, including tailings disposal @ $2.5/tonne of ore</td>
<td>0.35</td>
</tr>
<tr>
<td>Smelting @ $80/tonne of 30% Cu concentrate including sulfuric acid production</td>
<td>0.3</td>
</tr>
<tr>
<td>Electrolytic refining, excluding precious metals recovery</td>
<td>0.1</td>
</tr>
<tr>
<td>Sales and distribution</td>
<td>0.05</td>
</tr>
<tr>
<td>Local management and overhead</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Total direct operating cost</strong></td>
<td><strong>1.10</strong></td>
</tr>
</tbody>
</table>

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:

$$\text{Finance charges per tonne of copper} = \frac{\text{Finance charges, } \$/\text{year}}{\text{Copper production, tonnes/ year}}$$

$$= \frac{12\% \text{ per year} \times 100\% \times \text{total capital investment, } \$}{\text{Copper production, tonnes/ year}}$$

$$= 0.12 \times (\text{capital investment per annual tonne of copper})$$

or

$$\text{Finance charges per tonne of copper} = \text{\$1100 per tonne of copper}^*$$

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.
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 electorefining (with some additional treatment) and sold. Other orebodies contain MoS₂ 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 $10 \times 10^6$ tonnes of ore per year concentrator will cost $200 \times 10^6$.

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.

<table>
<thead>
<tr>
<th>Section</th>
<th>Percent of total investment cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ore handling, storage, conveying equipment</td>
<td>10</td>
</tr>
<tr>
<td>Semi-autogenous grinding mill, ball mills and size classifiers</td>
<td>50</td>
</tr>
<tr>
<td>Flotation cells and associated equipment</td>
<td>10</td>
</tr>
<tr>
<td>Dewatering equipment, tailings dam, concentrate loading facilities</td>
<td>30</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Cost per tonne of ore ($U.S.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crushing, conveying, storage</td>
<td>0.4</td>
</tr>
<tr>
<td>Semi-autogenous grinding, ball mill grinding, size classification</td>
<td>1.3</td>
</tr>
<tr>
<td>Flotation</td>
<td>0.4</td>
</tr>
<tr>
<td>Dewatering, filtering, drying, storage and loading of concentrate</td>
<td>0.2</td>
</tr>
<tr>
<td>Tailings disposal, effluent control, water recycle</td>
<td>0.15</td>
</tr>
<tr>
<td>Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>2.5</strong></td>
</tr>
</tbody>
</table>

Table 23.5. Concentrator operating costs by cost component. Expenditures on energy, manpower, supplies and overhead are shown. Ore cost is not included.

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent of concentrating cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrical energy</td>
<td></td>
</tr>
<tr>
<td>crushing and grinding</td>
<td>25</td>
</tr>
<tr>
<td>flotation and tailings disposal</td>
<td>3</td>
</tr>
<tr>
<td>other (including hydrocarbon fuel)</td>
<td>2</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>30</strong></td>
</tr>
<tr>
<td>Operating labor</td>
<td>5</td>
</tr>
<tr>
<td>Maintenance labor</td>
<td>5</td>
</tr>
<tr>
<td>Maintenance and operating supplies, including freight and handling</td>
<td>30</td>
</tr>
<tr>
<td>Reagents and grinding balls</td>
<td></td>
</tr>
<tr>
<td>reagents and lime</td>
<td>10</td>
</tr>
<tr>
<td>grinding media</td>
<td>15</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>25</strong></td>
</tr>
<tr>
<td>Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)</td>
<td>5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Item</th>
<th>Percent of smelter cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate handling and drying, including delivery of dry concentrate to smelting furnace</td>
<td>10</td>
</tr>
<tr>
<td>Oxygen plant</td>
<td>10</td>
</tr>
<tr>
<td>Flash furnace</td>
<td>20</td>
</tr>
<tr>
<td>Flash converter, including matte granulation and crushing</td>
<td>15</td>
</tr>
<tr>
<td>Cu-from-slag recovery equipment (electric furnace or flotation) including barren slag disposal</td>
<td>10</td>
</tr>
<tr>
<td>Anode furnaces and anode casting equipment</td>
<td>10</td>
</tr>
<tr>
<td>Gas handling system including waste heat boilers, electrostatic precipitators and sulfuric acid plant</td>
<td>25</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

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
- Mitsubishi
- Outokumpu flash
- Isasmelt
- Noranda
- 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.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Cost, $U.S. per tonne of concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentrate reception, storage and delivery to dryer</td>
<td>5</td>
</tr>
<tr>
<td>Flash furnace smelting including concentrate drying, gas handling and delivery of 70% Cu crushed matte granules to flash converting</td>
<td>20</td>
</tr>
<tr>
<td>Flash converting including delivery of molten copper to anode furnaces</td>
<td>20</td>
</tr>
<tr>
<td>Cu recovery from smelting slag</td>
<td>15</td>
</tr>
<tr>
<td>Anode-making including desulfurization and deoxidation of molten copper, anode casting and loading for transport to electorefinery</td>
<td>5</td>
</tr>
<tr>
<td>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</td>
<td>10</td>
</tr>
<tr>
<td>Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)</td>
<td>5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>80</strong></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Component</th>
<th>Percent of smelting cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen</td>
<td>10</td>
</tr>
<tr>
<td>Operating manpower, including supervision</td>
<td>20</td>
</tr>
<tr>
<td>Maintenance manpower, including supervision</td>
<td>10</td>
</tr>
<tr>
<td>Electricity (excluding electricity used for making oxygen)</td>
<td>10</td>
</tr>
<tr>
<td>Hydrocarbon fuel</td>
<td>5</td>
</tr>
<tr>
<td>Flux and refractories</td>
<td>5</td>
</tr>
<tr>
<td>Other maintenance supplies</td>
<td>35</td>
</tr>
<tr>
<td>Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)</td>
<td>5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
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>
<thead>
<tr>
<th>Component</th>
<th>Percent of total fixed investment cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode reception, weighing, straightening, lug milling, sampling equipment</td>
<td>10</td>
</tr>
<tr>
<td>Production electrorefining equipment including stainless steel blanks, polymer concrete cells, transformers, rectifiers, electrical distribution system</td>
<td>55</td>
</tr>
<tr>
<td>Electrolyte circulation and purification equipment including filters, heaters, pumps, storage tanks, reagent addition equipment, electrowinning cells</td>
<td>15</td>
</tr>
<tr>
<td>Cathode handling equipment including stripping, washing, weighing, sampling and bundling equipment</td>
<td>5</td>
</tr>
<tr>
<td>Anode (and purchased) scrap melting and anode casting equipment – including Asarco shaft furnace, holding furnace, pouring equipment and Hazelett anode caster</td>
<td>15</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Activity</th>
<th>Cost, $U.S. per kg of cathode Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode reception, weighing, straightening, lug milling, delivery to tankhouse*</td>
<td>0.010</td>
</tr>
<tr>
<td>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</td>
<td>0.050</td>
</tr>
<tr>
<td>Cathode handling including stripping, washing, weighing, quality control and delivery to loading docks</td>
<td>0.010</td>
</tr>
<tr>
<td>Anode scrap washing and melting, purchased scrap melting, anode casting and anode delivery to tankhouse</td>
<td>0.010</td>
</tr>
<tr>
<td>Cu recovery from slimes</td>
<td>0.005</td>
</tr>
<tr>
<td>Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)</td>
<td>0.005</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.090</strong></td>
</tr>
</tbody>
</table>

* 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.

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage of electrorefining cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating manpower, including supervision</td>
<td>30</td>
</tr>
<tr>
<td>Maintenance manpower, including supervision</td>
<td>10</td>
</tr>
<tr>
<td>Electricity</td>
<td>30</td>
</tr>
<tr>
<td>Maintenance materials</td>
<td>20</td>
</tr>
<tr>
<td>Reagents and fossil fuel</td>
<td>5</td>
</tr>
<tr>
<td>Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)</td>
<td>5</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>100</strong></td>
</tr>
</tbody>
</table>

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.

<table>
<thead>
<tr>
<th>Component</th>
<th>$U.S. per annual tone of copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heap leach system including leach pad, crusher, agglomerating drum, on-off heap building and removal equipment, piping, pumps, solution collection ponds etc.</td>
<td>1600</td>
</tr>
<tr>
<td>Solvent extraction plant including mixer-settlers, pumps, piping, storage tanks and initial extractant and diluent</td>
<td>400</td>
</tr>
<tr>
<td>Electrowinning plant including electrical equipment, polymer concrete cells, rolled Pb-Sn-Ca anodes, stainless steel cathodes, cranes, cathode stripping, washing and handling equipment</td>
<td>700</td>
</tr>
<tr>
<td>Utilities and infrastructure</td>
<td>500</td>
</tr>
<tr>
<td>Engineering services, contingency, escalation etc.</td>
<td>300</td>
</tr>
<tr>
<td><strong>Total (Dufresne, 2000)</strong></td>
<td><strong>3500</strong></td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Item</th>
<th>$/kg of copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heap leach operation including crushing, acid curing, agglomeration, on-off heap construction/removal, solution delivery and collection</td>
<td>0.10</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>0.05</td>
</tr>
<tr>
<td>Solvent extraction plant operation, including maintenance</td>
<td>0.03</td>
</tr>
<tr>
<td>Reagent make-up: extractant, diluent, guar and CoSO₄·7H₂O</td>
<td>0.04</td>
</tr>
<tr>
<td>Electrowinning tankhouse operation, delivering cathode plates to loadout platform</td>
<td>0.15</td>
</tr>
<tr>
<td>Local overhead (accounting, clerical, environmental, human resources, laboratory, management, property taxes, safety)</td>
<td>0.03</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>0.40</strong></td>
</tr>
</tbody>
</table>

Unfortunately, chalcopyrite ore (the world's largest source of copper) cannot be processed by heap leach/solvent extraction/electrowinning, Chapter 17. Chalcopryrite ores must be treated by conventional concentration/smelting/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/smelting. 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 electrefining 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/smelting/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


## Appendix A

### Stoichiometric Data for Copper Extraction

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW, kg/kg mol</th>
<th>% Metal</th>
<th>%O or S</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>101.96</td>
<td>52.9</td>
<td>47.1</td>
</tr>
<tr>
<td>CH₄</td>
<td>16.04</td>
<td>74.9</td>
<td>25.1</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>30.07</td>
<td>79.9</td>
<td>20.1</td>
</tr>
<tr>
<td>CO</td>
<td>28.01</td>
<td>42.9</td>
<td>57.1</td>
</tr>
<tr>
<td>CO₂</td>
<td>44.01</td>
<td>27.3</td>
<td>72.7</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>100.09</td>
<td>56.0% CaO</td>
<td>44.0% CO₂</td>
</tr>
<tr>
<td>CaO</td>
<td>56.08</td>
<td>71.5</td>
<td>28.5</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>151.99</td>
<td>68.4</td>
<td>31.6</td>
</tr>
<tr>
<td>CuCO₃·Cu(OH)₂</td>
<td>221.12</td>
<td>57.5</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.9 H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>36.2 O</td>
</tr>
<tr>
<td>(CuCO₃)₂·Cu(OH)₂</td>
<td>344.67</td>
<td>55.3</td>
<td>7.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.6 H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>37.1 O</td>
</tr>
<tr>
<td>Cu₂Cl(OH)₃</td>
<td>213.57</td>
<td>59.5</td>
<td>16.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1.4 H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>22.5 O</td>
</tr>
<tr>
<td>CuFeS₂</td>
<td>183.51</td>
<td>34.6 Cu</td>
<td>35.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30.4 Fe</td>
<td></td>
</tr>
<tr>
<td>Cu₅FeS₄</td>
<td>501.82</td>
<td>63.3 Cu</td>
<td>25.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.1 Fe</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>79.55</td>
<td>79.9</td>
<td>20.1</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>143.09</td>
<td>88.8</td>
<td>11.2</td>
</tr>
<tr>
<td>CuSiO₃·2H₂O</td>
<td>175.66</td>
<td>36.2</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>27.3 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>34.2 SiO₂</td>
</tr>
<tr>
<td>CuS</td>
<td>95.61</td>
<td>66.5</td>
<td>33.5</td>
</tr>
<tr>
<td>Cu₂S</td>
<td>159.15</td>
<td>79.9</td>
<td>20.1</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>159.60</td>
<td>39.8</td>
<td>40.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.1 S</td>
</tr>
<tr>
<td>CuSO₄·CuO</td>
<td>239.15</td>
<td>53.1</td>
<td>33.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>13.4 S</td>
</tr>
<tr>
<td>CuSO₄·2Cu(OH)₃</td>
<td>354.72</td>
<td>53.7</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>36.1 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>9.0 S</td>
</tr>
<tr>
<td>Compound</td>
<td>MW, kg/kg mol</td>
<td>% Metal</td>
<td>%O or S</td>
</tr>
<tr>
<td>---------------------------</td>
<td>---------------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>CuSO$_4$:3Cu(OH)$_2$</td>
<td>452.29</td>
<td>56.2</td>
<td>1.2 H</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>35.4 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>7.1 S</td>
</tr>
<tr>
<td>Cu$_2$SO$_4$</td>
<td>223.15</td>
<td>57.0</td>
<td>28.6 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>14.4 S</td>
</tr>
<tr>
<td>FeO</td>
<td>71.85</td>
<td>77.7</td>
<td>22.3</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>159.69</td>
<td>69.9</td>
<td>30.1</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>231.54</td>
<td>72.4</td>
<td>27.6</td>
</tr>
<tr>
<td>FeS</td>
<td>87.91</td>
<td>63.5</td>
<td>36.5</td>
</tr>
<tr>
<td>FeS$_{1.14}$</td>
<td>92.40</td>
<td>60.4</td>
<td>39.6</td>
</tr>
<tr>
<td>FeS$_2$</td>
<td>119.97</td>
<td>46.6</td>
<td>53.4</td>
</tr>
<tr>
<td>FeSO$_4$</td>
<td>151.90</td>
<td>36.8</td>
<td>42.1 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>21.1 S</td>
</tr>
<tr>
<td>Fe$_2$(SO$_4$)$_3$</td>
<td>399.87</td>
<td>27.9</td>
<td>48.0 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>24.1 S</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>18.02</td>
<td>11.2</td>
<td>88.8</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>84.31</td>
<td>47.8% MgO</td>
<td>52.2% CO$_2$</td>
</tr>
<tr>
<td>MgO</td>
<td>40.30</td>
<td>60.3</td>
<td>39.7</td>
</tr>
<tr>
<td>NiO</td>
<td>74.69</td>
<td>78.6</td>
<td>21.4</td>
</tr>
<tr>
<td>NiS</td>
<td>90.75</td>
<td>64.7</td>
<td>35.3</td>
</tr>
<tr>
<td>Ni$_3$S$_2$</td>
<td>240.25</td>
<td>73.3</td>
<td>26.7</td>
</tr>
<tr>
<td>NiSO$_4$</td>
<td>154.75</td>
<td>37.9</td>
<td>41.4 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20.7 S</td>
</tr>
<tr>
<td>PbO</td>
<td>223.20</td>
<td>92.8</td>
<td>7.2</td>
</tr>
<tr>
<td>PbS</td>
<td>239.30</td>
<td>86.6</td>
<td>13.4</td>
</tr>
<tr>
<td>PbSO$_4$</td>
<td>303.30</td>
<td>68.3</td>
<td>21.1 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>10.6 S</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>60.08</td>
<td>46.7</td>
<td>53.3</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>64.06</td>
<td>50.0</td>
<td>50.0</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>80.06</td>
<td>40.0</td>
<td>60.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>81.38</td>
<td>80.3</td>
<td>19.7</td>
</tr>
<tr>
<td>ZnS</td>
<td>97.44</td>
<td>67.1</td>
<td>32.9</td>
</tr>
<tr>
<td>ZnSO$_4$</td>
<td>161.44</td>
<td>40.5</td>
<td>39.6 O</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>19.9 S</td>
</tr>
</tbody>
</table>
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 ‘reverb’. It is heated by hydrocarbon fuel combustion.

Concentrate (moist, dry or roasted*) and flux are fed through feedholes along the

![Reverberatory Furnace Diagram](image)

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 SO₂ and (ii) to oxidize iron to iron oxide (Biswas and Davenport, 1994). The results of the roasting are (i) efficient SO₂ 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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Onahama Smelting &amp; Refining, Japan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of furnaces</td>
<td>2</td>
</tr>
<tr>
<td>Hearth size, w x l x h, m</td>
<td>a) $9.73 \times 33.55 \times 3.69$</td>
</tr>
<tr>
<td></td>
<td>b) $11.1 \times 33.27 \times 4.00$</td>
</tr>
<tr>
<td>slag layer thickness, m</td>
<td>0.6-0.9</td>
</tr>
<tr>
<td>matte layer thickness, m</td>
<td>0.4-0.6</td>
</tr>
<tr>
<td>active slag tapholes</td>
<td>1</td>
</tr>
<tr>
<td>active matte tapholes</td>
<td>4</td>
</tr>
</tbody>
</table>

**Burner details**

- number of burners: 6
- endwall or roof: endwall
- combustion 'air' temperature °C: (a) 300; (b) 30
- volume% O₂ 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% SiO₂/mass% Fe: 0.91
- Cu recovery, reverberatory slag: none
- Cu recovery, converter slag: recycle to reverb
- offgas, thousand Nm³/hour: 180
- vol% SO₂, 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:
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 Queneau, 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.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Boliden Limited Ronnskar, Sweden</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Number of electric furnaces</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>Hearth size, w x l x h, m</strong></td>
<td>$7 \times 24 \times 5$</td>
</tr>
<tr>
<td>slag layer thickness, m</td>
<td>1.5</td>
</tr>
<tr>
<td>matte layer thickness, m</td>
<td>0.8</td>
</tr>
<tr>
<td>active slag tapholes</td>
<td>2</td>
</tr>
<tr>
<td>active matte tapholes</td>
<td>2</td>
</tr>
<tr>
<td><strong>Electrical details</strong></td>
<td></td>
</tr>
<tr>
<td>furnace power rating, kW</td>
<td>23 000</td>
</tr>
<tr>
<td>usual applied power, kW</td>
<td>19 000</td>
</tr>
<tr>
<td>usual current, A</td>
<td>38 000</td>
</tr>
<tr>
<td>usual voltage between electrodes, V</td>
<td>180 (towards melt)</td>
</tr>
<tr>
<td>number of electrodes</td>
<td>6</td>
</tr>
<tr>
<td>diameter, m</td>
<td>1.2</td>
</tr>
<tr>
<td>material</td>
<td>self-baking</td>
</tr>
<tr>
<td>normal immersion in slag, m</td>
<td>0.1</td>
</tr>
<tr>
<td>electrode consumption, kg/tonne of new calcine</td>
<td>1.9</td>
</tr>
<tr>
<td>electrical energy consumption kWh/tonne of new calcine</td>
<td>300</td>
</tr>
<tr>
<td><strong>Feed details</strong></td>
<td></td>
</tr>
<tr>
<td>type of charge</td>
<td>roasted concentrate (calcine)</td>
</tr>
<tr>
<td><strong>Feed, tonnes/day (dry basis)</strong></td>
<td></td>
</tr>
<tr>
<td>calcine</td>
<td>930 (27% Cu)</td>
</tr>
<tr>
<td>silica flux</td>
<td>95</td>
</tr>
<tr>
<td>recycle smelting furnace dust</td>
<td>70</td>
</tr>
<tr>
<td>converter dust</td>
<td>15</td>
</tr>
<tr>
<td>molten converter slag</td>
<td>300</td>
</tr>
<tr>
<td>reverts</td>
<td>140</td>
</tr>
<tr>
<td>dried ashes (secondary feed)</td>
<td>260</td>
</tr>
<tr>
<td><strong>Production</strong></td>
<td></td>
</tr>
<tr>
<td>matte, tonnes/day</td>
<td>580 (51% Cu))</td>
</tr>
<tr>
<td>slag, tonnes/day</td>
<td>830 (1.3% Cu)</td>
</tr>
<tr>
<td>mass% SiO$_2$/mass% Fe</td>
<td>0.93</td>
</tr>
<tr>
<td>Cu recovery, electric furnace slag</td>
<td>Zn fuming/settling</td>
</tr>
<tr>
<td>Cu recovery, converter slag</td>
<td>in electric smelting furnace</td>
</tr>
<tr>
<td>offgas production, Nm$^3$/minute</td>
<td>580</td>
</tr>
<tr>
<td>vol% SO$_2$, leaving furnace</td>
<td>4.5</td>
</tr>
<tr>
<td>dust production, tonnes/day</td>
<td>70 (all recycled)</td>
</tr>
<tr>
<td>matte/slag/offgas temperatures, $^\circ$C</td>
<td>1180/1250/800</td>
</tr>
</tbody>
</table>
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).](image)
Table B.3. Operating details of Vanyukov furnace at Balkash, Kazakhstan, 1993.

<table>
<thead>
<tr>
<th>Smelter</th>
<th>Balkash, Kazakhstan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace size, inside brick</td>
<td></td>
</tr>
<tr>
<td>width × length × height, m</td>
<td>2 × 10 × 6</td>
</tr>
<tr>
<td>bath volume, m³</td>
<td></td>
</tr>
<tr>
<td>Feed details, tonnes/day</td>
<td></td>
</tr>
<tr>
<td>concentrate</td>
<td>~1800 (15% Cu)</td>
</tr>
<tr>
<td>flux</td>
<td></td>
</tr>
<tr>
<td>Blast details</td>
<td></td>
</tr>
<tr>
<td>number of operating tuyeres</td>
<td>16</td>
</tr>
<tr>
<td>tuyere diameter, cm</td>
<td>2</td>
</tr>
<tr>
<td>tuyere depth in slag, m</td>
<td></td>
</tr>
<tr>
<td>total blast flowrate, Nm³/h</td>
<td>16 000</td>
</tr>
<tr>
<td>volume% O₂ in blast</td>
<td>93</td>
</tr>
<tr>
<td>blast temperature</td>
<td>ambient</td>
</tr>
<tr>
<td>blast velocity at tuyere tip, m/s</td>
<td></td>
</tr>
<tr>
<td>Production details</td>
<td></td>
</tr>
<tr>
<td>matte grade, %Cu</td>
<td>45</td>
</tr>
<tr>
<td>slag % Cu from smelting furnace</td>
<td>1.5-2</td>
</tr>
<tr>
<td>Cu-from-slag recovery systems</td>
<td></td>
</tr>
<tr>
<td>Vanyukov slag</td>
<td>electric furnace (0.7% Cu after settling)</td>
</tr>
<tr>
<td>converter slag</td>
<td>reverberatory furnace</td>
</tr>
<tr>
<td>offgas production, Nm³/hour</td>
<td>33 000</td>
</tr>
<tr>
<td>volume% SO₂ in offgas</td>
<td>30</td>
</tr>
<tr>
<td>dust production, tonnes/day</td>
<td>20</td>
</tr>
<tr>
<td>Oxygen and fuel consumption</td>
<td></td>
</tr>
<tr>
<td>oxygen (98% O₂), kg/tonne of new concentrate</td>
<td>~300</td>
</tr>
<tr>
<td>natural gas, Nm³/tonne of new concentrate</td>
<td>0 (autothermal)</td>
</tr>
</tbody>
</table>

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%.
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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


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 Cu₂O 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 H₂SO₄/m³), 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 Cu₂Te, 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 de-
copperizing 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
electrorefinery, Section 16.5.1.

References

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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

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/m$^3$. 

Pregnant leach solution from leach
(3)
1000 m$^3$/hour

Raffinate to leach
(0.6)
1000 m$^3$/hour

Pregnant leach solution from leach
(3)
1000 m$^3$/hour

Strong organic
(4.8)

Weakened aqueous
(1.4)

Mixer

Settler

Extract parallel

Settler

Strongened organic
(4)

Raffinate to leach
(0.5)
1000 m$^3$/hour

1000 m$^3$/hour stripped organic (1.5)

Extract 2

Mixer

Settler

Extract 1

Mixer

Settler

Strip

Mixer

Enriched electrolyte to electrowinning
(45)

Loaded organic
(6.4)

Depleted electrolyte from electrowinning
(35)
490 m$^3$/hour
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<th>City</th>
<th>Province</th>
<th>2002 Refining capacity, kilotonnes cathode Cu/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bayin</td>
<td>Gangxu</td>
<td>60</td>
</tr>
<tr>
<td>Beijing</td>
<td>Beijing</td>
<td>10</td>
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<tr>
<td>Changjiang</td>
<td>Hainan</td>
<td>5</td>
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<tr>
<td>Changsha</td>
<td>Hunan</td>
<td>5</td>
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<tr>
<td>Changzhou</td>
<td>Jiangsu</td>
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<tr>
<td>Chengdu</td>
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<tr>
<td>Chongqing</td>
<td>Sichuan</td>
<td>15</td>
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<tr>
<td>Dabizhuang</td>
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<td>26</td>
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<tr>
<td>Daye</td>
<td>Hubei</td>
<td>110</td>
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<tr>
<td>Fuyang</td>
<td>Zhejiang</td>
<td>10</td>
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<tr>
<td>Guangzhou</td>
<td>Guangdong</td>
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<tr>
<td>Guixi</td>
<td>Jiangxi</td>
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<tr>
<td>Harbin</td>
<td>Heilongjiang</td>
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<tr>
<td>Huludao</td>
<td>Liaoning</td>
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</tr>
<tr>
<td>Jiangpu</td>
<td>Jiangsu</td>
<td>5</td>
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<tr>
<td>Jinchang</td>
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<tr>
<td>Jinlong</td>
<td>Anhui</td>
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<td>Jinquan</td>
<td>Gansu</td>
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<tr>
<td>Kunming</td>
<td>Yunnan</td>
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<td>Luoyang</td>
<td>Hunan</td>
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<td>Huangpu</td>
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<tr>
<td>Shanghai 2</td>
<td>Jiangsu</td>
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</tr>
<tr>
<td>Shenyang</td>
<td>Liaoning</td>
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<tr>
<td>Shenyang smelter</td>
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<td>Shenyang</td>
<td>Xixing</td>
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<tr>
<td>Tianjin</td>
<td>Heilongjiang</td>
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<tr>
<td>Tonling II</td>
<td>Anhui</td>
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<td>Wuhu</td>
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<tr>
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<tr>
<td>Zhongtiaoshan</td>
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<tr>
<td>Zhuzhou</td>
<td>Hunan</td>
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...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.

Dr. Davenport is Professor of Metallurgical Engineering at the University of Arizona, Dr. King is in the Design and Engineering Department of Phelps Dodge Mining Company, and Dr. Schlesinger is Professor of Metallurgical Engineering at the University of Missouri-Rolla.