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AN ASSESSMENT OF ENERGY REQUIREMENTS IN PROVEN AND NEW COPPER PROCESSES

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December 1980

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Department of Metallurgy and
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AN ASSESSMENT OF ENERGY REQUIREMENTS IN PROVEN AND NEW COPPER PROCESSES

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**December 31, 1980
Final Report**

**Prepared for

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PREFACE

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EXECUTIVE SUMMARY

A. OBJECTIVES AND SCOPE

At the request of the Department of Energy, the University of Utah, Arthur D. Little, Inc., Mountain States Research, Inc., and Ford, Bacon and Davis Utah Inc. have undertaken an assessment of energy expenditures in various copper producing processes. Objectives may be listed as follows:

- Determine energy expenditures in existing and recently developed copper technology;
- Aid government and industry in screening and developing processes which are least energy intensive;
- Provide information that will direct research toward constructive areas for energy conservation; and
- Compile and disseminate energy analyses for selected new technology areas to industry and government.

The processes selected for study along with the companies primarily concerned with analyzing each process are listed in Table A-1. The University of Utah acted as prime contractor for the project with Arthur D. Little, Mountain States Research and Ford, Bacon and Davis Utah, acting as principal sub-contractors. In most cases the University of Utah personnel acted as advisors and coordinators on each process.

It must be strongly emphasized that the analysis undertaken in this report is strictly on an energy basis and does not directly address economic considerations or, in some cases, the technological feasibility of the processes considered. These areas would have to be evaluated carefully before an overall decision could be made to adopt a given process. Likewise a complete evaluation would have to include the consideration of the nature of the ore, its composition and plant location and capacity in determination of process feasibility.

B. APPROACH

Several recent efforts for the estimation of copper processing energy requirements are evident in the literature. Articles by Kellogg (1974, 1977) and Kellogg and Henderson (1976) consider energy consumption for producing copper from nine pyrometallurgical processes. A study by Arthur D. Little (1976) delineates energy requirements in relation to pollution control requirements in some of the newer processes. Fairly complete assessments of energy use in conventional copper production have been attempted by Battelle Columbus Laboratories (1975) and by Gordian Associates (1975). A thorough and detailed analysis, however, of energy expenditures for the complete range of copper processing is not presently available.

1. Criteria for Process Selection

Ores of copper are classified as sulfide, native copper or oxide. Of these, sulfide porphyry deposits account for about 90% of the U. S. production, most of the world output, and most of the estimated commercial copper reserves of the world. Therefore, this study focuses on processes

TABLE A-1

COPPER PROCESSES EVALUATED/COMPANIES ASSIGNED FOR EVALUATION

Process	Section	Company
Mining Operations	1.2	Ford, Bacon and Davis Utah, Inc. and University of Utah
Mineral Processing Operations	1.3	Mountain States Research and Development and University of Utah
Gas Clean...	1.4	Arthur D. Little, Inc.
Acid Plant	1.5	Arthur D. Little, Inc.
Refining	1.6	Arthur D. Little, Inc.
In Situ Solution Mining	1.7	Mountain States Research and Development and University of Utah
Copper Cementation	1.8	Arthur D. Little, Inc.
Conventional Smelting	2.3	Arthur D. Little, Inc.
Impurity Control	2.4	Arthur D. Little, Inc.
Electric Furnace Smelting	2.5	Mountain States Research and Development
Outokumpu Flash Smelting	2.6	Arthur D. Little, Inc.
INCO Flash Smelting	2.7	Arthur D. Little, Inc.
Top Blown Rotary Converter Smelting	2.8	Arthur D. Little, Inc.
Noranda Continuous Smelting	2.9	Ford, Bacon and Davis Utah, Inc.
Mitsubishi Continuous Smelting	2.10	Arthur D. Little, Inc.
Queneau-Schuhmann Continuous Smelting	2.11	Arthur D. Little, Inc.
AMAX Dead Roast Blast Furnace Smelting	2.12	AMAX
Segregation Process	2.13	Ford, Bacon and Davis Utah, Inc.
Thermo Electron Chlorination Process	2.14	Mountain States Research and Development
Oxy-Fuel Reverberatory Smelting	2.15	University of Utah
Oxygen Sprinkle Smelting	2.16	Arthur D. Little, Inc.
Arbiter Ammonia Leach Process	3.2	Arthur D. Little, Inc.
Roast Leach Electrowin Process	3.3	Mountain States Research and Development
Cymet-Ferric Chloride Process	3.4	Arthur D. Little, Inc.
Sherritt-Cominco Process	3.5	Arthur D. Little, Inc.
Nitric-Sulfuric Acid Leach Process	3.6	Ford, Bacon and Davis Utah, Inc.
University of Utah - Martin Marietta Process	3.7	Arthur D. Little, Inc.
Electroslurry-Envirotech Process	3.7A	Envirotech Corporation
Roast/Sulfite Reduction Process	3.8	Ford, Bacon and Davis Utah, Inc.

that extract copper from sulfide ores. Sulfide ores, after mining, are primarily treated by crushing, grinding and froth flotation to produce a concentrate of sulfide minerals. In contrast, many oxide ores are not amenable to concentration and are treated with dilute sulfuric acid to dissolve the copper.

The extraction of copper from sulfide ores is conveniently divided into four segments:

- mining — ore containing 0.4 to 2% copper is blasted and excavated;
- beneficiation — copper minerals are crushed, ground and separated from the gangue materials to produce a concentrate containing about 25% to 30% copper;
- smelting — concentrates are smelted and reacted to produce anode copper containing 98% to 99% copper; and
- electrorefining — the anode copper is refined to produce over 99.9% pure cathode copper.

This report evaluates a wide range of processes covering the spectrum from those that have been in operation on a full scale to those on which data are still being gathered on a laboratory scale. These processes cover the treatment steps necessary for the production of cathode quality copper from sulfide resources.

The front-end processes for the production of concentrates (i.e., mining and beneficiation) are analyzed separately to define the important parameters that affect overall energy consumption in the production of copper. For the remainder of the analysis, a fixed concentrate input composition is assumed. Plants of conventional size (i.e., 100,000 tons/year of copper) for pyrometallurgical and hydrometallurgical processes are considered. The process criteria are:

Mill Feed Grade (Dry Basis)	Mill Concentrate Grade (Dry Basis)	Annual Plant Capacity
• 0.55% Copper	• 25% Copper • 28% Iron • 31% Sulfur	100,000 Tons Cathode Copper
Cut-Off Grade	Mill Recovery	Base for Comparison
• 0.29% Copper	• 87.5%	Conventional Reverberatory Smelting: 98.7% Recovery

The subject matter in the text is organized into three general groupings: Front-end Operations, Pyrometallurgy and Hydrometallurgy. Within each section, individual processes are presented in an essentially random sequence, reflecting the order in which the information was received and developed and the inclusion of additional processes during the course of this study. Summary information, however, is organized under the headings: Older Proven, Newer Proven and New Unproven for pyrometallurgical processes and Commercial Processes and New Unproven Processes for hydrometallurgical processes.

Table B-1 lists the processes analyzed to be compared to the conventional processes they replace. Production steps from mining through refining or reduction are indicated.

TABLE B-1

**PROCESS STEPS AND CLASSIFICATION USED IN THIS STUDY
COMPARISON IS MADE TO CONVENTIONAL SMELTING**

	Mining	Beneficiation	Smelting	Refining
Conventional Processes	Open Pit Mining	Grinding and Froth Flotation	Reverberatory	Electrorefining
Older Proven Process	Open Pit Mining	Grinding and Froth Flotation	Outokumpu Flash	Electrorefining
Older Proven Process	Open Pit Mining	Grinding and Froth Flotation	INCO Flash	Electrorefining
Older Proven Process	Open Pit Mining	Grinding and Froth Flotation	Electric Furnace	Electrorefining
Newer Proven Process	Open Pit Mining	Grinding and Froth Flotation	Noranda Continuous	Electrorefining
+ Newer Proven Process	Open Pit Mining	Grinding and Froth Flotation	Mitsubishi Continuous	Electrorefining
Newer Proven Process	Open Pit Mining	Grinding and Froth Flotation	Oxy-Fuel Reverberatory	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Top Blown Rotary Converter	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Queneau-Schuhmann Continuous	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Oxygen Sprinkle Reverberatory	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	AMAX Dead Roast Blast Furnace	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Segregation	Electrorefining
New Unproven Process	Open Pit Mining	Grinding and Froth Flotation	Thermo Electron Chlorination	Electrorefining

TABLE B-1 (Continued)

	Mining	Beneficiation	Leaching	Reduction
Commercial Hydrometallurgical Processes	Open Pit Mining	Grinding and Froth Flotation	Arbiter Ammonia	Electrowinning
Commercial Hydrometallurgical Processes	Open Pit Mining	Grinding and Froth Flotation	Roast-Leach	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Sherritt/Cominco	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Nitric-Sulfuric	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Acid Ferric Sulfate	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Electroslurry-Ferric Sulfate	Electrowinning
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Cymet Ferric Chloride	Hydrogen Reduction
New Unproven Processes	Open Pit Mining	Grinding and Froth Flotation	Roast/Sulfite	Ammonium Bisulfite
In Situ Solution Mining	Partial Underground Mining	None	Leaching in Place	Solvent Extraction — Electrowinning

2. Method of Analysis

The analysis involved the calculation/estimation of material balances for each process based on available data. It should be noted that, when available, actual operating data for unit operations have been used. In addition, several general processes, such as gas cleaning, sulfuric acid production, and electrorefining common to most processes were considered. Next, a Level 1 analysis was performed which calculated the fossil fuel equivalent of all forms of purchased energy consumed in the process, and credited for byproduct heat recovery only in those cases where such heat recovery was carried out in plant practice. In addition, a Level 2 analysis was performed where the fossil energy equivalent of the major materials consumed in each process was evaluated separately. Table B-2 lists the energy values for various energy sources and commodities utilized in this study. This analysis of individual processes was supplemented by a theoretical analysis of energy requirements to go from a pre-defined initial state (e.g., sulfide concentrates) to a pre-defined final state (e.g., blister copper at 1200°C, slag at 1200°C, and off-gases at 400°C), in order to estimate the minimum energy requirements. Since impurity behavior is a major impediment to the widespread adoption of some of the newer pyrometallurgical technology, it has been investigated separately.

TABLE B-2
ENERGY VALUES FOR FUELS,
OTHER ENERGY SOURCES AND COMMODITIES

Commodities	Unit	Million Btu per Unit
Metallurgical Coke	Net Ton	31.5
Distillate Fuel Oil	Gallons	0.139
Natural Gas	Cubic Foot	0.001
Electrical Energy	Kilowatt-hour	0.0105
Steam	Pound	0.0014
Carbon Electrode	Net Ton	82.0
Graphite Electrode	do	160.0
Limestone	do	0.104
Nitric Acid	do	14.2
Refractory	do	26.6
Sand (silica sand)	do	0.042
Oxygen	do	4.41
Lime	Pound	0.0027
Sulfuric Acid	Net Ton	0.83
Ammonia	Net Ton	41.73
Hydrogen	Net Ton	234.0
Scrap Iron	Net Ton	18.0
Nitric Acid	Net Ton	14.2
Ammonium Nitrate Blasting Agent	Net Ton	30.0

Source: U.S. Department of the Interior, Bureau of Mines Information Circular, IC 8781, 1978.

It is important to note that all pyrometallurgical processes are strictly comparable (i.e., the iron in the concentrate ends up as a silicate slag and the sulfur in the concentrate ends up as sulfuric acid). In the hydrometallurgical processes, the iron ends up as a variety of jarosites or iron oxides while the sulfur either remains in the elemental state or is converted to throwaway gypsum and/or jarosites. The byproduct sulfur has not been allowed any credit in energy balances. If such credit were allowed (on the basis of comparing this sulfur against Frasch sulfur), the energy per ton of cathode copper would decrease by about 6% but a similar credit would have to be given those processes producing sulfuric acid or liquid SO_2 .

Similarly, refractory consumption data for a wide variety of pyrometallurgical processes were not generally available and therefore refractory consumption was excluded from Level 2 analysis in many instances. However, such consumption appears to fall in the range of 20-50 lb of refractory per ton of cathode copper which is equivalent to less than 1% of the total energy consumed in cathode copper production. Similarly, no credit has been allowed for by-product metals.

In this energy analysis, actual operating data have been used for the various unit operations, when such data were available. This accounts for differences among similar unit operations. For these, no attempt has been made to rationalize these variations. For Level 2 values, broad variations are to be expected since consumables are process specific.

C. ASSESSMENT OF ENERGY CONSUMPTION

1. Mining and Concentration

Today open pit mining is extended to depths of as much as 1,500 feet below the rim. The energy use and dollar cost of hauling rock from such depths become limiting factors in determining the life of the surface mining operation. Energy use and dollar cost optimization represent separate analysis strategies. There is an increasing bias relative to energy optimization as its availability is constrained, as its unit cost goes up, as mining proceeds to ores of lower grade, and as environmental protection regulations increase. The cutoff grade significantly affects the tonnage of the ore going to the mill and the tonnage going to dump leaching. Using an average mill feed grade of 0.55% copper and a cutoff grade of 0.29% copper, the energy use in mining (Level 1 plus Level 2) is listed in Table C-1. The analysis is presented in terms of energy per ton of cathode copper produced and is based upon a copper recovery of 87.5% in concentrating and 98.7% by conventional smelting. From a sensitivity analysis which varies the cutoff grade, it can be shown that the energy per normalized ton of cathode copper charged to mining decreases, while that charged to milling increases. The resulting counter-active changes produce a small net energy difference in the overall energy requirement; although a minimum is indicated at a cutoff value of 0.4% copper.

The increased recovery of copper from dump leaching as the cutoff grade increases does not markedly decrease the average energy use per ton of cathode copper produced. This insensitivity results from the high energy use in current dump leaching practice. Conversely, the energy use per net ton of cathode copper produced is very sensitive to stripping ratio and pit depth.

Energy use in milling is very sensitive to mining cutoff grade when normalized in terms of cathode copper produced. The approximate energy use per net ton of ore milled (Level 1 plus

TABLE C-1
ENERGY USE IN MINING FOR A
STRIPPING RATIO OF 1.25

Unit	Million Btu's per Ton Cathode Copper	% Total Mining Energy*
Drilling	0.612	3.0
Blasting	3.895	19.4
Loading	1.849	9.2
Hauling	13.137	65.2
Ancillary	0.638	3.2
Total	20.131	100.0

*Level 1 plus Level 2.

Level 2) is 0.156 million Btu of which 60% is in the grinding step. Assuming an average recovery of 97.5% in concentration and 98.7% in conventional smelting, milling energy is 42.57 million Btu per net ton cathode copper when produced from a mill head ore grade of 0.55% Cu.

It appears that major improvement in energy use in milling will require optimized energy use in grinding. This conceivably may be achieved by the application of stabilizing control strategies in the grinding operation itself and in related operations such as flotation and classification. This analysis points to potential energy savings in the use of autogenous and semi-autogenous mills for certain copper sulfide ores. Also pebble mills may be an attractive option for grinding when viewed in terms of energy optimization.

The tonnage of ore mined and beneficiated depends upon the final recovery inherent in the pyrometallurgical or hydrometallurgical process used. The results of a sensitivity analysis are presented in Table C-2. Clearly the energy of mining and beneficiation is relatively insensitive to recovery for the range of 97.0 to 99.5 percent recovery.

TABLE C-2
ENERGY FOR MINING AND BENEFICIATION

End Process Recovery %	Million Btu/Ton Cathode Copper		
	Mining	Concentration	Total
97.0	20.48	43.32	63.80
97.5	20.38	43.09	63.47
98.0	20.27	42.87	63.15
98.5	20.17	42.66	62.83
98.7*	20.13	42.57	62.70
99.0	20.07	42.44	62.51
99.5	19.97	42.23	62.20

*Base Case is 98.7% recovery for conventional smelting and refining.

2. Pyrometallurgical Technology

Table C-3 lists the energy use evaluated for several older and newer commercial and proposed pyrometallurgical processes. Included in the table are Level 1 plus Level 2 values for each process. The range of values for each category are also listed. The mining and milling values may be adjusted relative to conventional smelting with a recovery of 98.7% according to Table C-2.

TABLE C-3
ENERGY USE IN COPPER PYROMETALLURGY TECHNOLOGY
FOR SMELTING AND REFINING
(Million Btu/Ton Cathode Copper)

Category	Process	Total	Range
		Level 1 plus Level 2	
OLDER PROVEN PROCESSES	Conventional Smelting (Green Charge)	35.16	30-44
	Conventional Smelting (Calcine Charge)	30.92	
	Electric Furnace Smelting	42.97	
	Outokumpu Flash Smelting	18.92	19-21
	INCO Flash Smelting	21.25	
NEWER PROVEN PROCESS	Noranda Continuous Smelting	24.00	20-29
	Mitsubishi Continuous Smelting and Converting	19.76	
	Oxy-Fuel Reverberatory Smelting	28.62	
NEW UNPROVEN PROCESSES	Top Blown Rotary Converter Smelting	23.56	20-24
	Queneau-Schuhmann Continuous Smelting	22.63	
	Oxygen Sprinkle Smelting	22.43	
	AMAX Dead Roast Blast Furnace Smelting	19.58+1.5*	
	Segregation Process	21.03	
	Thermo-Electron Chlorination Process	20.20	

To obtain the total energy required for producing a ton of cathode copper the energy for mining and concentrator operations must be added. For a 98.7% recovery in the smelting operation the estimated mining energy is 20.13 and concentrator energy is 42.57 million Btu/ton cathode copper.

*Value reported by AMAX for electro-refining is approximately 1.5 million Btu less than value used for other processes in this study; also, energy requirement for fugitive emissions control is not included.

It is important to note that the energy-based comparison amongst processes can be significantly different from an economic comparison between same processes since the labor and fixed capital requirements for the processes may vary considerably. Similarly, the processes produce different types of environmental intrusions (fugitive emissions, waste water, slag and sludge) and the costs or future potential cost of dealing with these streams may vary from process to process. What is presented here is a comparative discussion of the processes based on energy consumption alone.

Table C-3 shows that conventional smelting is energy intensive. It uses large quantities of hydrocarbon fuels, deriving little energy from the combustion of the sulfides. Hot calcine smelt-

ing (roast-reverberatory) practice is less energy intensive than green charge practice by approximately 4 million Btu, mainly resulting from lower fuel and air requirements and the resultant decrease in the volume of offgas which must be handled. The Oxy-Fuel process at about 29 million Btu shows considerable improvement over conventional smelting. More important, while sulfur recovery as acid in conventional smelting is below 70%, sulfur recovery in Calteones Oxy-Fuel smelting would be over 90%.

Electric Furnace Smelting is the most energy intensive of all of the pyrometallurgical processes analyzed in this study. The addition of fluid bed roasting could reduce the fuel requirements by approximately 3 million Btu's per ton of cathode copper.

It is evident (see Table C-3) that two of the older proven processes based on matte smelting, Outokumpu Flash Smelting and INCG Flash Smelting, fall in the lowest range of energy consumption (19-21 million Btu per net ton cathode copper produced). This is a significant improvement over conventional smelting and illustrates the important conclusion that with the many technological improvements incorporated in these processes over the last 30 years, there has been a significant improvement in energy efficiency. Newer proven processes (based on matte smelting) fall in the mid-range of energy consumption (19-29 million Btu/net ton cathode copper produced). These are the Mitsubishi, Noranda and Oxy-Fuel Processes. Of these the Mitsubishi and Noranda Processes are at the lower end of the range and are close in energy consumption to the flash smelting processes. It should be noted that improved reactor design in general also makes these processes more environmentally acceptable. This is particularly true for developments which reduce converter aisle-type operations in a process, reducing fugitive emissions.

Six processes are newer, unproven processes and fall into two categories. Three of these processes are based upon matte smelting. They are TBRC, Q-S, and oxygen sprinkle smelting. These three processes fall in the same energy range (20-24 million Btu/net ton cathode copper produced) as other newer processes based on matte smelting. Three processes, not based on matte smelting, are the AMAX Dead Roast Blast Furnace, Segregation and Thermo Electron processes. These processes similarly show relatively low energy usage. However, the energy values for the Amax Dead Roast Blast Furnace process would have to increase for controlling fugitive emissions.

The AMAX Dead Roast Blast Furnace process and the Segregation process, have been tested only on a pilot plant basis, but not on a commercial scale. The Segregation process has been tested on a commercial scale for refractory silicate ores but not on roasted calcines. It is difficult to analyze the Thermo Electron Corp. process comparatively, since background data are incomplete and are based on bench scale tests only.

As stated earlier, when available, actual operating numbers for the various unit operations have been used. This accounts for the variation in values presented for similar steps in Level 1 analyses. Some differences such as smelting energy and surplus steam generation are expected for the various pyrometallurgical processes. Also, although process units perform similar functions in different processes, operating conditions such as matte grade, degree of oxygen enrichment in smelting and converting, air preheat etc. vary considerably leading to differences in energy requirements. Other process steps should be similar. For these, no attempt has been made to rationalize the variations although subtle differences may, in fact, exist for the separate processes. Where the deviation is large, special note is made of the differences. Broad variations are

expected for Level 2 values since consumables are process specific. Table C-4 lists the Level 1 plus Level 2 values for unit operations within each process illustrating the degree of variation. Some of the major variations are:

- The energy requirements for electric smelting are highest reflecting to a large extent the inefficiency of power generation based on fossil fuels.
- The fugitive emissions control energy use for the Mitsubishi Process is approximately 25% of that attributed to other processes reflecting the transfer of molten matte through launders. For the Q-S Process no energy has been assigned for fugitive control, since all the processing will be done in a single reactor. For electric smelting, energy for fugitive emission is not listed separately but is included under cold gas cleaning. The energy for fugitives emission control is likely to be similar for the Segregation process and the Amax Dead Roast Blast Furnace process because they both involve handling of dusty calcines. Although Table C-4 shows 3.57 million Btu/ton for fugitive emission control in the Segregation process, the actual requirements need to be established for both processes.

The values shown in Table C-3 may be compared to the values reported by Kellogg and Henderson (1976) for several pyrometallurgical processes. This comparison is shown in Table C-5 where the Kellogg & Henderson values have been adjusted to the same basis as Table C-3 by adding an average value of 3.57 million Btu/ton copper for fugitive emission control and 4.69 million Btu/ton for electrorefining.

Evolutionary development of pyrometallurgical processes employing matte smelting chemistry may be viewed in terms of two major developments beyond conventional reverberatory smelting; namely, flash smelting and continuous processing. In the future, energy saving features, improved environmental acceptability, minimal loss of copper in the slag, large capacity, fugitive emission control and design features minimizing heat loss must receive special attention. The conventional reverberatory-Pierce Smith process is clearly obsolete. Flash furnace technology, now over 30 years old, and well proven, may be viewed as modern transitional-proven technology, while Mitsubishi and Noranda are modern continuous-proven processes. It is difficult to assess whether or not these latter two are transitional. Mitsubishi uses three smelting steps and, while it is effective in conserving on fugitive emission energy requirements, it deviates from a single reactor concept. The Noranda process is too new to assess from this point of view. It is continuous, but slag cleaning appears to be a problem. Oxygen sprinkle smelting by these criteria may be viewed as transitional, unproven, representing a potentially significant linking between older and newer technologies. The TBRC is difficult to analyze in the same framework as the other processes mentioned, except it must be considered at this point as somewhat unproven for large scale smelting of copper. It is limited in size, operates best on high grade mattes and has the added capability of fire refining. The Q-S process as designed is capable of going from copper feed to blister copper and falls in the category of modern and continuous-unproven processes. A similar version, the QSL (Queneau-Schuhmann-Lurgi) process for lead is now at the demonstration stage in Germany by Bundes Ministerium für Forschung und Technologie. The demonstration plant (250 tpd galena) is funded at a level of \$25 million U.S., one-half by German industry and one-half by the German government with tests to be completed by the end of 1982.

TABLE C-4

ENERGY (MILLION BTU/NET TON COPPER) COMPARING SIMILAR STEPS IN PYROMETALLURGICAL PROCESSES

Section	2.6	2.3a	2.3b	2.16	2.10	2.9	2.11	2.16	2.7	2.8	2.6	2.12
Process Designation	Electric Furnace Copper Smelting	Conventional Smelting, Wet Charge	Conventional Smelting, Dry Charge	Oxy-Fuel Reverberatory Smelting	Mitsubishi Continuous Smelting & Converting	Noranda Continuous Smelting	Quebec-Schuhmann Oxygen Process	Oxygen Sprinkle Smelting	INCO Flash Smelting	Top Blown Rotary Converter	Outokumpu Flash Smelting	AMAX Dead Roast - Blast Furnace
LEVEL 1												
Materials Handling:		.73	.73	.73	.66	.79	.66	.73	.73	.73	.67	
Dry or Roast:	2.67		.66	1.35	1.29	.80	1.47	1.72	1.86	1.86	1.23	1.58
Heat Recovery												4.73
SMELTING												
Fuel		26.01	14.60	9.27	6.46	3.72		1.38		.40	.80	10.88
kWh	19.03	.64	.64	.64	1.68	1.26		.64	.06	1.16		1.27
Surplus Steam		-10.00	-4.36	-3.71	-8.00	-1.82		-1.09			3.43	1.50
CONVERTING												
kWh	2.92	1.63	1.26	1.63	1.42	.37		1.26	0.94		.64	
Fuel	3.68	.64	.32	.60	.25	.09		.23				
Slag Cleaning					1.36	1.31					1.49	
GAS CLEANING												
Hot Gas	.78	4.03	2.63	1.27	.86		.13	.64	.69	.61	0.42	
Cold Gas	2.21	.25	.40	.48	.32	.69	.06	.24	.31	.34	0.21	.84
Fugitive Emissions		3.67	3.67	3.67	.89	3.67		3.67	3.67	3.67	3.67	
Acid Plant	4.74	2.27	3.87	4.61	4.08	3.10	4.30	3.91	3.19	4.09	3.86	4.18
Water		.10	.10	.10	.10		.10	.10	.10	.10	.10	
Anode Furnace Electrorefining	6.10	6.82	6.82	6.82	6.82	6.82	6.82	6.82	6.82	6.82	6.82	6.03
TOTAL LEVEL 1	<u>41.03</u>	<u>34.59</u>	<u>30.36</u>	<u>26.16</u>	<u>17.08</u>	<u>19.70</u>	<u>12.63</u>	<u>19.16</u>	<u>17.16</u>	<u>18.58</u>	<u>16.28</u>	<u>19.66</u>
LEVEL 2												
Misc. Materials					.63	.66	2.80			0.13	.04	
Oxygen				1.88	1.29	3.17	6.70	2.71	3.63	4.74	3.04	
Electrodes	.86				0.16							
Fluxes	.12	.04	.03	.04	.06	.02	.05	.03	.02	.02	.01	.03
Water		.08	.08	.08	.08		.08	.08	.08	.08	.08	
Anode Furnace Electrorefining	.61	.47	.47	.47	.47	.47	.47	.47	.47	.02	.47	.01
TOTAL LEVEL 2	<u>1.49</u>	<u>.69</u>	<u>.68</u>	<u>2.47</u>	<u>2.69</u>	<u>4.31</u>	<u>10.10</u>	<u>3.29</u>	<u>4.10</u>	<u>4.99</u>	<u>3.64</u>	<u>.04</u>
GRAND TOTAL	<u>42.52</u>	<u>35.18</u>	<u>30.93</u>	<u>28.63</u>	<u>19.77</u>	<u>24.01</u>	<u>22.63</u>	<u>22.44</u>	<u>21.26</u>	<u>23.57</u>	<u>20.87</u>	<u>19.69</u>

TABLE C-5

**COMPARISON OF TOTAL ENERGY (LEVEL 1 PLUS LEVEL 2)
WITH VALUES FROM KELLOGG AND HENDERSON (1976)
FOR SEVERAL PYROMETALLURGICAL PROCESSES**

Process	Total Energy Consumption Level 1 plus Level 2 (Million Btu/Net Ton Cathode Copper)	
	This Study	Kellogg and Henderson (1976) ^a
Conventional Smelting: Green Charge ^b	35.16	26.73
Conventional Smelting: Calorie Charge ^c	30.92	23.84
Electric Furnace Smelting ^d	42.97	32.55
Outokumpu Flash Smelting ^e	18.92	20.51, 23.69
INCO Flash Smelting ^f	21.25	18.20
Noranda Continuous Smelting ^g	24.00	20.53, 29.41
Mitsubishi Continuous Smelting ^h	19.76	22.21

- a. Add to Kellogg values, 3.57 million Btu/ton cathode copper for fugitive emissions and 4.69 million Btu/ton cathode copper for electrorefining.
- b. This study: no air preheat; Matte Grade - 42.0%.
Kellogg and Henderson: 72% preheated to 220°C, Matte Grade - 35%.
- c. This study: no air preheat; Matte Grade - 50.0%.
Kellogg and Henderson: 72% preheated to 220°C, Matte Grade - 43.5%.
- d. This study: no air preheat; Matte Grade - 41%.
Kellogg and Henderson: no air preheat, Matte Grade - 35%.
- e. This study: enriched air 36.5 wt % oxygen, preheated to 200°C, Matte Grade - 65%.
Kellogg and Henderson: (1) air preheat at 77% to 1000°C, low oxygen enrichment Matte Grade - 59%.
(2) air preheat 80% to 200°C, higher oxygen enrichment Matte Grade - 61.4%.
- f. This study: oxygen, Matte Grade - 50.45%.
Kellogg and Henderson: pure oxygen, Matte Grade - 54.3%.
- g. This study: oxygen enrichment, Matte Grade - 70% Cu.
Kellogg and Henderson: (1) Blister copper, no air preheat.
(2) Oxygen enrichment, Matte Grade - 75% Cu.
- h. This study: Oxygen enrichment (40.9%), no preheat, Matte Grade - 65%.
Kellogg and Henderson: air preheat 25% to 275°C.
moderate oxygen use, Matte Grade - 64.5%.

Following the above logic and using the data of this study, it appears that the reactor of the future, with a production capacity of 100,000 tons per year, most likely will be a single continuous reactor capable of minimizing convective and radiative heat loss, fugitive emissions, and effective in removal of impurities. Such a single reactor should meet the following conditions:

- Produce blister copper low in impurities;
- Produce a clean slag;
- Increase SO₂ concentration and minimize gas volume;
- Fully utilize the fuel energy in the copper-iron sulfide feed; and
- Provide close control over emissions.

For smaller operations, e.g., 25,000 tons per year, other options appear likely, e.g., the TBRC may be well suited to plants of this size as may be several hydrometallurgical processes.

3. Hydrometallurgical Technology

Table C-6 lists the Level 1 plus Level 2 energy requirements for the eight hydrometallurgical processes considered in this study. Energy usage for in situ solution mining is also included, and is discussed in Section C.4. The hydrometallurgical processes are grouped according to three ranges of energy (Level 1 plus Level 2) required. The total energy values, including mining plus beneficiation, are also listed in Table C-6. The table clearly shows that hydrometallurgical processes in general are more energy intensive than smelting. This comes mainly from high Level 2 components and ineffective use of the heat of reaction. The processes having lowest Level 2 components, viz., Roast-Leach-Electrowin, Cymet Ferric Chloride Leach, Electroslurry and Sulfite Reduction, are notably less energy intensive and, in terms of energy, are comparable with Conventional or Electric Furnace Smelting.

TABLE C-6
ENERGY USE IN COPPER HYDROMETALLURGICAL TECHNOLOGY
(Million Btu/Ton Cathode Copper)

Process	Concentrate to Refined Copper		Range (Mining to Refined Copper)
	Total Level 1 Plus Level 2	Range	
Roast Leach Electrowin*	30.45		
Cymet Ferric Chloride Leach	30.92	24-31	87-94
Roast/Sulfite Reduction	23.64		
Electroslurry—Envirotech	39.61		
U of U/MM Ferric Sulfate Acid Leach	49.45	40-50	103-113
Sherritt Cominco	48.13		
Arbiter Ammonia Leach*	62.05		
Nitric-Sulfuric Acid Leach	74.45	60-75	123-138
In Situ Solution Mining	—	—	approx. 80

*Processes which have been used commercially. To obtain the total energy required for producing a ton of cathode copper the energy for mining and concentrator operations must be added. For 98.7 percent recovery in the smelting operation the estimated mining energy is 20.13 and the concentrator energy is 42.57 million Btu/Ton of cathode copper.

All of these processes, with the exception of the Cymet Ferric Chloride Leach and the Sulfite Reduction process, employ electrowinning for metal reduction. Improvement in electrowinning thus presents an area for reduction in the overall energy use in these processes. Chemical reductants, used in the Cymet and Sulfite Reduction processes are clearly less energy intensive than conventional electrowinning. The Envirotech Electroslurry cell appears to be operable with approximately 25 to 30 percent less energy than conventional electrowinning.

Combination processes, using both pyrometallurgical and hydrometallurgical steps, are generally less energy intensive than all-hydrometallurgical processes. The combination processes are Roast-Leach-Electrowin, Cymet Ferric Chloride, Sherritt-Cominco, and Sulfite Reduction.

The all-hydrometallurgical processes in general are the most energy intensive. These are the Arbiter Ammonia Leach, the Nitric-Sulfuric Acid Leach and the Ferric Sulfate Leach. The Electrosolurry modification of the Ferric Sulfate Leach is less energy intensive than the University of Utah, Martin Marietta version based on electrowinning because of the lower cell voltage of the electrosolurry electrowinning step. The Arbiter Ammonia Leach is less energy intensive than the Nitric-Sulfuric Acid Process, resulting principally from the high heat of reaction since sulfide sulfur is oxidized all the way to sulfate. Improvements in the Nitric-Sulfuric Acid and Arbiter processes require a more effective recovery of waste heat.

In general, the high energy requirement for hydrometallurgical processes results from electrowinning, inefficient use of reaction heat, high process steam requirements, and large Level 2 components. It does appear that significant improvements can be made in energy usage by more effective waste heat recovery, new electrowinning technology, and the combination of alternate lower energy unit processes.

The Smelting-Electrorefining processes recover byproducts such as precious metals, selenium, and tellurium in the form of anode slimes. This stream of slimes is small, about 5 to 25 lb per ton of cathode. The slimes are treated by a combination of processes to recover these byproducts. Technology for the recovery of such byproducts from the hydrometallurgical processes is not as well developed. Furthermore, it will involve the handling and treatment of much higher volumes of solids residues (iron oxides and/or jarosites), about 3 to 6 tons per ton of cathode. This treatment is likely to entail more energy consumption than anode slimes treatment. An exception to this is the Sherritt-Cominco Process which produces only 0.7 tons of solid residue per ton of cathode copper, thus enhancing precious metals recovery. In addition this process can recover the associated metal values such as molybdenum and zinc.

One of the major apparent benefits of hydrometallurgical processing is the absence of significant emissions to the air from process units. In pyrometallurgical processing, on the other hand, the control of emissions is expensive in both energy and economic terms. This has to be weighed against the increased potential for water pollution. In this analysis, we have allowed for a significant amount of energy for the control of fugitive emissions in pyrometallurgy (about 4 million Btu per ton of cathode). In spite of this, there is a significant difference in energy consumption between the two types of processes generally in favor of pyrometallurgy.

Of all the processes proposed, Roast/Sulfite Reduction has the greatest potential for competing with smelting processes in terms of energy usage. However, the process is unproven. Also, effective recovery of heat from the roasting step by an auxiliary heat exchange system seems capable of reducing the reported values appreciably for both the Roast Leach and Sulfite Reduction.

The construction of hydrometallurgical process plants capable of producing 100,000 tons of copper per year seems unlikely, at least in the next decade. Application to smaller tonnages is more likely, i.e., less than 25,000 tons per year of finished copper. The hydrometallurgical process most likely to succeed in the future will have to be designed to recover process heat in a useful form and will require vastly improved electrowinning technology or use chemical reductants.

4. In Situ Solution Mining

The in situ extraction of copper from a deep-seated deposit appears to be the least energy consuming process of all the extraction procedures investigated in spite of only 50% overall recovery assumed for this technique. The major energy saving factors are reduced energy involved in mining, the elimination of the concentration step, and more effective use of intrinsic heats of reaction under autoclave conditions in place. The estimated energy requirements (Level 1 plus Level 2) of about 80 million Btu's per ton cathode copper are at least 15 to 20% lower than the pyrometallurgical processes considered and about 25 to 75% lower than the hydrometallurgical techniques investigated.

The energy requirements are based on an assumption that only 50% of the copper is recoverable in this process. If higher recoveries are achievable, then the in situ extraction would be even more attractive for recovering copper from deep-seated deposits. On the other hand, the in situ technique is not a proven process, and experimental work is needed to demonstrate that the 50% recovery is possible. It should also be noted that such techniques would be applicable only where the geological structure permits containment of the pregnant solution.

D. RECOMMENDATIONS FOR FUTURE RESEARCH

In the course of this study, a variety of evolutionary and new energy saving ideas have been identified which have significant potential for decreasing the energy consumed in copper production. These ideas generally relate to unit operations which could be utilized by many of the processes discussed in this report. However, in all cases, additional research and evaluation are necessary to verify this potential for energy saving. These ideas are presented below with a short discussion of their significance.

1. Mining/Dump Leaching

Mining energy is about 21% of the energy consumed in copper production. If the downstream processes are not efficient and do not recover most of the contained copper, the contribution of mining energy towards the production of cathode copper would greatly increase. The areas for further research and evaluation in mining are:

- evaluation of alternatives for ore and waste haulage, e.g., the use of belt conveyors versus trucks in mines;
- the trade-off between the use of more blasting agents for additional breakage in the mine versus primary and secondary crushing; and
- optimization of cut-off grade in order to define the trade-off between energy consumption in dump leaching.

The study shows that dump leaching is more energy intensive than commonly realized. Areas for further research are:

- studies on fundamentals of dump leaching; and
- studies to improve aeration and rate of copper extraction in dump leaching.

2. Grinding/Concentration

Grinding and concentration consume about 45% of the energy used in the production of cathode copper, with grinding being the major energy consumer. Since their introduction during the last part of the 19th century, tumbling mills have proven to be superior to other grinding equipment for a very wide variety of applications. However, they are still quite inefficient in that no more than 1-2% of the energy consumed is used for the creation of new surface. Because of the large quantity of energy consumed in tumbling mills, even a small improvement can have a significant impact on energy conservation. The areas for further research and evaluation (which would generally benefit all industries using tumbling mills) are:

- the use of pebble milling in copper ore grinding where pebbles of hard rock such as quartzite are substituted for ore (autogenous) or steel grinding media;
- research on stabilizing control strategies in grinding, classification and flotation;
- evaluation of optimal energy consumption in size reduction by trade-offs between blasting, crushing, grinding and regrinding;
- development of techniques for more efficient classification to prevent the unnecessary recycling of fines to the grinding mill; and
- evaluation of alternative grinding devices such as attrition mills which might have higher grinding efficiencies.

3. Pyrometallurgy

Pyrometallurgical processes are most effective when the following conditions are met:

- exothermic heat of reaction is used to melt the charge materials;
- discontinuous batch processing is minimized;
- the heat content of the off-gases is recovered in waste heat boilers;
- an optimum degree of oxygen enrichment is used;
- the process produces strong sulfur-dioxide-containing streams suitable for sulfuric acid manufacture;
- the throwaway slag is low in copper; and
- the process has minimal emissions of fugitives to the working environment.

The areas for potential research/evaluation are:

- The use of waste heat recovered from hot off-gases to dry and preheat concentrates. At present, most or all the newer smelting processes use an external source of fuel for this purpose. Energy savings of 5-10% are conceivable by effective waste heat recovery.
- The pyrometallurgical slag cleaning processes could be improved to reduce the copper content of the throwaway slags and increase the copper recovery. Energy consumption is sensitive to increased recovery since mining and concentration energy could be proportionately decreased for a given production. A 1% increase in recovery amounts to approximately 1 to 2 million Btu savings in energy because of the high mining and concentration energy values. Since the slag is available to such

processing in the molten state, the procedure requires conditions which will maximize the reduction and separation of the copper. It should be noted that the Q-S process best addresses these questions conceptually.

- Continuous one-step smelting processes are energy efficient as compared to two-step processes because of better utilization of heats of reaction. In addition, a hot-matte transport step and the attendant heat loss and fugitive emissions are eliminated. Several of the new generation of pyrometallurgical processes can be operated in continuous one-step fashion. However, the potential for transfer of arsenic, antimony and bismuth to the metallic copper phase in such processes requires special design criteria. Current electrorefining technology is generally inadequate for handling significant levels of these impurities in anode copper. Therefore, research on unit operations which would remove these impurities from blister copper prior to electrorefining in a single continuous reactor would be very desirable. The successful implementation of this research would lead to true one-step smelting of copper concentrates and may result in a saving of 10-20% of the energy used in smelting. Potential approaches would include slagging and/or vaporization of the impurities. Future research for a large capacity copper smelting process for optimizing energy usage, environmental control and minimizing metal loss should be centered around the development of a single continuous reactor.
- The flue dusts collected in pyrometallurgical processing are rich in volatile impurities such as arsenic, zinc, and lead. Because of the high copper content (over 5%), these dusts are generally recycled. However, when impurity concentrations reach such levels that this recycling has a deleterious effect on copper quality, the dusts have to be stockpiled or discarded. This reduces copper recovery and represents a significant energy loss. Appropriate processes for flue dust treatment would prevent this loss and also recover valuable byproducts.
- Steam recovered from waste heat in smelters is used to generate electric power to drive the blowers in the acid plant and for converter air. If the smelter had an adjoining electrolytic refinery, the low level steam, after a topping steam turbine cycle, could be used for electrolyte heating. A detailed assessment of utility requirements in a smelter/refinery complex is necessary to quantify the potential for energy saving using this approach.

4. Hydrometallurgy

While hydrometallurgical processes show a higher level of energy consumption than pyrometallurgical processes, they are at an early state of development and, therefore, offer considerable potential for improvement. The areas for research and evaluation are:

- Research to decrease energy consumption in electrowinning is important since electrowinning consumes 21-24 million Btu's per ton of cathode copper or almost 20% of the total. This energy could be reduced by a direct approach to increase the efficiency of electrowinning by lowering overpotentials and by investigating alternative anode reactions. Another approach would be to avoid the use of electric energy for reduction (which incorporates the inefficiencies in electric power generation) and use, instead, other reductants such as hydrogen, sulfur dioxide, and other reducing gases or coal.

- Research is desirable to optimize the transfer of heat from the exothermic leaching reactions to the reactants more effectively. This would involve major modifications in reactor design.
- Research in hydrometallurgy process development most likely should move towards processes which pretreats the chalcopyrite feed to provide a more suitable feed material and either avoids electrowinning by using chemical reductants or uses some totally new, low energy electrowinning step.
- It may be possible to generate electrical energy while recovering copper by treating copper concentrates in a slurry electrode/fuel cell configuration. Research in this area has potential for energy savings in the future.

5. In Situ Solution Mining

While all of the research ideas discussed earlier increase conventional reserves by reducing energy requirements and costs, in situ solution mining is unique in that it adds low grade deep-seated deposits (which cannot be exploited economically by conventional technology) to the reserves of available copper.

A multi-faceted R & D program is desirable for optimizing the overall extraction of copper by in situ leaching techniques including a demonstration phase under field operating conditions to improve the technique to obtain higher recoveries than the 50% recovery assumed in this study. Specifically, such a program would include work on:

- actual oxygen or air consumption related to the type and extent of mineralization;
- application of recent developments in blasting stressed rock with flooded joints;
- weathering and leaching characteristics of copper porphyry ores under extended period of ore-solution contact;
- quantification of reactions with host rock potentially capable of complexing copper and consuming lixiviant; and
- modeling and simulation for optimization.

E. ENERGY SAVINGS POTENTIAL

The energy savings potential of the research ideas presented in Section D is not uniform. Table E-1 shows estimates of this energy savings potential in terms of million Btu's per ton of cathode copper in the first numerical column. Since the U.S. produces about 2 million tons of copper from primary sources, the total potential for energy savings in the U.S. would be approximately 2 million times these numbers if we assume that each technique was successfully adapted to primary copper production. The actual savings that could be realized would vary considerably. For example, improvements in mining and milling would be applicable to the production of other ores and minerals or mineral products, such as cement. On the other hand, some of the techniques (e.g., flue dust treatment) are probably necessary only for a fraction of the concentrates used in primary copper production.

The second column shows the estimated probability of success in each area. The probabilities are designated "very high" and "high" if the approach has already been demonstrated in some fashion and requires technology transfer. The probability is designated "medium" if the direction of research and development is reasonably well defined but requires further work. Finally, the probability is designated "low" if the direction of research is not fully defined.

TABLE E-1
CHARACTERIZATION OF RESEARCH IDEAS

	Potential Energy Savings MMBtu/Ton	Probability of Success ²	R&D Cost Implication ³	Range of Applicability	Type of Research ⁵
Mining					
Haulage vs. trucks	4	VH*	1	R	S,D
Blasting vs. crushing/grinding	Trade-off	H	1-2	R	S,D
Concentration vs. dump leaching	20-25	H	1	R	S,D
Fundamentals of dump leaching					
Increase aeration and copper extraction	10-20	M	2-3	R,G	L,P,D
Grinding					
Pebble mill autogeneous	4	M	2	R	S,L
Stabilizing control					
Optimal energy control	13	M	2-3	?	S,L
New classification techniques					
Other milling devices	NA ¹	L	1-2	G	L,P
Pyrometallurgy					
Waste heat for drying	0.7	H	1	R,G	S
Pyrometallurgical slag cleaning	2	M	3	R,G	S,L,P,D
Impurity removal from blister	2	M	3	R,G	S,L,P,D
Flue dust treatment	1	L	2-3	R	S,L,P,D
Waste heat steam/cogeneration	4-5	VH*	1	R	S
Single continuous reactor technology	4-7	H	3-4	G	P,D
Hydrometallurgy					
Electrowinning	8	L	3	G	S,L,P,D
Use of alternate reduction schemes	15	H	3	G	S,L,P,D
Reactor design for optimum heat transfer	3	H	1-2	G	S,D
In Situ Mining	2D	M	4	R,G	S,L,D

*Where applicable.

1. NA - Not available for "blue sky" type of ideas.
2. VH - Very high - approach has been demonstrated successfully elsewhere in the industry.
H - High - approach based on technology transfer but not demonstrated.
M - Medium - direction of research is known; needs further work.
L - Low - direction of research not fully defined.
3. \$0.1 Million = 1; \$1 Million = 2; \$10 Million = 3; \$100 Million = 4.
4. R = Retrofit; G = Grassroots.
5. L = Laboratory; P = Pilot plant; D = Demonstration; S = Study.

The third column shows our assessment of the R&D cost implications. The fourth column characterizes each idea in terms of its potential for retrofit into existing plants versus its applicability to new, grassroots plants. This is an indication of the rate at which these ideas may be adopted, if successful. The last column shows the type of research necessary before the techniques will be adopted by industry.

Finally, it is important to address concepts not included in the specific recommendations as stated, or listed in Table E-1. Any process should be considered from the origin of the ore (mining) to the finished product as a total system. In this context significant energy conservation may result by matching individual steps to optimized energy conservation. Matching ore chemical and physical characteristics, minor and major impurities, and potential for by-product recovery with the process steps selected may have significant energy conservation implications.

Examples are:

- trade off between explosives and primary crushing in the open pit;
- bulk flotation followed by grinding and selective flotation;
- concentrate pretreatment before smelting or hydrometallurgical processing; and
- merging of hydrometallurgical and pyrometallurgical steps.

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1.0 FRONT-END OPERATIONS

1.1 INTRODUCTION

The various processes contributing to the production of a refined cathode copper product fall into two clearly defined categories, first the front-end processes of mining, concentration, and dump leaching, and second the subsequent processes of extraction and refining the copper concentrate product or the reduction of the copper in the dump leaching solution.

For the purpose of this analysis, the concentrate feed to the extraction and refining processes is assumed to conform to standard specification. We can thus consider these extraction and refining operations on an independent basis, conversion taking place from a standard feed to a standard product.

By contrast the front-end processes are open-ended on both sides; the mining operations being tied to the physical characteristics of the orebody and to the configuration of the mine, and the production requirements of both mining and concentrating depending on the conversion efficiency (percent recovery of contained copper) of the extraction and refining processes.

1.2 MINING OPERATIONS

1.2.1 Introduction

Some 90% of all copper ore mined in the U.S. comes from openpit operations (Engineering & Mining Journal, June 1977). While the balance must ultimately swing towards the mining of deep-seated deposits by underground or remote mining methods as the near-surface deposits become exhausted, the dominant role of openpit mining may be expected to continue or even increase in the nearer term of, say, the remainder of this century. In view of the complexities and variations of underground mining methods, and their relatively small contribution, this study is restricted to an examination of energy demand for surface mining operations only.

Two significant parameters affect energy demand in openpit mines, the physical dimensions of the excavation and the grade of ore sent to the mill. The operation of hauling broken ore and waste rock accounts for a major portion of the energy consumption; thus energy consumption is dependent on the vertical and horizontal dimensions of the excavation. As the pit becomes deeper, the energy for moving broken rock will increase, firstly because of the increased lift and haul distance to be travelled, and secondly because the ratio of waste to ore may increase with depth. The planning of openpit mines is today extended to depths of as much as 1,500 feet below the pit rim. The energy and dollar cost of hauling rock from such depth may dictate the economic life of surface mining.

The average mill-head grade of copper ore mined in the U.S. has shown a continuously decreasing trend since the start of this century, despite the fact that the real price of copper metal has not increased. Technological improvements in mining and processing methods have reduced unit costs, while concurrently, the richer ores have become exhausted and replaced by lower grade ore. Consequently, more ore must now be mined and treated to produce a given amount of copper metal. While we may expect technological innovation to continue at least at the same tempo as in the past, it must be remembered that the incentive in the past was to replace expensive manpower by cheap energy. Increased mechanization usually results in higher energy consumption

per unit of production. As the cost of energy increases, the conflict between energy optimization and dollar optimization is likely to resolve itself, that is, as energy becomes more costly the profit motive of private enterprise will focus more attention on energy conservation, and technological innovation and economic policy decisions will be directed toward this objective.

A further consideration of growing significance in the past decade has been the increasing emphasis on environmental protection through government regulation. Compliance with the requirements of these regulations will undoubtedly add to the energy and dollar cost of the mining and extraction operations, reflecting on mining policy in terms of higher cut-off grade and curtailment of the economic life of the mine. In view of the above factors, the trend of falling average mill head grade may well be reduced, or even reversed.

1.2.2 Method of Analysis

The principal objective of this investigation is to determine the order of magnitude of energy consumption for each of the sequential processes required to produce a final cathode copper product. Two main subdivisions are recognizable — the front-end operations of mining and treating the ore to produce a copper sulfide concentrate, and the subsequent operation of extraction and refining to produce a cathode copper product. While the extraction and refining processes are independent of the front-end operations (assuming a standard concentrate composition) the converse is not necessarily true; loss of metal during refining affects the tonnage of ore to be mined, crushed, milled and concentrated by flotation (per ton of cathode copper produced). The total energy attributable to a particular extraction and refining process must therefore take account of its metal recovery factor as reflected in the front-end energy requirement.

The energy assessment for the mining operations is contingent on the physical characteristics of the ore body and the pit conformation. An initial attempt was made to obtain actual energy consumption data for operating openpit mines in the U.S.A. However, the mining companies were unwilling to divulge such information, although it is known that the relevant data is submitted in the form of routine reports to the Department of Energy. Consequently, it was decided to revert to an analytical type of assessment based on hypothetical mineralization and mining models. It is believed that this approach gives estimates of acceptable definition, and has the added advantage that the model parameters can be varied at will to ascertain their sensitivity to change. These models are described below.

1.2.2.1 The Mineralization Model

Mineral values are not evenly distributed throughout an ore body. Values ranging from high to low tenor usually follow a law of probability such that the occurrence of some values is more common than that of other values. This probability density distribution will vary from deposit to deposit.

In an openpit mine it is usually necessary to mine the low grade ground in order to gain access to the payable high grade ore. Only rock above a predetermined cut-off value is sent to the plant for treatment. The low grade rock below this value goes to the waste dump or to surface leach dumps for recovery of some of the copper content by acid leaching.

The mineralization model used in this simulation is typical of a porphyry copper deposit although it does not necessarily correspond to any particular deposit. It is assumed that the

average copper value of blocks of ore of minable size is log-normally distributed within the ore body such that the mean value of the ore body is 0.45% Cu, and the logarithmic variance of values is 0.2(%) Cu (U.S. House of Representatives, June 1976). This probability density distribution is shown graphically in Figure 1.2-1. (a)

It follows that as the cut-off grade is increased the tonnage available for mining is reduced, while the average value of the tons mined is increased. Mathematically this relationship may be expressed as follows:

$$\text{Fraction of total tons above cut-off grade} = \int_{g_c}^{\infty} f(x) \cdot dx$$

$$\text{Average grade of tons above cut-off grade} = \frac{\int_{g_c}^{\infty} x \cdot f(x) \cdot dx}{\int_{g_c}^{\infty} f(x) \cdot dx}$$

The grade/tonnage relationship is shown graphically in Figure 1.2-1 (b), and is tabulated in Table 1.2.1. A cut-off grade of 0.29% Cu is chosen as a base for this analysis, that is, 70% of the tonnage mined from the ore body will go to the mill at an average value of 0.55% Cu, and 30% of the tonnage mined from the ore body will go to surface leach dumps at an average grade of 0.22% Cu.

1.2.2.2 The Mine Model

Figure 1.2.2 is a cross section through a typical openpit mine exploiting a roughly cylindrical ore body extending vertically in depth. The model is based on the following assumptions:

Vertical depth below rim (H)	= 750'
Dynamic slope angle of sidewalls (θ)	= 30°
Ave. slope of haul roads in pit	= 6%
Surface haul to dumps	= 2500 ft. @ 6% grade
Surface haul to primary crushes	= 2500 ft. level
Overburden/ore body stripping ratio $\left(\frac{AC}{CB}\right)$	= 1.25
Mill head value of ore	= 0.55% Cu
Value of flotation concentrate	= 25% Cu
Value of flotation tails	= .069% Cu
i.e., recovery factor ore to concentrate	= 87.455%
Recovery factor concentrate to cathode copper	= 98.67%
i.e., recovery factor ore to cathode	= 86.29%
Primary cathode copper produced per year	= 100,000 tons
Tonnage Notation: (Refer to Figure 1.2.2)	
TO = Tons ore sent to mill (DB)	
TM = Tons mined from ore body (CB)

FIGURE 1.2-1 (a) LOG-NORMAL DISTRIBUTION OF Cu GRADES

FIGURE 1.2-1 (b) GRADE/TONNAGE RELATIONSHIP

TABLE 1.2-1

GRADE/TONNAGE RELATIONSHIP

Cut off Value (% Cu)	Tons > COV* (%)	Average Grade (% Cu)	
		Tons > COV	Tons < COV
0	100	.45	—
.22	85	.50	.17
.29	70	.55	.22
.34	58	.60	.24
.40	48	.65	.27
.45	39	.70	.29
.50	32	.75	.31
.55	26	.80	.32

* COV = Cut off value

FIGURE 1.2-2 THE MINE MODEL

TD = Tons ore sent to dump leach (CD)
 TS = Tons overburden stripped (AC)
 TW = Total tons mined from ore body not sent to mill (AD)
 TT = Total tons mined (AB)

Stripping Ratio Notation (Refer to Figure 1.2.2)

RSM = Ratio of tons of overburden stripped to tons mined from ore body
 RDO = Ratio of tons ore sent to dump leach to tons of ore sent to mill
 RSO = Ratio of tons of overburden stripped to tons of ore sent to mill
 RWO = Ratio of total tons mined from ore body not sent to mill to tons of ore sent to mill

 $RSM = TS/TM = AC/CB$
 $RDO = TD/TO = CD/DB \text{ ---- } CD = DB \cdot RDO$
 $RSO = TS/TO = AC/DB \text{ ---- } AC = DB \cdot RSO$
 $RWO = TW/TO = AD/DB \text{ ---- } AD = DB \cdot RWO$
 $RSM = TS/TM = AC/CB \text{ ---- } CB = AC \cdot RSM$

Examples of calculations:

0.55% = ore grade
 .8629 = fractional recovery from ore to cathode copper.
 100,000 = tons of cathode copper/yr.

$$\begin{aligned}
 \text{Tons to mill (TO)} &= \frac{100,000 \times 2,000}{.55 \times 20 \times .8629} \\
 &= 21.0706 \times 10^6 \text{ tons/year}
 \end{aligned}$$

$$RSM = 1.25$$

$$RDO = 30/70 = .4286$$

$$TD = TO \times RDO = 21.0706 \times 10^6 \times .4286 = 9.0309 \times 10^6$$

$$TM = TO + TD = (21.0706 + 9.0309) \times 10^6 = 30.1015 \times 10^6$$

$$TS = TM \times RSM = 30.1015 \times 10^6 \times 1.25 = 37.6268 \times 10^6$$

$$TW = TS + TD = (37.6268 + 9.0309) \times 10^6 = 46.6577 \times 10^6$$

$$TT = TW + TD = (46.6577 + 21.0706) \times 10^6 = 67.7283 \times 10^6$$

$$RWO = TW/TO = 46.6577 \times 10^6 / 21.0706 \times 10^6 = 2.2144$$

$$RSO = TS/TO = 37.6286 \times 10^6 / 21.0706 \times 10^6 = 1.7857$$

1.2.3 Analysis of Energy Demand in an Openpit Mine

Energy utilization in an openpit mine is analyzed in the context of the above models and in relation to the headings below, using typical values extracted from published literature and operating mine data. The energy consumption attributable to each operation is shown diagrammatically in Figure 1.2.3 in terms of Btu per short ton of refined cathode copper produced. For the particular model used in this analysis, the overall energy attributable to the mining operation is 27.999 million Btu per ton of refined cathode copper produced.

1.2.3.1 Drilling

The estimate of the energy utilization for drilling operations is based on published data of drilling equipment, and tonnage duties for 4 large copper mines in the State of Arizona. The calculated average energy consumption amounts to 904 Btu per short ton of broken rock produced. In terms of our model, this converts to 0.612×10^6 Btu per ton of cathode copper produced (see Appendix 1.2.3.1).

FIGURE 1.2-3 ENERGY REQUIREMENTS FOR EACH OPERATION IN MINING

Drilling is a relatively small user of energy, accounting for some 3.0% of the total energy consumed in the mining operation. (See Fig. 1.2.3.) No significant energy saving developments in drilling technology are anticipated in the foreseeable future.

1.2.3.2 Blasting

It is considered that explosives are a primary source of energy and that the operation of rock fragmentation is an energy function. It is therefore necessary to convert explosive energy into coal equivalent in the same way as has been done for electric power and diesel fuel.

The explosive agent used in openpit mines is primarily ANFO, ideally a mixture of 94.5% ammonium nitrate plus 5.5% fuel oil. The energy value of ammonium nitrate is estimated as 30.0 million Btu per ton (this value will vary depending on the production process used to produce ammonia whether from primarily natural gas feedstock or as a by-product from steel plant coking ovens.) A weighted average blasting agent factor of 0.27 lbs of explosives per ton of rock blasted is derived in Appendix 1.2.3.2. We can calculate the energy value of 1 lb of blasting agent (ANFO) in terms of its equivalent coal energy as follows:

$$\begin{aligned} 945 \text{ lb. Ammonium Nitrate} &= 0.945 \times 30 \times 10^6 / 2000 \\ &= 14175 \text{ Btu} \\ .055 \text{ lb. Fuel Oil} &= .055 \times 138690 \\ &= 7268 \text{ Btu} \\ 1 \text{ lb. Blasting Agent} &= 21443 \text{ Btu Coal Energy} \end{aligned}$$

Neglecting fuses, detonators and primers to initiate the explosion, we calculate the blasting energy consumption for our model as follows:

$$\begin{aligned} \text{Blasting Energy} &= .27 \times 21443 \text{ Btu/ton Rock} \\ &= 5790 \times 67.7283 \times 10^6 \text{ Btu (total)} \\ &= 3.895 \times 10^6 \text{ Btu/ton Cathode Copper} \end{aligned}$$

In terms of this model, blasting accounts for 19.4% of the total energy used in mining (Table 1.2.3). It is clear that any increase in the cost of energy will be reflected as a substantial rise in the cost of explosives. It may be anticipated that this rise in cost will stimulate research into more efficient use of explosives and could substantially modify present philosophies regarding the optimization of explosive utilization in relation to the other mining activities such as loading and hauling.

1.2.3.3 Loading

We assume an average power utilization factor for loading equipment of 0.6 kWh per bank cubic yard (BCY) of copper ore of density 4500 lbs./BCY. (Pfleider, Surface Mining, p. 439).

$$\frac{.6 \times 2000 \times 10239}{4500} = 2730 \text{ Btu/ton rock.}$$

$$\frac{2730 \times 67.7283 \times 10^6}{100,000} = 1.849 \times 10^6 \text{ Btu/ton cathode copper}$$

The energy used for loading operations will vary relative to the conditions of loading, the equipment used, and the nature of the shot rock. The indicated energy utilization of 1.849×10^6 Btu/ton of cathode copper represents only some 9.2% of the total energy used in mining, compared with 19.4% for explosives (Fig. 1.2.3).

Mine operators continuously seek to optimize fragmentation with respect to the overall economics of drilling, blasting, loading, hauling and primary crushing. Under conditions of relatively cheap abundant energy, preference is given to production equipment utilization, that is, the blasting operation is designed to produce a fragmentation size grading with minimum representation of large rocks which may adversely affect the loading operation, consequently, the fine end of the spectrum is unnecessarily over-represented. As energy becomes less plentiful and more costly, it can be expected that the bias of attention will swing toward more effective use of explosive energy.

1.2.3.4 Hauling

The traditional method of hauling rock in openpit mines is by means of a fleet of rear dump trucks which may range in size from 30 tons to 250 tons carrying capacity. The weight of the empty truck is some 75% of the live load. This nonproductive weight must be moved twice the distance of the live load, up the incline carrying the load, and return empty. A significant part of the total energy consumption is used in moving the carrier. Such inefficient use of energy invites examination of alternative forms of transportation of broken rock.

Two large openpit copper mines in the State of Arizona have introduced continuous conveyor belt systems as a partial replacement of truck haulage. Broken ore and waste is hauled by truck from the active benches to primary crushers located at a central point within the pit. The crushed rock is moved by conveyor belt to surface, either to the waste dump or to the mill. These systems are described respectively by J. J. Coille and F. W. Sweitzer. Operating statistics covering a significant continuous period of truck hauling and conveyor transportation have been confidentially provided by one of these mines. The analyzed results are summarized in Appendix 1.2.3.3 in relation to a synthetic unit of performance representing the product of tons moved by effective level feet traveled (TELF).

Consider the effective work performed in hauling rock up an incline by dump truck, neglecting the nonproductive work of moving the carrier up and down the slope:

$$\begin{aligned} \text{Effective work per ton} &= \text{Slope distance} \times (\text{Rolling resistance} + \text{Gravity resistance}) \\ \text{Rolling resistance} &= 40 \text{ lb./ton for a normal mine haulage road} \\ \text{Gravity resistance} &= (20 \times \% \text{ grade}) \text{ lb./ton} \\ \text{Effective work per ton} &= SD(40 + 20 \times \% \text{ grade}) \end{aligned}$$

The product $SD(2 + \% \text{ grade})$ is a proportional measure of the effective work accomplished, equivalent to moving one ton of rock through an equivalent level distance (ELF) of $SD(2 + \% \text{ grade})$.

$$\text{Total Effective Work} = \text{Tons} \times SD(2 + \% \text{ grade}) \text{ TELF.}$$

An estimate of the energy consumed for transporting broken rock can now be made in respect to the mine model previously discussed. (See Fig. 1.2-4.) Assume conventional rock hauling by rear dump truck operating at an average energy utilization factor of 0.2963 Btu/TELF as derived in Appendix 1.2.3.4.

In Figure 1.2.4 we have:

$$\begin{aligned}
 H &= \text{Depth of pit} \\
 HT &= \text{Average lift for overall tonnage} \\
 HS &= \text{Average lift for overburden stripping} \\
 HM &= \text{Average lift for tons mined from ore body} \\
 \frac{AC}{AB} &= \frac{TS}{TT} = \frac{37.6268}{67.7283} = .5556 \\
 AB &= 750/\sin 30^\circ = 1550 \\
 AC &= 1500 \times .5556 = 833' \\
 CB &= 1500 - 833 = 667' \\
 HT &= 750/2 = 375' \\
 HS &= 1/2 AC \sin 30^\circ = 208' \\
 HM &= 2 HS + 1/2 CB \sin 30^\circ = 583' \\
 \text{Stripping duty} &= TS \times \text{Slope Dist} \times (2 + \% \text{ grade}) \\
 &= 37.6268 \times 10^6 \times 208 \times \frac{100}{6} \times (2 + 6) \\
 &= 1.0435 \times 10^{12} \text{ TELF}
 \end{aligned}$$

Add duty for surface transportation of ore and waste to primary crushers and dumps respectively:

$$\begin{aligned}
 \text{To Dumps} &= TW \times \text{Slope Dist} (2 + \% \text{ grade}) \\
 &= 46.6577 \times 10^6 \times 2500 \times 8 \\
 &= 933154 \times 10^6 \text{ TELF} \\
 \text{To Primary Crushers} &= TO \times \text{Slope Dist} (2 + \% \text{ grade}) \\
 &= 21.07 \times 10^6 \times 2500 \times 2 \\
 &= 1.05 \times 10^{11} \text{ TELF} \\
 \text{Mining Duty} &= TM \times \text{Slope Dist} (2 + \% \text{ grade}) \\
 &= 30.10 \times 10^6 \times 583 \times \frac{100}{6} \times 8 \\
 &= 2.40 \times 10^{12} \text{ TELF} \\
 \text{Total Hauling Duty} &= 4.42 \times 10^{12} \text{ TELF} \\
 \text{Energy/ton Cathode Copper} &= 4.42 \times 10^6 / 100,000 \\
 &= (13.137 \times 10^6 \text{ Btu, by computer})
 \end{aligned}$$

Referring to Figure 1.2.3 it can be seen that the hauling operation accounts for 65.2% of the total energy, consumed by openpit mining under the assumed conditions of the model.

FIGURE 1.2-4 AVERAGE HAUL LIFT DUTY

In Appendix 1.2.3.3 it is shown that at the mine concerned the installation of a conveyor belt system to partially replace truck haulage resulted in a saving of some 30% in energy consumption. While the use of belt conveyors would not be feasible for all openpit mine configurations, it is clear that rock transportation is one area where very thorough research and development will pay big dividends in terms of savings in energy and dollar costs, especially as openpit mines grow in depth and extent in the future.

1.2.3.5 Ancillary Operations:

The ancillary operations associated with openpit mining are extremely diverse and their energy consumption is difficult to estimate. However, the total energy consumed by these operations is relatively small so that an error in estimation will have little if any effect on the overall outcome of this investigation. The following estimates are made (See Appendix 1.2.3.4):

Auxiliary mobile equipment	= 0.599×10^6 Btu/ton Cu
Dewatering	= 0.016×10^6 Btu/ton Cu
Reclamation equipment	= 0.021×10^6 Btu/ton Cu
Revegetation	= 0.202×10^6 Btu/ton Cu
Total	0.638×10^6 Btu/ton Cu

It is shown in Figure 1.2.3 that ancillary operations account for some 3.2% of the total energy consumption for mining operations.

1.2.4 Sensitivity Analysis

Three basic parameters may substantially affect the energy consumption of the front-end operations of mining and/or copper sulfide concentration. These are the average grade of the ore treated, the overburden to orebody stripping ratio (RSM), and the pit depth below the surface rim. The sensitivity of the model to changes in these parameters is tested by computer in relation to conventional extraction practice of sulfide concentration, reverberatory smelting, fire converting and electro-refining.

1.2.4.1 Sensitivity to Changes in Cut-off Grade

The grade/tonnage relationship given in Table 1.2.1 will apply, provided the mineralization model does not change. However, it must be remembered that some of the contained copper in the reject tonnage below cut-off grade may subsequently be recovered by means of dump leaching (see section 1.2.5). Provisionally neglecting this possible recovery of additional copper, the sensitivity of the model to change in cut-off grade is shown in Table 1.2.2.

TABLE 1.2.2

EFFECT OF VARYING CUT-OFF GRADE

Cut Off Grade (% Cu)	Millhead Grade (% Cu)	Tons Milled $\times 10^6$	Btu $\times 10^6$ /ton Cath. Copper Produced			
			Mining	Conc.	Refining	Total
0	.45	26.6005	17.4	53.7	35.2	106.3
.22	.50	23.515	18.3	47.5	35.2	101.0
.29	.55	21.070	20.1	42.6	35.2	97.9*
.34	.60	19.086	22.2	38.6	35.2	95.9
.40	.65	17.444	24.7	35.2	35.2	95.1
.45	.70	16.061	28.1	32.4	35.2	95.8

*Standard Reference

It can be seen in the above tabulation that the effect of lowering the cut-off grade will be to decrease the energy per ton of cathode copper produced for the mining operation, while increasing that for the concentrating operation. For this model the counter-active changes result in a very small net change in overall energy requirement, although a minimum is indicated at a cut-off value of .34% Cu.

Let us now consider the effect of recovering some of the copper content of the reject ore below the cut-off grade by dump leaching (Sect. 1.2.5). Reference to Table 1.2.3 shows that the tonnage of reject ore will increase as the cut-off grade is increased, and its average grade will also increase; in other words the potential recovery of copper by dump leaching will be substantially increased. The energy cost of this additional copper is estimated in Sect. 1.2.5 at 93.74 million Btu/ton. The average effect of a change in cut-off grade is tabulated below.

TABLE 1.2.3

OVERALL EFFECT OF VARYING CUT-OFF GRADE

Cut-off Grade (% Cu)	0	.22	.29	.34	.40	.45
Tons Milled ($\times 10^6$)	26.60	23.52	21.07	19.09	17.44	16.06
Mill-head Grade (% Cu)	.45	.50	.55	.60	.65	.70
Copper Produced (Tons)	100,000	100,000	100,000	100,000	100,000	100,000
Btu/ton Copper ($\times 10^6$)	106.3	101.0	97.9	95.9	95.1	95.7
Tons Leached ($\times 10^6$)	0	4.15	9.03	13.82	18.90	25.12
Dump Grade (% Cu)	0	.17	.22	.24	.27	.29
Copper Produced (Tons)	0	2,351	6,622	11,056	17,007	24,284
Btu/ton Copper ($\times 10^6$)	0	93.7	93.7	93.7	93.7	93.7
Total Tons Treated ($\times 10^6$)	26.60	27.67	30.10	32.91	36.34	41.18
Total Cu Produced (Tons)	100,000	102,351	106,622	111,056	117,007	124,284
Ave. Btu/ton Cu ($\times 10^6$)	106.3	100.8	97.6	95.7	94.9	95.3
% Resource Recovery	.835	.822	.787	.750	.715	.671

The above estimates are based on broad assumptions regarding mineralization characteristics, pit conformation and plant layout. Nevertheless it is apparent that an interesting scope for optimization studies exists in this area — that is, in the trade-off of energy conservation versus resource recovery. Changes in technology or design could well result in material changes in the selection of cut-off grade for a particular mine.

1.2.4.2 Sensitivity to Changes in Stripping Ratio

Table 1.2.4 indicates the way the energy consumed in mining varies with the overburden to orebody stripping ratio (RSM).

TABLE 1.2.4

EFFECT OF VARYING STRIPPING RATIO

Stripping Ratio (RSM)	Btu x 10 ⁶ /ton Cathode Copper Produced			
	Mining	Conc.	Refining	Total
1.00	17.79	42.57	35.17	95.53
1.25	20.13	42.57	35.17	97.87*
1.50	22.47	42.57	35.17	100.21
1.75	24.81	42.57	35.17	102.55
2.00	27.15	42.57	35.17	104.89
2.50	31.84	42.54	35.17	109.57

*Standard Reference.

1.2.4.3 Sensitivity to Changes in Depth

The energy expended in transporting broken rock is a function of the lift and horizontal distance moved. (Refer to Section 1.2.3.4.) This relationship is reflected in the total energy for mining as shown in Table 1.2.5.

TABLE 1.2.5

EFFECT OF VARYING DEPTH OF PIT

Depth of Pit (Feet)	Btu x 10 ⁶ /ton Cathode Copper Produced			
	Mining	Conc.	Refining	Total
500	24.67	42.57	35.17	102.95
750	28.00	42.57	35.17	106.28*
1000	31.36	42.57	35.17	109.64
1250	34.71	42.57	35.17	112.99
1500	38.05	42.57	35.17	116.33

*Standard Reference.

1.2.5 Dump Leaching

Dump leaching accounts for some 30% of the primary copper produced in the United States. While much of this comes from the treatment of old existing low grade copper dumps, it is clear that the recovery of some of the copper content of currently mined low grade ore should be taken into consideration in the overall assessment of the energy content of domestic copper production.

For the purpose of this analysis it is assumed that all the low grade ore below the cut-off value will be systematically placed in finger dumps suitable for current acid leaching. (Refer to the mineralization model section 1.2.2.1, and Table 1.2.1.) The base condition for this analysis calls for a cut-off grade of .29% Cu, giving 30% of mineralized ore below cut-off grade sent to the leach dumps at an average value of .22% Cu.

The energy for dump leaching is predominantly required for the circulation of the leachate solutions; this in turn is essentially a function of the lift and horizontal distance from the cementation plant to the top of the leach dumps. The following specifications are assumed:

Finger Dumps: 150' Vert x 400' flat top x 800 base.
Lift from plant to top of dump 450'
Hor. Dist. from plant to dump 5000'
Tons leached per year (TD in sect. 1.2.2.1) = 9.0309×10^6 tons @ .22% Cu
 $9.0309 \times 10^6 \times .22 \times 20$ = 39.7360×10^6 lbs Cu/year
@ 33% recovery = 6622.667 tons/year
@ 360 days per year = 36.792 lbs/day
Leachate concentration .5 gr/litre = 4.2 lbs/1000 U.S. gal.
Daily Circulation = 8.7600×10^6 gal./day
= 6083 gal./min.

From Ingersoll Rand Hydraulic Data Tables for 14" I.D. pipe we get:

Q = 3077 gpm
V = 6.42 ft/sec
H_v = .64 ft
H_f = 1.58 ft/100'

Pumped Flow of barren solution

Gravity Head = 450 ft
Spray Head = 50 ft
Velocity Head = 1 ft
Friction Head = 79 ft
Fittings = 40 ft
620 ft

Q = $6083 \times .13369$
= 813 ft³/min

Return flow of pregnant solution

Minm. Head for free flow = $(5000 \times .0158) + 1 = 80$ ft.
Therefore gravity head of 300 ft will effect return flow.

$$\begin{aligned}
 \text{Water Horsepower} &= \frac{H \times Q \times 62.4}{33,000} \\
 &= \frac{620 \times 813 \times 62.4}{33,000} \\
 &= 953 \text{ H.P.} \\
 \text{Pump H.P. @ 70\% efficiency} &= 1362 \text{ H.P.} \\
 \text{Energy per day} &= 1362 \times .745 \times 24 \\
 &= 24,346 \text{ KW hr/day} \\
 &= 249.28 \times 10^6 \text{ Btu/day} \\
 \text{Specific Energy} &= \frac{249.28 \times 10^6 \times 2000}{36,792} \\
 &= 13.551 \times 10^6 \text{ Btu/ton Cu.}
 \end{aligned}$$

On the basis of the above assumed conditions we have 6622 tons per year of copper extracted by dump leaching low grade ore (below cut-off grade) at a front-end energy cost of 13.551×10^6 Btu per ton of contained copper. The gross energy cost per ton of cathode copper produced must take account of the subsequent refining processes. Assume that dump leach ore does not carry any cost of mining, and that the cement copper is introduced into the reverberatory smelting furnace with the copper sulfide concentrate feed. The gross energy cost will then be:

$$\begin{aligned}
 \text{Energy for circulating solutions} &= 13.55 \times 10^6 \text{ Btu/ton Cu} \\
 \text{Energy for cementation (Sect. 1.8)} &= 45.05 \times 10^6 \text{ Btu/ton Cu} \\
 \text{Energy for refining (Sect. 2.3)} &= 35.14 \times 10^6 \text{ Btu/ton Cu} \\
 \text{Total Energy} &= 93.74 \times 10^6 \text{ Btu/ton Cu}
 \end{aligned}$$

1.2.6 Conclusion

The energy attributable to mining is to a large extent dependent on the physical parameters of the individual mine concerned, in particular on the nature of mineralization, the cut-off grade demarcating 'ore to mill' from 'low grade ore to dumps,' the overburden to ore stripping ratio, and the depth and dimensions of the pit. Reference to Section 1.2.4 indicates the extremely wide range of possible variation in energy requirement.

In addition to the sensitivity to internal mining parameters, the energy required by the mining operation per ton of cathode copper produced is a function of the recovery factor in the succeeding processes of copper sulfide concentration and refining. The lower the recovery in these processes the more ore must be provided by the mining operation to produce the final target of 100,000 tons of refined cathode copper. This reflected additional energy demand in the front-end processes should be taken into account in the assessment of alternative processes.

This report highlights certain areas where further research may be fruitful in the context of energy conservation. These are:

- Rock hauling
- Explosive utilization
- Optimization of cut-off grade taking account the trade off between conventional concentration and dump leaching.

With the rapidly rising cost of energy it is considered that normal economic motives will tend to stimulate accelerated research in the above areas in the future.

1.2.7 References

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APPENDIX 1.2.3.1

Energy Consumption: Blasthole Drilling

The calculation of direct energy consumption for blasthole drilling is based on published equipment provision for four large open pit copper mines (Engineering and Mining Journal, June 1977) and the manufacturer's estimates of unit energy consumption for the relevant equipment.

Mine A

Operating Data: S-45R Rotary Drills
190,000 tons mined per day
5 drills/shift x 3 shifts/day x 7.25 hr/day = 108.75 hr/day

Diesel Fuel

108.75 hr/day x 12.86 gal/hr = 1,399 gal/day
1399 gal/hr x 138.690 Btu/gal = 194,027,310 Btu/day

Lube Oil

@ 1.5% of Diesel Fuel = 21 gal/day
21 gal/day x 148.690 Btu/gal = 3,122,490 Btu/day
Total Direct Energy = 197,149,800 Btu/day

Mine B

Operating Data: 5-40R Rotary Drills
2-60R Rotary Drills
135,000 tons mined per day
7 drill shifts per day
7 drill shifts/day x 7.25 hr/shift = 50.75 hr/day
Assume use of drills is proportional to number of drills.

$$\begin{aligned}40R \text{ } 50.75 \text{ hr/day} \times 5/7 &= 36.25 \text{ hr/day} \\60R \text{ } 50.75 \text{ hr/day} \times 5/7 &= 14.5 \text{ hr/day}\end{aligned}$$

Diesel Fuel

$$\begin{aligned}40R \text{ } 36.25 \text{ hr/day} \times 10.71 \text{ gal/hr} &= 388 \text{ gal/day} \\60R \text{ } 14.5 \text{ hr/day} \times 19.29 \text{ gal/hr} &= 280 \text{ gal/day} \\688 \text{ gal/day} \times 138,690 \text{ Btu/gal} &= 95,418,720 \text{ Btu/day}\end{aligned}$$

Lube Oil

$$\begin{aligned}\text{@ } 1.5\% \text{ of Diesel Fuel} &= 10 \text{ gal/day} \\10 \text{ gal/day} \times 148,690 \text{ Btu/gal} &= 1,486,900 \text{ Btu/day} \\ \text{Total Direct Energy} &= 96,915,620 \text{ Btu/day}\end{aligned}$$

Mine C

Operating Data: 4-45R Rotary Drills
4-60R Rotary Drills
256,000 tons mined per day
5 drills per shift 3 shifts per day
15 drill shifts/day x 7.25 hr/shift = 108.8 hr/day
Assume use of drills is proportional to number of drills

$$\begin{aligned}45R \text{ } 108.8 \text{ hr/day} \times 4/8 &= 54.4 \text{ hr/day} \\60R \text{ } 108.8 \text{ hr/day} \times 4/8 &= 54.4 \text{ hr/day}\end{aligned}$$

Diesel Fuel

$$\begin{aligned}40R \text{ } 54.4 \text{ hr/day} \times 12.86 \text{ gal/hr} &= 699.6 \text{ gal/day} \\60R \text{ } 54.4 \text{ hr/day} \times 19.29 \text{ gal/hr} &= 1,049.4 \text{ gal/day} \\ \text{Total} &= 1,749.0 \text{ gal/day} \\1,749.0 \text{ gal/day} \times 138,690 \text{ Btu/gal} &= 242,658,810 \text{ Btu/day}\end{aligned}$$

Lube Oil

$$\begin{aligned}\text{@ } 1.5\% \text{ of Diesel Fuel} &= 26 \text{ gal/day} \\26 \text{ gal/day} \times 148,690 \text{ Btu/gal} &= 3,865,940 \text{ Btu/day} \\ \text{Total Direct Energy} &= 246,434,750 \text{ Btu/day}\end{aligned}$$

Mine D

Operating Data: 4-60R Rotary Drills
 107,400 Tons mined per day
 4 drill shifts per day 1 shift per day
 7.5 hr/shift
 4 drills/shift x 7.5 hr/shift = 30.0 hr/day

Diesel Fuel

60R 30 hr/day x 19.29 gal/hr = 579 gal/day
 579 gal/hr x 138.690 Btu/gal = 80,301,510 Btu/day

Lube Oil

@ 1.5% of Diesel Fuel = 9 gal/day
 9 gal/day x 148,690 Btu/gal = 1,338,210 Btu/day
 Total Direct Energy = 81,639,720 Btu/day

<u>Mine</u>	<u>Tons Mined Per Day</u>	<u>Energy Equivalent Btu/day</u>
A	190,000	197,149,800
B	135,000	96,915,620
C	256,000	246,434,750
D	107,400	81,639,720
Total	688,400	622,139,890

Average Energy = 622,139,890 Btu/day
 688,400 tons mined/day
 = 904 Btu/ton mined

APPENDIX 1.2.3.2

Energy Consumption: Explosives Utilization

Derivation of the powder factor used in calculation of blasting energy use is accomplished in the following manner:

<u>Mine</u>	<u>Tons Mined per Year</u>		<u>Powder Factor lb/ton</u>		<u>lb Blasting Agent Used per Year</u>
1	39,514,000	x	0.20	=	7,902,800
2	27,108,000	x	0.27	=	7,319,160
3	36,583,486	x	0.43	=	15,380,898
4	57,046,000	x	0.25	=	14,261,500
5	18,672,100	x	0.62	=	11,576,702
6	145,264,340	x	0.224	=	32,510,159
Total	324,187,926	x	(0.27)	=	88,951,219

$$\frac{88,951,219 \text{ lb ANFO/yr}}{324,187,926 \text{ T/yr}} = 0.27 \frac{\text{lb ANFO}}{\text{T}}$$

The tonnage-weighted-average blasting agent use for six large open pit copper mines is 0.27 lb/T.

APPENDIX 1.2.3.3

Energy Consumption: Rock Hauling

The following tabulation is a summary of actual operating statistics covering the transportation of broken rock by dump truck and conveyor belts for a continuous period of nine months, as provided confidentially by a large openpit copper mine in the State of Arizona.

TRUCK HAULING (Waste and Ore)

Ore and Waste Rock hauled	= 3.898×10^8 short tons
Average slope distance	= 5730 feet
Average Vertical Lift	= 221.5 feet
Average gradient	= 3.87%
Total Effective work units	= 1.311×10^{12} TELF
Diesel fuel consumed	= 2,759,279 gallons
*Coal energy equivalent	= 3.827×10^7 Btu
Lube oil consumed	= 39,361 gallons
*Coal energy equivalent	= 5.89×10^9 Btu
Total Energy Consumption	= 3.886×10^{11} Btu
Unit Energy consumed	= 0.2963 Btu/TELF

WASTE ROCK CONVEYING

Waste rock transported	= 2.064×10^7 short tons
Slope length of conveyor system	= 7,079 feet
Vertical lift	= 414 feet
Average gradient	= 5.86%
Total effective work units	= 1.149×10^{12} TELF
Electric power consumed	= 2.0924×10^7 kWhr
*Coal energy equivalent	= 2.142×10^7 Btu
Unit energy consumed	= 0.1865 Btu/TELF

WASTE ROCK CRUSHING

Waste rock crushed	= 2.064×10^7 short tons
Electric power consumed	= 4.581×10^6 kWhr
Coal energy equivalent	= 4.69×10^{10} Btu
Unit Energy consumed	= 2,272 Btu/ton

ORE CONVEYING

Ore transported	= 2.214×10^7 short tons
Slope length of conveyor system	= 18,216 feet
Vertical lift	= 457 feet
Average gradient	= 2.51%
Total effective work units	= 1.819×10^{12} TELF
*Coal energy equivalent	= 3.533×10^7 kWhr
Unit energy consumed (ore)	= 0.1989 Btu/TELF
Mean unit energy (ore and waste)	= 0.1941 Btu/TELF
*Coal energy equivalents	
1 gal. diesel fuel	= 138,690 Btu
1 gal. Lube oil	= 149,690 Btu
1 kWhr	= 10,239 Btu

Significant unit energy consumption figures extracted from the above tabulation are:

Truck Hauling	= 0.2963 Btu/TELF
Conveyor Transportation	= 0.1941 Btu/TELF
Waste Rock Crushing	= 2272 Btu/ton

Considering only the existing conveyor system we have:

Energy Consumed	- Waste crushing	= 4.69×10^{10} Btu
	- Waste conveying	= 2.142×10^{10} Btu
	- Ore conveying	= 3.617×10^{11} Btu
	- Total	= 6.229×10^7 Btu
Haul Duty	- Waste conveying	= 1.149×10^{12} TELF
	- Ore conveying	= 1.819×10^{12} TELF
	- Total	= 2.968×10^{12} TELF

If the above hauling duty were to be performed by dump trucks operating at an average unit energy factor of 0.2963 Btu/TELF, the total energy consumption would amount to 879.338×10^6 Btu. The energy saved by the conveyor installation is therefore 256.461×10^6 Btu, or some 30% of the equivalent all truck system. On a 12 month basis the saving would amount to 341.948×10^6 Btu, or the coal equivalent energy of 2.5 million gallons of diesel fuel per year. In areas where electric power is generated from coal the conversion to conveyor belt system would have the added attraction of reducing the demand for scarce diesel fuel by some 6.3 million gallons per year.

APPENDIX 1.2.3.4

Energy Consumption: Ancillary Operations

The following broad estimates are made of energy consumed by operations in an open pit mine:

	<u>Btu/ton Copper</u>
1. Auxiliary Mining Equipment	0.399×10^6
2. Pit Dewatering	0.016×10^6
3. Reclamation Equipment	0.021×10^6
4. Revegetation	<u>0.202×10^6</u>
Total	0.638×10^6

1. Auxiliary Mining Equipment

	No. of Units	X	Fuel Consumption gal/hr	X	Shifts/ Day	X	Days/ Year	X	Utilization 70%	=	Gallons per Year
Track Dozers	12		14		3		312		0.7		110,000
Rubber Tired Dozers	4		11		3		312		0.7		28,800
F.E. Loaders	3		18		3		312		0.7		35,400
Graders	5		7		3		312		0.7		23,000
Water Trucks	2		9		3		312		0.7		12,000
ANFO Trucks	2		6		1		312		0.7		2,600
Pickups (Gasoline)	60		2		3		312		0.7		78,600

Total Diesel = 211,800 gal/yr

Total Gasoline = 78,600 gal/yr

Diesel Fuel and Gasoline

$$211,800 \text{ gal/yr} \times 138,600 \text{ Btu/gal} = 2.9355 \times 10^{10} \text{ Btu/yr}$$

$$78,600 \text{ gal/yr} \times 125,800 \text{ Btu/gal} = 0.9888 \times 10^{10} \text{ Btu/yr}$$

Lube Oil

$$@ 1.5\% \text{ of fuel use} = 4356 \text{ gal/yr}$$

$$4356 \text{ gal/yr} \times 148,690 \text{ Btu/gal} = 0.0647 \times 10^{10} \text{ Btu/yr}$$

$$\text{Total Energy Use} = 3.989 \times 10^{10} \text{ Btu/yr}$$

$$\frac{3.989 \times 10^{10} \text{ Btu/yr}}{100,000 \text{ T Cu/yr}} = 0.399 \times 10^6 \text{ Btu/ton Cu}$$

2. Pit Dewatering

Assumed Data: Precipitation – 10 inches/year
Pit Diameter – 3,000 ft
Pit Depth – 750 ft
Length of pipe for pumping 2000 ft
No evaporation or precipitation

$$\text{Pit area} = \pi r^2 = 3.14 \times (1500)^2 = 7.068 \times 10^6 \text{ ft}^2$$

$$\text{Volume of precipitation} = 7.08 \times 10^6 \text{ ft}^2 \times \frac{10 \text{ in.}}{\text{yr}} \times \frac{\text{ft}}{12 \text{ in.}} = 5.89 \times 10^6 \frac{\text{ft}^3}{\text{yr}}$$

$$\frac{5.89 \times 10^6 \frac{\text{ft}^3}{\text{yr}} \times 7.48 \frac{\text{gal}}{\text{ft}^3}}{525,960 \frac{\text{min}}{\text{yr}}} = 93.8 \frac{\text{gal}}{\text{min}} \text{ pumping duty}$$

Assume evaporation rate equals the ground water infiltration rate to the pit; therefore total pumping duty for pit dewatering is 84 gal/min.

Pumping	4" CI pipe, 84 gal/min velocity = 2.14 ft/sec friction loss = 0.83 ft/100 ft
Gravity Head	750 ft
Friction Head	17 ft
Velocity Head	--
Fittings @ 50% H _f	8 ft
Total Head	775 ft

$$Q = 84 \text{ gal/min} \times 0.13369 \text{ ft}^3/\text{gal} = 11.23 \text{ ft}^3/\text{min}$$

$$\text{Water Hp} = \frac{HQ \times 62.4}{33,000} = \frac{775 \times 11.23 \times 62.4}{33,000} = 16.5 \text{ Hp}$$

$$\text{Pumping Efficiency @ 70\%} = \frac{16.5 \text{ Hp}}{0.7} = 23.5 \text{ Hp}$$

Energy Requirement

$$\begin{aligned}
 &23.5 \text{ Hp} \times 0.754 \frac{\text{kWh}}{\text{Hp}} \times 24 \frac{\text{hr}}{\text{day}} = 420 \frac{\text{kWh}}{\text{day}} \\
 &420 \frac{\text{kWh}}{\text{day}} \times 10239 \frac{\text{Btu}}{\text{kWh}} = 4.3 \times 10^6 \frac{\text{Btu}}{\text{day}} \\
 &\frac{4.3 \times 10^6 \frac{\text{Btu}}{\text{day}} \times 365.25 \frac{\text{day}}{\text{yr}}}{100,000 \frac{\text{T Cu}}{\text{yr}}} = 0.016 \times 10^6 \frac{\text{Btu}}{\text{Ton Cu}}
 \end{aligned}$$

3. Reclamation Equipment

Assume that reclamation proceeds at the same rate as the dumps are built with suitable delay in time to allow leaching of the dumps to proceed to completion.

From previous calculations, the finger dumps will hold 6000 tons per foot of dump.

$$\frac{47.1991 \times 10^6 \text{ T/yr}}{6000 \text{ T/ft}} = 7,866 \text{ ft of dump/year}$$

Area to be reclaimed is the top and the outward end of the dump. The sides of the dump will only be reclaimed at the completion of mining.

Top Area of Dump

$$400 \text{ ft wide} \times 7,866 \text{ ft long} = 3,146,400 \text{ ft}^2$$

End Area of Dump

400 ft wide at top, 800 ft wide at bottom, 249 ft slope

$$\frac{400 \text{ ft} + 800 \text{ ft}}{2} \times 249 \text{ ft} = 149,400 \text{ ft}^2$$

Total dump area reclaimed each year = 3,259,800 ft²

The dump will be covered with 0.5 ft of topsoil

$$\frac{3,259,800 \text{ ft}^2 \times 0.5 \text{ ft}}{27 \text{ ft}^3/\text{yd}^3} = 60,367 \text{ yd}^3/\text{yr}$$

Assume scraper production rate of 125 yd³/hr, at an approximate 3000 ft haul distance.

$$\frac{60,367 \text{ yd}^3/\text{yr}}{125 \text{ yd}^3/\text{hr}} = 483 \text{ hr/yr}$$

Also assume for this job that a dozer and a grader are required for the same length of time as the scraper.

Fuel Consumption				
Scraper	483	hr/yr x 15.8 gal/hr	=	7,631 gal/yr
Dozer	483	hr/yr x 10.0 gal/hr	=	4,830 gal/yr
Grader	483	hr/yr x 5.8 gal/hr	=	2,801 gal/yr
Total Diesel Fuel				= 15,262 gal/yr

Energy Consumption

Diesel fuel 15,262 gal/yr x 138,600 Btu/gal = 2.115 x 10⁷ Btu/yr

Lube Oil

@ 1.5% of Diesel Fuel = 229 gal/yr

229 gal/yr x 148,690 Btu/gal = 3.405 x 10⁷ Btu/yr

Total 2.149 x 10⁷ Btu/yr

$$\frac{2.149 \times 10^7 \text{ Btu/yr}}{100,000 \text{ T Cu/yr}} = 2.1 \times 10^4 \text{ Btu/ton Cu}$$

4. Revegetation

The sprinkling system is calculated for a finger dump 1522 ft long. For reclamation of the total waste, a dump with a total length of 7866 ft is required per year. Several wells will be required to obtain the amount of water required for reclamation purposes.

Assume sprinkling duty required is three hours per day, 270 days/year.

For a 1522 ft long dump with spray nozzles on 100 ft centers, 60 nozzles are required at 25 gal/min each at 35 lb/in².

$$60 \times 25 \text{ gal/min} = 1500 \text{ gal/min}$$

$$3 \text{ hr/day} \times 270 \text{ day/yr} = 810 \text{ hr/yr sprinkling required}$$

Assume for pumping duty:

Wells average 800 ft deep at 2000 ft from dump
 Dumps 150 ft high
 Gravity head = 950 ft

For each section, the distribution line is a 10 inch line 3750 ft long. Laterals are 6 inch line with 2250 ft required.

Main Distribution Line

10 inch 3750 ft long carrying 1500 gal/min.
 Velocity head = 0.6 ft
 Friction head = 1.25 ft/100 ft (Cast Iron Pipe)
 $3750 \text{ ft} \times 1.25 \text{ ft}/100 \text{ ft} = 47 \text{ ft}$

Laterals

3-6 inch lines total length of pipe 2250 ft carrying 500 gal/min
 Velocity head = 0.5 ft
 Friction head = 2.02 ft/100 ft (Cast Iron Pipe)
 $2250 \text{ ft} \times 2.02 \text{ ft}/100 \text{ ft} = 45 \text{ ft}$

Gravity Head	=	950 ft
Pressure Head	=	81 ft
Friction Head	=	92 ft
Fittings @ 50% H_f	=	46 ft
Velocity Head	=	1 ft
Total Head		1170 ft

$$Q = 1500 \text{ gal/min} \times 0.13369 \text{ ft}^3/\text{gal} = 200 \text{ ft}^3/\text{min}$$

$$\text{Water Hp} = \frac{HQ \times 62.4}{33,000} = \frac{1170 \times 200 \times 62.4}{33,000} = 442 \text{ Hp}$$

$$\text{@ 70\% efficiency } \frac{442}{0.7} \text{ Hp} = 631 \text{ Hp required for one 1522 ft section.}$$

$$\frac{7866 \text{ ft of dump/yr}}{1522 \text{ ft}} = 5.17$$

$$631 \text{ Hp} \times 5.17 = 3262 \text{ Hp required for total dump}$$

$$3262 \text{ Hp} \times 0.745 \frac{\text{kWh}}{\text{Hp}} \times 810 \text{ hr/yr} = 1.968 \times 10^6 \text{ kWh/yr}$$

$$1.968 \times 10^6 \text{ kWh/yr} \times 10.239 \text{ Btu/kWh} = 2.0155 \times 10^{10} \text{ Btu/yr}$$

$$\frac{2.015 \times 10^{10} \text{ Btu/yr}}{100,000 \text{ T Cu/yr}} = 202 \times 10^6 \text{ Btu/ton Cu}$$

1.3 MINERAL PROCESSING OPERATIONS

Beneficiation of copper sulfide ores is accomplished by size reduction and froth flotation. Several tons of ore must be handled to produce one ton of copper. The finer the grind for liberation the higher the energy requirements per pound of copper. Also, the harder the ore the greater the energy requirement for any specific grind.

Figure 1.3-1 illustrates a typical flowsheet for a copper concentrator. For purposes of this study crushing is done in three stages to minus $\frac{3}{8}$ -inch size and grinding in a single stage ball mill in closed circuit with cyclones to 15 to 20 percent on 65-mesh. The coarse rougher concentrate is reground for final mineral liberation. This flowsheet was chosen because it represents a fair percentage of operating mills.

1.3.1 Material Balance

For the material and energy requirements of a copper concentrator without molybdenum recovery, a porphyry ore containing 0.55 percent copper was selected. The porphyry type ore was considered typical since approximately 88 percent of copper ores in the United States are from porphyry ore deposits in the western states. The 0.55 percent copper is the weighted average of all ore grades from producing porphyry copper mines in the United States as published by the USBM Minerals Commodities Profile (1977).

Froth flotation has been known and widely practiced for over fifty years. This method is employed for all copper sulfide ores from porphyry deposits. Information on froth flotation theory and practice is available in a two volume compilation (Fuerstenau, 1976).

The recovery of copper from ore to concentrate is assumed to be 87.5 percent. The concentrate grade is set at 25 percent copper, 28 percent iron, and 31 percent sulfur. These assumptions are used to calculate the copper material balance shown in Table 1.3-1.

1.3.2 Energy Balance

Tabulation of the energy requirements is shown in Table 1.3-2 and Table 1.3-3. It is evident from Table 1.3-2 that the major electrical energy consuming step in the process is the primary grinding step (process step 2). The actual percentage of level 1 energy input is 72%. The crushing and flotation steps (process steps 1 and 3) also require sizable amounts of electrical energy, while regrinding, filtering, and pumping of new and recycled water each requires a relatively small amount of electrical energy. Table 1.3-3 also shows that steel liners and cast balls represent a sizable energy expenditure as consumed items. Most steel consumption is in crushing and grinding, constituting 65% of the level 2 energy requirement. Flotation reagent production requires very little energy.

Energy used to produce grinding balls, ball mill liners, and crusher liners has been variously stated. In some cases scrap steel is the basic raw material while in other cases new steel is the basic raw material. Two and a half tons of scrap represents the same energy as one ton of new steel (Kellogg, 1977). Production energy of new steel slabs is given as 22×10^6 Btu per ton. The same article shows the production energy for steel slabs, grey iron, and steel castings as 24.9×10^6 Btu per ton. The same author (Kellogg, 1976) shows the energy requirements for steel balls and liners as 36×10^6 Btu per ton. Another author (Makhjani, 1972) gives the production energy for high grade steel alloys as 202×10^6 Btu per ton. This figure does not seem to apply but it has been

TABLE 1.3-1 MATERIAL BALANCE COPPER SULFIDE CONCENTRATOR

BASIS: 1 Ton Concentrate (25% Cu, 28% Fe, 31% S)
 0.55% Ore Grade - 87.5% Recovery
 0.07% Tailings Grade

Stream No.	Description	Solids (Tons)	Water (Tons)	Other (Lbs)
1	Ore Feed	51.95		
2	Steel Liners			0.061
3	Crushed Ore Slurry (70%)	51.95	22.26	
4	Steel Balls			1.5
5	Steel Liners			0.1
6	Flotation Feed Slurry (30%)	51.95	121.22	
7	Frothers			0.07
8	Promoters			0.08
9	Lime			3.0
10	Concentrate Slurry (75%)	1.00	3.00	
11	Regrind Slurry (20%)	1.90	7.60	
12	Steel Liners			0.004
13	Steel Balls			0.04
14	Regrind Recycle (20%)	1.90	7.60	
15	Tailings to Thickener	50.95	118.33	
16	Tailings Overflow		19.37	
17	Tailings Underflow (34%)	50.95	98.96	
18	Tailings Return		62.60	
19	Fresh Water Makeup		36.36	
20	Water Return		98.96	
21	Filtration Recycle Water		2.89	
22	Copper Concentrate	1.00	0.11	

TABLE 1.3-2

ENERGY REQUIREMENTS

Level 1

FOR COPPER SULFIDE CONCENTRATOR

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON OF ORE	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON OF ORE
1	Crushing	KWH	1.85	0.0105	0.019425
2	Grinding	KWH	8.89	0.0105	0.093345
3	Flotation	KWH	1.16	0.0105	0.012180
5	Filtration	KWH	0.19	0.0105	0.002520
*	Regrinding	KWH	0.24	0.0105	0.001995
*	New Water	KWH	1.63	0.0105	0.009555
*	Recycle Water	KWH	0.91	0.0105	0.017115
				TOTAL	0.156135
	*Not Shown on Flowsheet				

TABLE 1.3-3

ENERGY REQUIREMENTS
FOR COPPER SULFIDE CONCENTRATOR

Level 2

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON OF ORE	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON OF ORE
1	Crushing A) Liners	LB	.06	0.018	0.00108
2	Grinding A) Balls	LB	1.50	0.018	0.027
	B) Liners	LB	0.10	0.018	0.0018
3	Flotation A) Frothers	LB	3.00	0.0041	0.0123
	B) Promoters	LB	0.08	0.02	0.0016
	C) Lime	LB	0.07	0.02	0.0014
*	Regrinding A) Liners	LB	0.04	0.018	0.00072
	B) Balls	LB	0.004	0.02	0.00008
				TOTAL	0.04598
	*Not shown on flowsheet				

used by others. The energy requirements for high carbon ferro-chromium is given as 61×10^6 Btu per ton (Battelle, 1975). Most of the liners in use today are chromium-molybdenum type while the grinding balls are low alloy steel. In this calculation the value of 18,000 Btu per pound given by H.H. Kellogg for liners and grinding balls is used since it seems to more nearly represent the use of scrap iron, new iron, and alloys. The electrical energy conversion factor is taken from the same article. The energy use, per ton of ore milled, was obtained from private communication with one of the latest copper plants built. Direct kWh meter readings are taken from each step of the process. These total kWh readings are converted to kWh per ton by dividing by the tons processed. The kWh or Btu per pound of copper is directly dependent upon the recoverable copper content of the ore.

1.3.3 Impact of Autogenous Grinding

The significant contribution of iron, and steel consumption to the total energy requirement for conventional grinding is of particular interest in view of the development of autogenous grinding technology in the mineral processing industry. The consumption of iron and steel can be reduced considerably when the ore is self grinding. Many operations in Europe now practice either autogenous or semi-autogenous grinding and the state of the art for this technology was discussed at a recent autogenous grinding conference in Trondheim, Norway, June, 1979. Based on the analysis of this data (Digre, 1979) and the use of standard relationships which have been developed for conventional grinding (Mular and Bhappu, 1978) the energy effectiveness of conventional grinding can be compared to that of autogenous grinding. Figure 1.3-2 presents this comparison for a typical copper ore with a work index WI of 13.1 kWh/ton and abrasion index AI of .095. Here the total energy required for grinding by various methods is plotted versus an autogenous grinding factor. The autogenous grinding factor, β , gives a measure of the energy inefficiency of self-breakage for the ore and is defined as the ratio of the operating work index for autogenous grinding to a standard laboratory ball mill work index as established by a Bond grindability test or the equivalent thereof. The overall energy requirement for each alternative has been calculated as:

$$\begin{aligned} \text{TOTAL ENERGY REQUIRED FOR COMMINUTION} = & \\ & (\text{NET CRUSHING ENERGY}/\epsilon_C) \\ & + \beta (\text{NET BALL MILL ENERGY}/\epsilon_B) \\ & + \left(\frac{\text{STEEL CONSUMED AS MEDIA \& LINERS}}{\text{ENERGY "CONTENT" OF STEEL}} \right) \\ & + \text{ENERGY FOR COMMINUTION CIRCUIT AUXILIARIES} \end{aligned}$$

Of course, the energy consumption for conventional grinding and pebble grinding is independent of the autogenous grinding factor, whereas the energy consumption in autogenous grinding will reflect the extent to which self-breakage contributes to the energy economy. Available data indicates that the autogenous grinding factor for copper ores is generally between 1.35 and 1.6 with occasional values as low as 0.75. When β is small the energy required for autogenous grinding is less than that required for conventional grinding, since the inefficiency of autogenous breakage is more than offset by the elimination of media requirements, however, when the inefficiency exceeds 45-50% ($\beta = 1.45-1.50$) the advantage of no media expense disappears. The comparisons shown in the figure are not indisputable, but are based on the best available data. These data do indicate that for copper ores which are very amenable to autogenous grinding, a reduction in

FIGURE 1.3-2 COMPARISON OF ENERGY REQUIRED FOR CONVENTIONAL, AUTOGENOUS, AND PEBBLE GRINDING OF TYPICAL COPPER ORES

energy requirements of up to 10% may be possible. Further reductions may be possible through the use of pebble milling although the energy cost associated with the production of pebbles must be taken into consideration.

1.3.4 Improvements in Operating Efficiency

One method of reducing the energy requirement (Btu/Ton) for an existing mineral processing plant involves improving the operating efficiency by increasing the production rate at a fixed power input. A major source of operating inefficiency is often uncontrolled fluctuations in the quality of the ore coming into the plant. During the last decade significant advances have been made in the development of on-line instrumentation for mineral processing systems including: particle size analyzers, mass flow measurement systems, solid phase and liquid phase composition analyzers. In addition, inexpensive and reliable computers for process control have become available. In many instances stabilizing control strategies have been developed for grinding (Herbst and Rajamani, 1979) and flotation circuits (Cooper and Paakinen, 1979); typical improvements in throughput (or equivalently energy efficiency) have been on the order of 5-10%. Optimizing control strategies (Herbst and Rajamani, 1979a) promise even greater improvements but to date none have been implemented in U.S. copper concentrators.

Similarly another important factor in determining the capacity of a closed grinding circuit is the efficiency of size separation. Size separation (classification) is typically accomplished with mechanical classifiers or hydrocyclones, the latter being preferred in the design of new plants. It is intuitively evident that if misplaced fine material of the desired size range is being returned along with coarse material to size reduction, the mill capacity will be reduced correspondingly. Under these circumstances, the mill will be regrinding material which is already of a suitable size. If, on the other hand, the fine material is not misplaced in the coarse material stream, the mill will have a greater capacity and the fresh feed rate can be increased.

The effect of classifier efficiency on the grinding circuit capacity is revealed in at least two computer simulation studies (Herbst; Grandy and Fuerstenau 1973). (Luckie and Austin 1975). In one analysis, examination of the results reveals that the grinding circuit capacity could be increased by as much as 50 percent by improved classifier efficiency. The results from another simulation suggest the grinding circuit capacity could be increased by as much as 64 percent if perfect size separation could be achieved. In view of the fact that the efficiency (as measured by the coefficient of separation which represents the fraction of feed material separated ideally) of most hydrocyclones, even under the best of circumstances, is only 50 percent and that the efficiency of mechanical classifiers is even lower, considerable improvement in grinding circuit capacity could be achieved by improved classifier efficiency.

Considerable potential exists for the optimization of entire plant (and mine) performance. Traditional ideas concerning the "best" size for run of mine ore, primary crusher product, secondary crusher product, primary grinding product and secondary grinding product may change if the energy economy of the overall size reduction process is taken into account. In addition integrated grinding and flotation circuit performance may be improved from an energy efficiency point of view by reducing the extent of size reduction (and therefore liberation) in the primary grinding circuit. In this emerging process strategy, locked particles in the small mass rougher concentrate are reground to achieve the final high degree of liberation required for the production of the specified grade of cleaner products. The solution of these and other integrated optimization problems promises to improve significantly the overall energy economy of existing mineral processing plants.

1.3.5 Effect of Declining Head Grades

Declining head grades will result in higher costs and energy requirements for copper extraction in the future. The overall effect of ore grade on energy consumption for various ore types has been estimated (Kellogg, 1979) and is depicted in Figure 1.3-3.

In terms of energy accounting for mineral processing operations, the head grade will have a direct effect on the total energy requirement of the process for two reasons. First, more ore must be processed to recover the same amount of copper from a lower head grade ore and second, as the head grade drops the ore will probably have to be ground finer to achieve the same recovery. If the energy input per ton ore is maintained constant, the recovery must drop; it appears to be a reasonable assumption, based on plant observations, that the copper content of the flotation tailing will remain approximately constant. The significance of this effect is presented in Table 1.3-4. As a result of the constant tail assay assumption, it is seen that the recovery decreases from 90.3% to 76.9% as the head assay decreases from 0.7% Cu to 0.3% Cu. The energy per ton of ore remains constant at 202,115 Btu. However, the energy per ton of concentrate more than doubles when the head assay drops from 0.7% Cu to 0.3% Cu. This increase corresponds to an increase in energy per ton of copper contained in the concentrate from 32 million Btu to 88 million Btu.

Some questions may be raised regarding the change of liberation size with a decrease in head assay and the increased energy that may be required to achieve the desired level of liberation. Neither good enough data nor accurate enough mathematical models are available to evaluate the effect in a rigorous manner, however, this effect was evaluated using simple liberation models (Gaudin, 1939; Weigel and Li, 1967) and it was found to be insignificant for low grade materials such as the copper porphyry ores under consideration.

1.3.6 Conclusions and Recommendations

1.3.6.1 Conclusions

Concentrators include standard and well-established unit operations. No major developments requiring less energy have been introduced in concentration in the last few decades. However, several minor modifications in process strategy which may be considered to be fine tuning of the circuit, offer promise for modest energy savings. Crushing and grinding are the major energy consuming steps in the process and any improvement in these steps would have the largest impact as far as energy input is concerned. The use of large flotation cells has improved process efficiency and lessened energy usage.

1.3.6.2 Recommendations

Improved energy conservation in mineral processing operations can be effected by efforts to implement existing technology and by the development of a concerted research program to establish new technologies for energy conservation.

1.3.6.2.1 Implementation of Existing Technology

- 1) Application of existing stabilizing control strategies for grinding and flotation
- 2) Careful evaluation of the potential of autogenous or pebble grinding versus conventional grinding on an ore by ore basis
- 3) Optimal allocation of energy between blasting, crushing, grinding and regrinding.

FIGURE 1.3-3 ENERGY-ORE GRADE RELATIONSHIPS FOR VARIOUS SOURCE MATERIALS, Kellogg (1978)

TABLE 1.3-4 EFFECT OF HEAD GRADE
ON TOTAL ENERGY CONSUMPTION

Head <u>Assay</u>	Tail <u>Assay</u>	Recovery <u>Percent</u>	Tons Ore per <u>Ton Concentrate</u>	BTU per <u>Ton Ore</u>	MM BTU per <u>Ton Concentrate</u>	MM BTU per Ton of Cu <u>in Concentrate</u>
0.30	0.07	76.9	108.4	202,115	21.91	87.64
0.35	0.07	80.2	89.0	202,115	18.00	72.00
0.40	0.07	82.7	75.5	202,115	15.27	61.08
0.45	0.07	84.7	65.6	202,115	13.26	53.04
0.50	0.07	86.2	58.0	202,115	11.72	46.88
0.55	0.07	87.5	51.9	202,115	10.50	42.00
0.60	0.07	88.6	47.0	202,115	9.51	38.04
0.65	0.07	89.5	43.0	202,115	8.69	34.76
0.70	0.07	90.3	39.6	202,115	8.00	32.00

1.3.6.2.2 New Research

- 1) Development of more efficient classification devices for closed circuit grinding
- 2) Development of optimizing (as opposed to stabilizing) control strategies for grinding and flotation
- 3) Identify and develop more efficient reduction devices for copper ores.

1.3.6.3 References

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1.4 GAS CLEANING

1.4.1 Introduction

All unit operations, i.e., roasting, smelting and converting in copper smelting produce an off gas containing sulfur dioxide and particulates. Gas cleaning comprises the removal of particu-

lates from all gas streams while still hot in electrostatic precipitators. Those gas streams with sulfur dioxide concentrations high enough to require sulfur dioxide removal in an acid plant are further cleaned to ensure efficient acid plant operation. These strong sulfur dioxide gas streams are cooled and the remaining dust removed in spray towers (or venturi scrubbers). Electrostatic precipitators remove acid mist from the gas and makes it ready for treatment in a contact acid plant.

1.4.2 Process Description

A flowsheet depicting gas cleaning in a conventional smelter (roast/smelt/convert) is presented in Figure 1.4-1.

1.4.2.1 Hot Gas Cleaning

Hot gas cleaning is normally done separately on the roaster, smelting furnace, and converter with recycle of the recovered dust back into the smelting furnace. The principal purpose is to recover copper contained in the dust.

The off-gas stream typically contains sulfur dioxide, some sulfur trioxide, water vapor, and other volatiles (metal oxides, sulfides, etc.). If the temperature of the gas drops below the acid dew point (about 400°F), acid mist can condense as sulfuric acid (H_2SO_4) presenting severe corrosion problems. Cyclones, bag filters, and settling flues have been used to remove the dust, but current practice generally is to use electrostatic precipitators.

The physical properties of the off-gas are such that maximum efficiency in the electrostatic precipitators is attained at about 700°F and around 100°F (i.e., minimum resistivity). Since the gas cannot be cooled below about 400°F because of the acid mist problem, the higher temperature operation is normally preferred (about 400-600°F).

The off-gas leaving the smelting furnace is cooled in a waste heat boiler to the range of 400-600°F before passing into the hot electrostatic precipitator. The off-gas leaving the converter passes through flues where a significant portion of the dust is removed. Also the gas is cooled with water sprays, with radiating flues, by dilution, or with waste heat boilers to about 400-600°F before entering the hot electrostatic precipitator. In practice, normally, the temperature at which hot electrostatic precipitators operate ranges from about 400-600°F. ASARCO operates hot electrostatic precipitators at 240-300°F in order to control the volatiles, principally arsenic. The resistivity of the dust is controlled by acid conditioning, i.e., spraying acid or injecting sulfur trioxide from the acid plant and by monitoring the acidity of the dust. Enough acid is added so as to provide conditioning but not to cause excessive corrosion.

Depending upon the discharge temperature, the off-gas from the roaster may or may not be cooled before passing into a dust removal device (separate electrostatic precipitators or cyclone, or blending with off-gas from smelting furnace/converter).

1.4.2.2 Cold Gas Cleaning

Following hot gas cleaning, the separate off-gas streams to be treated for sulfur dioxide recovery are usually combined before being fed into cold gas cleaning. Whereas the purpose of the hot gas cleaning is to remove dust to recover its copper value, the purpose of cold gas cleaning is to remove dust to prevent fouling of the acid plant. This is usually accomplished in a spray tower, although some installations have used venturi scrubbers or both.

FIGURE 1.4-1 GAS CLEANING IN COPPER SMELTING

In the spray towers the off-gas is scrubbed with weak sulfuric acid removing most of the remaining dust. At the same time, the gases are cooled allowing any acid mist to condense. The gases may be further cooled in an indirect cooling tower before entering a mist precipitator (usually an electrostatic precipitator) which removes the last traces of dust and reduces the amount of water vapor contained in the gas stream. Cooling and mist elimination are important factors in controlling the overall water balance in the acid plant.

1.4.3 Key Variables

The economics of gas cleaning/acid plants are determined by several key variables, the gas volume, sulfur dioxide concentration, water vapor concentration and free oxygen.

1.4.3.1 Design

In general, copper smelters produce several off-gas streams from the roasting, smelting, and converting operations. The roasting off-gas tends to be high in sulfur dioxide, relatively low in volume and relatively constant (especially fluid-bed units, to a lesser degree in multi-hearth units). The smelting off-gas ranges from very high volume-low sulfur dioxide (less than 2% sulfur dioxide) on conventional reverberatory furnaces to low volume-high sulfur dioxide (more than 50% sulfur dioxide on some of the newer technologies) and is usually relatively constant. Converter off-gas tends to be high sulfur dioxide (average 5% sulfur dioxide) but the volume fluctuates drastically during the blow; the sulfur dioxide also tends to vary, being higher on the finish blow than on the slag blow.

1.4.4 Energy Requirements

The energy requirements for hot and cold gas cleaning are presented in Table 1.4-1

1.4.5 Fugitive Emissions Control

In this section we have estimated the energy requirements associated with fugitive emissions control at a smelter producing 100,000 tons of copper per year. The emission control system is based on building enclosure, especially of the converter aisle and secondary hooding of process equipment. The collected gases would be filtered in a baghouse and exhausted via the main stack. This system roughly corresponds to the type of fugitive emissions control used in some foreign smelters.

The fugitive gas stream is essentially at ambient temperature and is much larger than the other streams from the process units which are also ultimately exhausted via the main smelter stack. As a consequence, the stack gas will require reheating to increase buoyancy and achieve the proper degree of dispersion necessary to meet NAAQS (National Ambient Air Quality Standards). The energy requirements for fugitive emissions control is estimated to be 340 kWh per ton copper or 3.57 million Btu per ton of copper. It is assumed that heat necessary to provide buoyancy is provided by waste heat.

1.4.6 References

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TABLE 1.4.1

ENERGY REQUIREMENTS

Level 1

GAS CLEANING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Hot gas cleaning	Thous. SCF		0.00336	
2	Cold gas cleaning	Thous. SCF		0.00126	

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1.5 ACID PLANT

1.5.1 Introduction

All unit operations in copper smelting, i.e., roasting, smelting, and converting produce an off-gas containing sulfur dioxide and particulates. Environmental control regulations require the removal of sulfur dioxide from rich gas streams (above 4-5% sulfur dioxide); weak streams may be vented after particulate removal. Current practice in the United States for sulfur dioxide recovery involves the treatment of gas streams from roasting, new smelting furnaces and converting in contact plants which fix the sulfur dioxide as sulfuric acid; reverberatory furnace gases are vented after particulate removal.

1.5.2 Process Description

Figure 1.5-1 shows a flowsheet for an acid plant treating gas from cold gas cleaning as described in section 1.4. In a contact process acid plant, the gas entering the plant from cold gas cleaning is first dried in scrubbing towers using moderate (78%) and/or strong (94/96%) sulfuric acid to remove any water vapor. Downstream of the driers a blower is used to move the gas through the remaining equipment.

The incoming gas, containing sulfur dioxide and oxygen is passed over a vanadium pentoxide catalyst where it reacts to form sulfur trioxide

The gas stream is then passed through an absorption tower where the sulfur trioxide is absorbed in sulfuric acid forming more concentrated acid. ASARCO reports using a 98 percent acid with the strength of acid controlled within close limits to ensure good absorption.

Reaction 1.5.1 is an equilibrium reaction. The conversion ratio is a function of temperature and concentration. To maximize conversion to sulfur trioxide (and hence sulfur dioxide removal) and to meet pollution control requirements, most modern plants use a double contact/double absorption (DC/DA) scheme where the gas passes through a catalyst (converter) bed, is cooled, and passes through a second (and possibly third) converter bed followed by an absorber (for sulfur trioxide removal). The gas then passes through a third and fourth converter bed (with interstage cooling) followed by a pass through a second absorber. Off-gas from the final absorber is vented to the atmosphere and typically contains less than 500 ppm sulfur dioxide.

In the older single contact/single absorption (SC/SA) plants, the gas would pass through several beds of the converter and into the absorption tower only once resulting in a lower conversion efficiency (about 95%). A DC/DA plant operates at a higher conversion efficiency (about 99.5 percent conversion) than an SC/SA plant and complies with current U.S. environmental regulations.

1.5.3 Key Variables

The design and operating economics of an acid plant treating waste gas from a copper smelter are determined by four key variables, the gas volume, sulfur dioxide concentration, water vapor concentration, and free oxygen.

The design of a contact acid plant is dependent upon the maximum gas flow rate, the maximum sulfur dioxide concentration, and the minimum sulfur dioxide concentration. In copper smelting, the blended gas feed to the acid plant varies in both gas volume and concentration (due mainly to cyclical converter operations). One of the main objectives is to maintain as much as possible constant gas flow/concentration and to design the system to ensure autothermal operation over the range of operating conditions. The required heat exchange surface increases with decreasing sulfur dioxide concentration and the system therefore is sized based on the lowest expected concentration.

Sulfuric acid plants generally consume both electrical and thermal energy in normal use. Electrical energy is used primarily to supply power to the gas blowers ($\Delta p \approx 10$ psig), in the electrostatic precipitators and in pumping the acid and cooling water. Since power consumption in these operations is essentially a function of gas volume, electrical energy consumption per MSCF (thousand standard cubic feet) is expected to be constant, independent of sulfur dioxide in the gas stream. Also, as noted earlier, smelters are subject to widely fluctuating gas volumes and sulfur dioxide concentrations which tend to increase energy consumption over that given by the "average" design conditions.

The thermal energy requirement is primarily for preheating the incoming gas stream when the sulfur dioxide content is low. A sulfuric acid plant can be a net consumer of energy, a net producer of energy or have zero net energy consumption, depending upon the type of plant (SC/SA vs. DC/DA), the thermal efficiency of the plant design, and the inlet sulfur dioxide concentration. Generally, most newer DC/DA plants require 4.5-5 percent sulfur dioxide in the inlet gas stream to operate autogenously (zero external thermal energy required). If the sulfur dioxide concentration drops below this level, the incoming gas stream has to be preheated to supply the required energy. Below 3-4 percent sulfur dioxide, most sulfuric acid plants are not operated. It is expected that below about 5 percent sulfur dioxide, the thermal energy consumption will rise rapidly; above 5 percent sulfur dioxide, the plant is a potential net producer of energy. This energy can be recovered but is generally dissipated to the atmosphere. Thus an acid plant associated with reverberatory smelting or other processes which produce gas streams with 1-2 percent sulfur dioxide would require significant amounts of thermal energy.

1.5.3.1 High Grade Sulfur Dioxide Streams

The advent of stricter environmental protection regulations and process improvements using tonnage oxygen have led to higher sulfur dioxide concentrations in the smelting furnace off-gas. Such processes include, for example, the INCO Flash Process (80% sulfur dioxide) and the Outokumpu Flash Smelter (10-20% sulfur dioxide).

With contact acid plants, allowing for sufficient excess oxygen to maximize conversion to sulfur trioxide, the stoichiometry of reaction 1.5.1 limits the maximum sulfur dioxide concentration in the inlet gas to 16% (at 1.1:1 ratio of oxygen to sulfur dioxide). In practice at least 50 percent excess oxygen over stoichiometry is required, putting a practical limit of about 11 percent (Rinckhoff, 1977) unless oxygen is added to the gas stream. Higher grade sulfur dioxide process gas must be diluted with air to no more than this concentration.

The conventional DC/DA process can be used on feed gas containing up to 8.5-9.0 percent sulfur dioxide. In maintaining an autothermal operation, the loss of heat as sensible energy to the incoming gas and product acid is balanced against the heat released by conversion of sulfur dioxide to sulfur trioxide and absorption of the sulfur trioxide. For gas streams containing about 5-9 percent sulfur dioxide, this balance can be maintained by adjusting the heat transfer surface and the cooling water rate. Increasing sulfur dioxide concentrations result in temperature rises in the converter beds leading to greater duties on the heat exchangers.

Beyond 8.5-9.0 percent sulfur dioxide, additional heat transfer surface would be required to remove the excess heat generated in the unit and to avoid overheating in the converter beds. Lurgi has proposed the use of a split gas stream along with an economizer/evaporator to remove the excess heat and allow processing of 16 percent sulfur dioxide with no loss in efficiency. In principle, it should be possible to treat even stronger sulfur dioxide streams and export low pressure steam to other process units. To the best of our knowledge, no one is currently operating an acid plant on gas over 9 percent sulfur dioxide.

In some instances where the market is available, liquid SO_2 or elemental sulfur can be produced.

1.5.4 Energy Balance

Energy requirements for DC/DA acid plants are presented as a function of gas volume and sulfur dioxide concentration in Table 1.5-1. As noted earlier, acid plant energy consumption is related to sulfur dioxide concentration and volume. At sulfur dioxide concentrations of less than 5 percent, thermal energy is needed to preheat the incoming gas and forms a significant part of the total energy use. Above 5 percent sulfur dioxide, preheating is not required and energy is only consumed in the pumps and blowers. It is assumed that concentrated sulfur dioxide streams (more than 9 percent volume sulfur dioxide) would be diluted with air to 9 percent sulfur dioxide before being processed in the acid plant.

1.5.5 References

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TABLE 1.5-1		ENERGY REQUIREMENTS			Level 1
DC/DA ACID PLANT					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	SO ₂ concentration of gas to acid plant				
	A) 4-5% SO ₂ *	Thous. SCF		$(-1.1098 \times \% \text{ SO}_2) + 5.5592$	
	B) 5-9% SO ₂	Thous. SCF		$(6 \times 10^{-4} \times \% \text{ SO}_2) + 7.2 \times 10^{-3}$	
	C) 9% and above Volume of gas is diluted to 9% SO ₂	Thous. SCF		0.0126	
*Assume acid plant will shut down below 4% SO ₂					

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1.6 REFINING

1.6.1 Introduction

Copper produced by pyrometallurgical or hydrometallurgical processes is generally electrolytically treated to produce 99.99+ % pure cathode copper. Blister copper produced by pyrometallurgical processes is fire refined and cast into anodes. These anodes are electrorefined. During electrorefining, copper is electrochemically dissolved from the impure anodes and then selectively plated in pure form onto copper cathodes. About 95 percent of all copper produced is by electrorefining, the remainder being produced by electrowinning of dissolved copper produced by hydrometallurgical processes (Biswas and Davenport, 1976).

Figures 1.6-1 and 1.6-2 present flowsheets (block and schematic) for the production of cathode copper from blister copper. The principal steps are (a) fire refining and anode casting; (b) electrorefining.

1.6.2 Fire Refining and Preparation of Anodes

Blister copper from converting contains approximately 0.02-0.03 percent dissolved sulfur and 0.5 percent dissolved oxygen, while that from continuous copper-making processes contains 0.5-2.0 percent sulfur and 0.2 percent oxygen. At these levels, the sulfur and oxygen combine during solidification to form blisters of sulfur dioxide in and on cast metal. Since anodes must be strong, thin, and smooth surfaced for electrorefining, this prohibits anode casting directly from blister copper.

Fire refining is used to sequentially remove sulfur (and traces of other oxidizable impurities) and oxygen from liquid blister copper. There are two steps involved, the first is oxidation of the sulfur with air, to a level of 0.001 - 0.003% sulfur in the copper; and the second is elimination of oxygen which has dissolved in the copper during the previous step. This step (called "poling" because wooden poles were once used for this purpose) reduces oxygen content in the copper from about 0.6 percent to 0.05 percent by introducing hydrocarbons into the molten copper.

FIGURE 1.6-1 REFINING OF BLISTER COPPER

FIGURE 1.6-2 TYPICAL FLOWSHEET FOR ELECTROLYTIC COPPER REFINERY

Some hydrogen dissolves during the poling step and this combines with some of the residual oxygen to evolve steam during casting, which offsets metal shrinkage and leads to the production of a flat anode surface.

The principal reactions in fire refining are:

(1) Sulfur removal

(2) Oxygen removal

(3) Steam Formation and Metal Shrinkage

In a majority of cases, anodes are fire refined directly from molten copper produced in converters. Occasionally, however, the blister copper is cast for transport to a distant electrolytic refinery where it is remelted for anode preparation. In this case, scrap copper and scrap anodes are also remelted with the cast blister copper.

Fire refining is carried out in rotary-type refining furnaces resembling Peirce-Smith converters or in reverberatory furnaces. The rotary type predominates where the molten blister copper is treated directly, while reverberatory furnaces are necessary where the melting of solid charge is practiced. The temperature of operation is about 1130-1150°C. which provides sufficient superheat for the subsequent casting of anodes. There is very little heat produced by the refining reactions, and some combustion of fuel is necessary to maintain the temperature of the furnace.

Rotary furnaces have one or two tuyeres for introducing gas into the molten metal. Gas flow rates and pressures are on the order of 5-15 Nm³min⁻¹ and 2.5-6 atm., respectively. Air is blown through the tuyeres to oxidize the charge until the sulfur content is lowered to 0.001-0.003 percent. The oxygen is then removed (to about 0.05-0.02%) from the copper by blowing natural gas, reformed natural gas, or propane through the tuyeres. The correct "end point" is determined by casting a sample of the copper (which should set to a flat surface) or by continuously analyzing for oxygen with an oxygen probe (Scholes, 1974). The liquid metal is then covered with low sulfur coke to prevent reoxidation of the copper. Older modifications of this process, which are still being used in some cases, include introducing air via steel lances and lowering poles of green wood into the copper for the oxygen removal step.

Use of hearth furnaces has been largely discontinued except in electrolytic refineries where scrap and/or blister copper were melted (Biswas and Davenport, 1976). In the reverberatory furnace, air and hydrocarbons are introduced via steel lances that are submerged in the molten bath.

Copper anodes are cast flat in open copper molds on a large rotating wheel. The wheel is rotated to bring an anode mold into casting position beneath the copper stream. The newly poured anodes are cooled by sprays of water as the wheel rotates and are stripped from their molds after a one-half rotation. Accuracy of anode thickness is an important aspect of anode casting. Thickness must be as uniform as possible to ensure that during electrorefining all anodes in a refining cell reach the end of their useful refining cycle at the same time. Automatic control of the weight of each pour of copper is now practiced in many plants (Outokumpu, 1972; Biswas and Davenport, 1976).

Anodes normally weigh 300-400 kg, but there are widespread variations from plant to plant (Schloen and Forbes, 1961). Anodes are approximately 0.9-1.0 m square and 4-5 cm thick and are generally cast with lugs to provide support for themselves when in electrolytic cells.

A recent development in the casting of anodes is the use of the Hazelett continuous-strip type of casting system (Itakura et al., 1974). In this system the copper is cast in the gap between two coincidentally moving water-cooled steel bands to form a continuous strip of anode copper, 1 m wide and 1-2 cm thick. This strip can either be cut into anodes with lugs or can be sheared into pieces about 1 m long and notched on the sides. The latter are supported by prefabricated hanger bars attached to the notches.

1.6.3 Electrorefining

Electrorefining serves to eliminate impurities from copper which are harmful to its electrical and mechanical properties and to separate valuable impurities, such as gold and silver, which can then be recovered as byproduct metals.

Figure 1.6-1 also shows the flowsheet of copper refining.

In electrorefining, an electrical potential is applied between a copper anode and a copper cathode, which are both immersed in an acidified copper sulfate solution. Copper is electrochemically dissolved from the anode into the electrolyte, producing copper cations and electrons. These are conducted towards the cathode, at which the electrons and the Cu^{++} cations recombine and plate onto the cathode to produce copper metal.

The principal reactions are as follows.

Cathodes are thin sheets of high purity copper that are prepared in a "starting sheet" section by a 24-hour electrodeposition of copper onto titanium or hard-rolled copper blanks. The starting sheets are 0.3-0.5 cm thick and they weigh about 5 kg.

The principal impurities in anode copper (As, Bi, Fe, Ni, Pb, Sb, Se, and Te, Ag, and Au) are usually present in quantities large enough to be worth recovering.

The impurities that go into solution do not deposit on the cathode because they are higher in the e.m.f. series than copper. These are eventually removed by purification of the electrolyte. Insoluble impurities either adhere to the anodes or are deposited on the bottom of the cell. These slimes can be further processed for recovery of precious metals. The most troublesome of these impurities are those that form "float slimes," i.e., precipitated arsenates of antimony and bismuth that absorb on or are occluded on cathodes (Braun, et al., 1976).

Electrorefining is carried out in a multiple (parallel) system in which all anodes in a cell are at one electrical potential and all the cathodes are at a second (lower) potential and the electrodes provide parallel paths for current flow. Each anode is placed between two cathodes so that all of the anodes electrochemically dissolve at approximately the same rate. Series connections have been used in the past.

Cells are connected in series to form sections (26-40 cells per section) and each section can be isolated electrically and chemically for the operations of inserting and removing cathodes and anodes, cleaning anode residues, and maintenance. The total voltage across a group of sections varies from 100 to 250 volts depending on the line voltage into the plant.

Cathodes of one cell are in direct connection (i.e., at the same potential) with anodes of the next cell. Connections can be made using either the Walker system or the Whitehead system (Biswas and Davenport, 1976). In the Whitehead system, connections are made by seating the cathode support in a groove in the leg of an anode of the adjacent cell. In the more commonly used Walker system, connections are made by supporting the cathodes of one cell and the anodes of the adjacent cell on a common copper distributor bar.

To prevent accidental short circuiting, anodes and cathodes are accurately spaced in the cells by means of fixed position cranes. Cells are monitored continuously by gaussmeters, computer or infrared scanning, for any short circuiting that may occur during deposition.

Cathodes usually reach their maximum weight in 12-14 days, and they are then replaced by a fresh set of starter sheets. Anode life is approximately 30 days so that two cathodes can be produced from each anode. Cathodes, after removal, are washed and transported to the cathode melting furnace for casting into commercial shapes. About 85 percent of the anodes dissolves, the undissolved remains are washed, melted, and recast as new anodes.

The electrolyte in the refining cell generally contains about 40-50 Kg/m³ copper, 175-225 Kg/m³ free H₂SO₄, some impurities and organic brightening and smoothing agents. Because resistance of the solution to the passage of current is about 50-65% of the total resistance and resistance decreases with an increase in temperature, the electrolyte is usually maintained at a temperature of 60-65°C by steam heat.

The electrolyte continuously circulates, at an approximate rate of 0.015 m³/min., to carry away dissolved impurities from the cells and to ensure uniform copper ion concentrations at the electrode surfaces. Soluble impurities such as iron, zinc, and nickel tend to accumulate in the electrolyte and as a result of this buildup, circuit resistance and power consumption may increase. It is therefore desirable to remove these impurities periodically. Usually, a portion of the electrolyte is bled continuously to a purification circuit, where the copper is recovered by electrowinning and impurities are removed. The electrolyte is then returned to the system.

Organic agents are added to the electrolyte to brighten and smooth the cathode deposit. The most common reagent is bone glue, which is composed of natural proteins. The action of the glue in smoothing is due to its adsorption on the surface of newly formed copper grains. Any grain which tends to grow out excessively adsorbs a nonconductive layer of glue which renders it less conductive than the rest of the cathode surface and its growth is hindered. Other organic additives that can be used are hydrolyzed casein, thiourea, sulphonated wood fibers, and petroleum liquors.

1.6.4 Material Balance

Table 1.6-1 shows a material balance, per ton of blister copper. In making this material balance, the effect of anode scrap from the electrolytic refinery is not shown. Anode scrap represents 15-20% of the anode by weight and is usually recycled to the converters in order to make use of the excess heat available. Where this is not possible, anode scrap is remelted in the anode furnace.

1.6.5 Energy Requirements in Refining of Blister Copper to Cathodes

Tables 1.6-2 and 1.6-3 present level 1 and level 2 energy requirements for the refining of blister copper to cathodes. This analysis assumes that the anode scrap which represents 15-20% of the anodes by weight is recycled to the converters where excess heat is available for melting. No additional energy is associated with the recycle of anode scrap to converters.

Where the refinery is situated away from the smelter, anode scrap is usually charged to the anode reverberatory furnace. In the reverb, scrap is melted and partially fire-refined. After the melt is oxidized to saturation with Cu_2O (oxygen content 0.8% to 0.9%), the poling step is carried out until the oxygen content is around 0.2 percent. In some operations electric furnaces are used, simplifying this aspect of the process. Offgases may be ducted to a waste heat boiler for the production of high pressure steam which can provide the major portion of steam required in the electrolytic refinery. Gases from the waste heat boiler are sent to a baghouse for dust collection. The molten copper is cast into anodes for electrolytic refining. The energy requirement for melting is 4.41 million Btu per ton of copper scrap recycled as shown in Table 1.6-4. Anode scrap represents 15-20 percent of the anodes by weight used in electrolytic refining.

1.6.6 Electrorefining of Copper at High Current Densities

Cathode current densities generally range from 170 to 240 amps/m². High current densities are desirable because total rate of copper production is directly proportional to current density. With normal techniques, however, current densities above 250 amps/m² tend to cause anode passivation (the anode stops dissolving) and a decrease in cathode purity.

A new technique, periodic current reversal, which involves periodically reversing the direction of the direct current for short spans of time (e.g., 200 seconds forward, 10 seconds reverse) has permitted the use of current densities up to 400 amps/m², without loss of cathode purity.

From figures given in various references (Imai, 1968; Kitamura et al., 1976; Palacios and Pesquera, 1976; Ikeda and Matsubara, 1976; Morisaki and Ikeda, 1968), general trends for steam and power consumption vs. current density have been developed (see Figure 1.6-3). Cell voltage and power consumption naturally increase with a rise in current density. Higher resistance in the solution and bus bars caused by an increased cell voltage tends to increase the resistance heating of the electrolyte in a cell. This is supported experimentally by Imai, 1968. Because of this effect, steam consumption necessary for heating the electrolyte decreases as current density increases.

TABLE 1.6-1 FIRE REFINING & ELECTROREFINING						
[TONS PER TON BLISTER COPPER]						
STREAM NO.	(1)		(4)		(5)	
STREAM NAME	BLISTER COPPER		SLAG FROM AF		OFF GASES FROM AF	
COMPOSITION	wt.	wet wt. %	wt.	wet wt. %	wt.	wet wt. %
Cu	0.98	98				
Fe	0.001	0.10	.0007	12.15		
S	0.009	0.90				
O _{Fe*}	0.0015	0.15	.0002	3.47		
SiO ₂						
Al ₂ O ₃						
CuO + MgO						
Others	0.0085	0.85	.00486	84.38		
H ₂ O					0.3675	7.15
SO ₂					.00118	0.23
O ₂						
CO					.10811	21.04
CO ₂					.36787	71.58
N ₂						
TOTAL	1.0	100.00	.00576	100.00	.51391	100.00
TEMP. (°F)		2100		2100		2100
STATE		L		L		G

*Oxygen associated with FeO and Fe₃O₄

**Hydrogen and carbon contents in natural gas

TABLE 1.6-1 (cont.)

FIRE REFINING & ELECTROREFINING
[TONS PER TON BLISTER COPPER]

STREAM NO.	(6)		(7)		(8)			
STREAM NAME	STEAM FROM AF		ANODE Cu		CATHODE Cu			
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %		
Cu			.97499	99.5	.980	99.991		
Fe			.00029	0.03				
S			.00003	0.003				
O _{Fe} *			.00098	0.10				
SiO ₂								
Al ₂ O ₃								
CaO + MgO			.00364	0.37	.00001	0.001		
Others	.0097	100.0						
H ₂ O								
SO ₂								
O ₂								
CO								
CO ₂								
N ₂								
TOTAL	.0097	100.0	.98492	100.0	.98001	100		
TEMP. (°F)		1832		60		60		
STATE		G		S		S		

*Oxygen associated with FeO and Fe₃O₄

TABLE 1.6-2 ENERGY REQUIREMENTS Level 1					
FIRE REFINING AND ELECTROREFINING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	<u>Fire Refining</u>				
	A) Fuel Oil	GAL	7.5	0.130	1.043
	B) Electrical Energy	KWH	10.0	0.0105	0.105
2	<u>Electrorefining</u>				
	A) Electrical Energy	KWH	280.0	0.0105	2.94
	B) Steam	LBS	1240.0	0.0014	1.736
				TOTAL	5.824

TABLE 1.6-3 ENERGY REQUIREMENTS Level 2					
FIRE REFINING AND ELECTROREFINING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	<u>Fire Refining</u>				
	A) Natural Gas	SCF	200.0	0.0010	0.200
	B) Metallurgical coke	TON	0.001	31.50	0.252
2	<u>Electrorefining</u>				
	A) Sulfuric Acid	TON	0.0167	0.83	0.014
	B) Glue	TON	0.00003	40.00	0.0012
	C) Thiourea	TON	0.00003	40.00	0.0012
	D) Hydrochloric acid	TON	0.000002	9.25	0.00002
				TOTAL	0.468

TABLE 1.6-4

ENERGY REQUIREMENTS

Level 1

MELTING ANODE SCRAP IN REVERBERATORY FURNACE

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	<u>FIRE REFINING</u>				
	A) Distillate fuel oil	Gal.	35	0.139	4.87
	B) Natural gas, poling	SCF	560	0.001	0.56
2	C) Metallurgical coke	NET TON	0.008	31.5	0.25
	<u>ELECTRO REFINING</u>				
	A) Electrical energy	KWH	20	0.0105	0.21
	B) Steam (waste heat credit)	LBS	-1060	0.0014	-1.48
				TOTAL	4.41

FIGURE 1.6-3 TRENDS FOR STEAM AND POWER CONSUMPTION VERSUS CURRENT DENSITY IN ELECTROREFINING

This trend towards higher current density will reduce the overall cost of electrorefining although the energy consumption will increase. For a new electrorefinery, the breakdown in operating costs is approximately as follows (Arthur D. Little, 1976):

Electricity	2.3%
Other utilities	1.8
Chemicals and materials	7.9
Labor	19.9
Fixed Costs (including return on capital)	68.1
TOTAL	100.0%

This breakdown shows that incentives for cost savings and technological change in electrorefining will be to decrease the fixed cost component (by increasing the rate at which copper is refined) and through automation. For example, if current density is increased from 200 amps/m² to 350, the copper production would increase by approximately 70-75 percent while energy consumption would increase only by 30 percent per ton of product. The overall cost reduction resulting from this would be about 35-40 percent.

1.6.7 References

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1.7 IN-SITU EXTRACTION OF DEEP SEATED COPPER DEPOSITS

1.7.1 Introduction

In situ mining is the in-place extraction of metals from their ores located within the confines of a mine. The material to be leached may include fractured or unfractured ore, stope fill, caved material, and ores in permeable zones. Alternately, it may be ore dumps, heaps, slag piles, and tailing ponds. These materials represent an enormous, untapped potential source of all types of metals.

The field of in situ mining encompasses the following steps:

- (1) The preparation of ore for subsequent in-place leaching,
- (2) The flow of solutions and ionic species through rock masses and within rock pores,
- (3) The leaching of minerals with inexpensive and possibly regenerable leaching reagents under conditions prevailing in-place,
- (4) The generation and regeneration of such solution, and
- (5) The recovery of metals or their compounds from the metal-bearing solutions.

Accordingly, the overall scope of this potential mining method embraces interdisciplinary science and technology requiring application of principles of basic sciences, mineral technology, hydrology and economics. A flow diagram of the in situ extraction of copper is depicted in Figure 1.7-3.

1.7.2 Model Design

To assess the energy impact of in situ extraction of copper, a specific model must be designed which builds upon data available for a typical copper porphyry ore. Laboratory results obtained by researchers at Lawrence Livermore Laboratory (LLL) (Braun, et al., 1974) were used as a basis for calculation. The LLL laboratory study involved the leaching of a run-of-mine copper porphyry ore from the San Manuel Mine (Magma Copper Company, Arizona). In the test, 5.8×10^3 kg (6.38 tons) were leached in 1.52 cubic meters of solution for 717 days at 90 degrees centigrade and 400 psia oxygen over pressure. The copper curve of Figure 1.7-1 illustrates the experimental results obtained, where the fraction of the copper extracted is plotted against the number of days. The San Manuel ore was observed to weather appreciably, accelerating the rate of extraction.

An initial analysis suggests that hydrofracturing for access to a porphyry type deposit with highly disseminated copper and iron sulfides is least likely to be successful. This was, in fact, the result of the Safford field study carried out recently by Kennecott Copper Corporation. At the other end of the spectrum is complete rubblization such as could result by block caving mining or by nuclear rubblization as suggested by the Lawrence Livermore Laboratory experiment (Braun, et al., 1974). Block caving or nuclear rubblization results in an inter-particle porosity of approximately 30 to 40 percent. While a nuclear device is capable of generating an approximate 35 percent porosity without ore withdrawal, conventional explosives appear unlikely to be usable without some ore withdrawal. Also, any caving technique will produce upwards of 40 percent porosity if freely falling fragments pack randomly. As the space becomes more confined, lower and lower porosities occur in an ascending chimney of rock.

FIGURE 1.7-1 COMPARISON OF WEATHERING AND NON-WEATHERING ORE. DASHED LINE USED FOR DESIGN CALCULATIONS. UPPER CURVE IS FOR LLL EXP-1 USING SAN MANUEL ORE AT 90°C AND 400 PSIA OXYGEN

If conventional explosives, followed by block caving, were employed to simulate the LLL experiment, a void for the explosive would amount to approximately 15 percent of the total volume. Clearly, simulation of the LLL design with conventional explosives is not warranted. This has led us to a design which we refer to as "uniform rubblization" and is an approach employing explosives to shatter the ore into a pattern of free space generated through the joint efforts of Mountain States Engineering and the departments of Mining Engineering and Metallurgical Engineering at the University of Utah.

The design for field application is based upon an ore unit consisting of a cubic block 1,000 feet on a side. Four to possibly eight such blocks may be accessed by one shaft in one 1,000-foot layer. Multiple layers in depth may also be accessed by the shaft providing rubblization proceeds from the bottom of the deposit upward. Considering one unit only, the design incorporates the generation of a minimum of 8 percent porosity by mining lamellae 10 feet in height every 100 feet of depth. Pillars 10 feet on a side would be generated with 20-foot spacing between pillars. Ten such lamellae would be developed in each 1,000-foot ore unit. The 8 percent minimal porosity was arrived at on the basis of explosive rubblization producing a mean rock fragment diameter of 10 centimeters with average crack openings of approximately 3 millimeters. Uniformity is achieved by phased rubblization using conventional explosives. The explosive would be loaded into bore holes produced by drilling from each room and pillar section. Delayed detonation would be employed to attenuate the explosive shock-wave.

For purposes of calculation leading to laboratory experimental design, a typical copper porphyry ore containing 0.7 percent copper and a pyrite to chalcopyrite ratio of 2.0 to 1 will be considered. The bulk ore density is taken as 150 pounds per cubic foot. One unit block would contain 75×10^6 tons of ore. Using an average grade of 0.7 percent copper, a unit would contain approximately one billion pounds of copper. Successful exploitation would depend upon a recovery of approximately 50 percent of the copper in a 5-year period. Rubblization of ore in-place against a free surface requires 0.25 (open pit) to 1.0 pound of explosive per ton of ore depending upon the degree of rubblization required. Using a value of 0.5 pound of explosive per ton of ore, a unit block would require 37.5 million pounds of ANFO explosive. By detonating the blast into free space produced by mining, minimal random packing should occur resulting in a fairly uniform distribution of fracturing throughout the ore body. The permeability is estimated to be approximately ten to one hundred fold greater than the surrounding unbroken rock.

Leaching would be carried out using modified bore-hole mining technology with a pattern of down pumping, outpumping, and oxygen injection holes. In operation, continuous oxidation would proceed by oxygen injection into the ore body while a slow, continuous flow of solution is injected and removed. Oxygen would be introduced as needed, probably resulting in two-phase flow. The solution flow rate used in the following analysis is based upon a typical flow rate used in dump leaching of 0.25 gallon per square foot per hour. If the free flowing solution volume of the rubblized deposit is 8 percent of the total volume, the free liquid or pore volume would be 8×10^7 cubic feet or 2.7×10^6 liters. At the above flow rate, approximately 100 days would be required for one pore volume of liquid to pass through the rubblized deposit. For purposes of calculation, the depletion of contained copper during each pore volume transfer will be considered small compared to the total. Approximately 20 pore volumes will be considered in the calculation.

1.7.2.1 Oxygen Consumption and the Acid Balance

For an ore having a pyrite to chalcopyrite molar ratio of 2 to 1, 11.75 moles of oxygen are required for each mole of copper produced assuming the iron is oxidized to the plus three valence state and all sulfur is oxidized to sulfate. The overall reactions are:

The iron would precipitate as hydrated oxides and as jarosite salts depending upon the solution chemistry. The five moles of acid generated induce accelerated weathering of gangue constituents. Dynamic buffering of the system in steady-state represents a balance between the acid producing reactions involving the sulfide minerals and the acid consuming reactions involving the sulfide and the gangue minerals. The gangue mineral reactions will vary greatly depending upon the mineral make-up of the ore. Typically important gangue reactions would be those involving calcite and feldspar. Potassium feldspar reacts in the sequence:

The overall reactions would be:

The previous work carried out at LLL indicated that enhanced leaching occurred as a result of the weathering of the host rock.

1.7.2.2 Calculated Copper Extraction

In Figure 1.7-1 the upper curve, as mentioned, illustrates the laboratory results for the LLL experiment in which relatively extensive weathering occurred. The bottom curve represents the calculated extraction for a dense non-weathering ore which is limited by diffusion through pores. It is assumed the 50 percent passing diameter is 10 centimeters and the ore size distribution follows the log normal relationship. The dashed curve of Figure 1.7-1 represents a modestly weathering ore. The dashed curve is represented by the equation:

$$1 - \frac{2}{3}\alpha - (1 - \alpha)^{2/3} = 1.86 \times 10^5 t$$

where α is fraction of copper extracted and t = days. The above equation is considered conservative for a typical porphyry type mineralization. Based on the working curve, the copper released expressed as grams per liter, total cumulative tonnage, and tons per day were calculated. Also, using an oxygen efficiency of 0.85 the oxygen requirement was evaluated. The calculated results are summarized in Table 1.7-1.

TABLE 1.7-1

CALCULATED PRODUCTION DATA FOR IN SITU EXTRACTION FROM ONE BLOCK:

ONE PORE VOLUME (PV) = 2.27×10^4
 RETENTION TIME = 100 days

Pore Volume	Time (days)	Fraction Reacted	[Cu ²⁺] gpc	Total Cu Produced (Million Tons)	Daily Avg. Cu Production tons/day	Oxygen Requirement tons/day	Oxygen Requirement Cumulative Total (tons)
1	100	.110	21.3	0.053	531	3,690	3,690
2	200	.170	11.6	0.082	290	2,016	5,706
3	300	.210	7.74	0.101	193	1,341	7,047
4	400	.240	5.80	0.116	145	1,008	8,055
5	500	.270	5.80	0.130	145	1,008	9,063
6	600	.290	3.90	0.140	97	674	9,737
7	700	.310	3.90	0.150	97	674	10,410
8	800	.330	3.90	0.160	97	674	11,090
9	900	.350	3.90	0.169	97	674	11,760
10	1000	.370	3.90	0.179	97	674	12,430
11	1100	.385	2.90	0.186	73	507	12,940
12	1200	.400	2.90	0.193	73	507	13,450
13	1300	.415	2.90	0.200	73	507	13,960
14	1400	.430	2.90	0.208	73	507	14,460
15	1500	.445	2.90	0.215	73	507	14,970
16	1600	.460	2.90	0.222	73	507	15,480
17	1700	.470	1.90	0.227	48	334	15,810
18	1800	.480	1.90	0.232	48	334	16,140
19	1900	.490	1.90	0.237	48	334	16,480
20	2000	.500	1.90	0.242	48	334	16,810

Figure 1.7-2 illustrates the calculated results. There is a marked fall-off in solution concentration with time, beginning with very high initial solution concentrations. The horizontal upper (dashed) line of Figure 1.7-2 represents a theoretical continuous production level capable of producing 100,000 tons of copper per year (270 tons per day). Clearly there would be great difficulty in designing an extraction plant to handle the effluent from one unit block. Field production would require initial control of copper extraction either by limiting flow to progressively greater portions of the unit block or by limiting the oxygen flow rate. Phasing in additional rubblized blocks would be required after approximately 200 days to provide a continuous level of production at 270 tons per day.

The solid curves of Figure 1.7-2 refer to maximum production at oxygen saturation. If five years is taken as the effective time for 50 percent removal, we note from Figure 1.7-2 that the 435,000 tons (actually 49 percent of the copper) could be produced from a single unit block in five years by operating at a continuous rate of 130 tons per day or 47,500 tons per year as indicated by the lower dashed line. Beyond five years the rate of production would fall off since the rate of extraction would shift from rate of solution withdrawal to rate of oxygen diffusion into the ore fragments.

1.7.3 The Mining Plan

The mining plan is based upon a 1,000-foot cube of porphyry copper containing 0.70 percent copper with a pyrite to chalcopyrite ratio of 2 to 1. The cube extends from 500 feet to 1500 feet below the permanent water table. The cube contains 7.5×10^9 metric tons of the above mineralization in a major zone of barren porphyry. It is to be leached in-place by a procedure to be described which outlines the preparation of the cube for leaching. Leaching will be over a 5-year period and copper recovery is expected to be 50 percent.

The energy required to prepare and leach the cube is estimated to be 4,921,000 million Btu's, expended over a period estimated at approximately 10 years.

The development program entails the establishment of an underground mine, the extraction of 8 percent of the ore body to create voids, the installation of solution seals surrounding the ore body (if required), and all other procedures that would enhance leaching and recovery following the shattering of the ore-cube.

The development program will be carried out on a work schedule of 24 hours per day, 340 days per year.

1.7.3.1 Site Selection

Choose the shaft site most favorable to surface plant topography and to skirt 200 feet away from the exact mid-point of one side of the ore cube. Bear in mind the surface plant will include all the normal buildings and facilities to support a medium sized underground mining operation including dump space for 8.0×10^9 kg of waste and space to install a pad to heap leach more than 5.0×10^9 kg of ore.

1.7.3.2 Shaft Installation

Drill a pilot PQ wireline core hole at the shaft site to 2,600 feet in depth for detailed data on lithology and water to be encountered in sinking.

FIGURE 1.7-2 CALCULATED RECOVERY RATE (tons/day) AND TOTAL TONNAGE PRODUCED FROM A UNIT BLOCK OF COPPER PORPHYRY ORE

By truck mounted equipment, excavate the first 50 to 100 feet of shaft and concrete from collar to competent ground. As this is being accomplished the headframe, hoist, compressor, building, and other surface ancillaries can be in the process of installation.

When the shaft achieves 1,460 feet depth, cut a station to serve the injection well field platform. At the 1,600 foot level and each 100 feet below the 2,510 level, cut an appropriate station.

Sink to 2,600 feet below collar and install between the 2,510 and bottom levels the 800 MT capacity pocket, skip loading device, and station. The 2,510 level station will be much larger than others to accommodate the first aid station, minor repairs shop, and emergency supplies.

1.7.3.3 Ore Pass Raise

This system of 6-foot by 6-foot raises will be designed on a 70 degree slope reversed between each level (1,460-2,510 levels) to act as retarders against free-fall velocity. The ore pass system will be in the pillar between shaft and ore body and will be connected with each level by a separate, short 5-foot by 5-foot raise at 70 degrees from a level grizzly with 24-inch openings. The 2,510 level will serve as the main grizzly location with a retarder-feeder admitting the muck from the ore pass to the grizzly with bars at 12-inch spacings immediately above the pocket.

1.7.3.4 Ventilation and Shaft

The four-compartment shaft will utilize the two center compartments for counter-balance hoisting, one compartment for service lines and manway, while the other will be smooth-lined for ventilation air downcast from surface blower. The other compartment will serve as upcast air until the second opening has been installed.

1.7.3.5 The Emergency Escapeway

Upon achieving the 2,510 level, a drift will be started toward the opposite side of the ore block on that level. It will extend 200 feet beyond the ore block into the wall rock directly opposite the shaft, at which point an up-reamed, 6-foot diameter shaft will be bored, using 13 $\frac{3}{4}$ -inch pilot hole from surface. This second connection with surface will be concrete lined to 5-feet inside diameter and will serve as a ventilation exhaust conduit and an emergency man escapeway.

1.7.3.6 Mining for Voids

To create the needed 8 percent voids to blast to in the ore block, 10-foot horizontal, room-and-pillar slices will be mined at 100-foot intervals in the ore block and one such slice will be made immediately under the block. The number of these slices will depend on the time frame chosen to complete the overall development program. If a 3,000 tons per day shaft facility is installed, the overall development program is estimated to consume 9 years. With a 9,000 ton per day shaft, that period could be 6 years. If leaching is started on the lower one-third of the ore body, production of copper could begin at one-third to one-half of the above time frame. There will be approximately 7,000,000 tons of ore and development waste removed from the shaft and the capital cost for excavating and transporting the materials will be approximately double for the 9,000 over the 3,000 ton per day capacity.

1.7.3.7 Preparation for the Rubblization of the Ore Block

As a slice is nearing completion, special drilling equipment can be moved in to drill 4-inch diameter holes in preparation for the rubblization blast.

1.7.3.8 Placement of the Leach Reagent Injection Platform

Forty feet above the top of the ore block, 8,300 feet of 6-foot by 7-foot drift will be driven to serve 81 injection holes on 100-foot centers. The drift from a shaft station 1,460 feet below collar will carry the oxygen and leach solution headers to the grid of 8-inch holes drilled into the top of the broken ore after rubblization.

1.7.4 Energy Consumption in Mining and Fracturing

1.7.4.1 Electric Power

The mine surface and underground plants will ultimately have 3,050 connected horsepower with an average over the first 1½ years of 20 percent (610 HP) connected, and 100 percent connected the remaining 6½ years of the 8-year mine development period.

Energy expended: 1,605,000 million Btu = 6.76×10^6 Btu/ton copper

1.7.4.2 Diesel Power

Principal consumption is by load-haul-dump units underground (assuming public electric power is delivered to the site in place of diesel generator).

114,000 million Btu = 0.07×10^6 Btu/ton copper

1.7.4.3 Other Petroleum

17,000 million Btu = 0.07×10^6 Btu/ton copper.

1.7.4.4 Explosives

Using a 0.5 pound of explosive per ton of material broken including detonators, boosters, etc., for total blasted metric tons = 75,806,384,568,000 million Btu = 2.14×10^6 Btu/ton copper.

1.7.4.5 Bore Escape Shaft (Electric)

This 6-foot diameter shaft will be upreamed through a 13¾-inch pilot hole from surface and the following energy use could be combined with "Electric Power."

8,000 million Btu = 0.03×10^6 Btu/ton copper.

1.7.4.6 Underground Drilling of Blast Holes

The approximate 4,600 holes on 10-foot centers, 50-feet deep can be drilled by special lowhead drills capable of vertical up and down drilling 4-inch to 6-inch diameter holes. Power can be either electric or diesel.

1,324,000 million Btu = 5.57×10^6 Btu/ton copper.

1.7.4.7 Total Energy Expended in Mining

5,353,000 million Btu = 22.54×10^6 Btu/ton copper (47,500 tons per year copper for 5 years)

1.7.5 Energy Consumption in Copper In-Situ Extraction

In this in-situ leaching process, the oxidation of chalcopyrite and pyrite is carried out by pumping oxygen in the fractured ore. About 13,160 pounds of oxygen are required to obtain one ton of copper assuming 85 percent oxygen efficiency. This oxygen requirement represents an energy consumption of 23.7 million Btu's per ton of copper produced as shown under Energy Use Level 2 (Table 1.7-3). Moreover, the oxidation of sulfides underground produces sufficient sulfuric acid for leaching of the copper values.

On the other hand, the reaction of oxygen with sulfides is an exothermic one producing about 57.3 million Btu's of energy per ton of copper oxidized, nearly half of which is consumed in heating the leach solution and the ore in-place up to 90 degrees centigrade. Mountain States Research and Development's (MSRD) calculations indicate that about 29.6 million Btu's are required for heating the leach solution and the fractured ore in-place. This results in the surplus of about 27.7 million Btu's energy. However, MSRD believes that this surplus energy is not in a usable form and no credit is allowed in the energy balance.

The copper values from the leach solution will be recovered using the solvent extraction-electrowinning (SX-EW) process to obtain directly salable cathode copper as shown in the flowsheet (Figure 1.7-3). In the proposed flowsheet, 3,000 gallons per minute of leach solution averaging 8.0 grams per liter copper will be processed in an appropriate SX-EW plant to produce 130 tons per day of cathode copper at an efficiency of 90 percent.

The energy requirement for the SX-EW process as calculated by MSRD amounts to about 24 million Btu's per ton cathode copper produced. Additional energy requirements in the overall process include 1.4 million Btu's for pumping of the leach solution (3,000 gallons per minute) and 29.6 million Btu's for heating the solution and ore in-place to 90 degrees centigrade. It should be noted that much of the heat, once generated, will be retained in the fractured ore underground and the above energy requirement represents additional energy needed to make up the heat losses sustained during leaching and processing.

The energy uses in the proposed in-situ leaching process under level 1 and Level 2 are summarized in Table 1.7-2 and Table 1.7-3 respectively.

As can be seen, the total energy required for producing one ton of cathode copper by in-situ extraction including both Levels 1 and 2, amounts to 80.6 million Btu's. This quantity is in line with the energy required by other hydrometallurgical and pyrometallurgical processes including mining and concentration. One would expect that the in-situ extraction would be less energy intensive than other conventional mining and surface processing methods. In reality, the process is less energy consuming per unit of copper, but the recovery is about 50 percent as compared to about 85 to 90 percent for conventional mining and surface processing methods. This observation clearly pinpoints the need for research and development resulting in higher recoveries than 50 percent.

FIGURE 1.7-3 COPPER IN SITU LEACHING

TABLE 1.7-2		ENERGY REQUIREMENTS			Level 1
INSITU LEACH PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	<u>Mining and Fracturing Leaching</u>				22.5
	A) Pumping Solution				1.4
	B) Heating Solution and ore in place				29.6
	<u>Solvent Extraction</u>				24.0
	<u>Electrowinning</u>				-29.6
	Energy Produced in the Process* (oxidation of sulfides)				
				TOTAL	47.9
*Energy produced in the oxidation of sulfides is actually 57.3×10^6 Btu, but we are accounting for only heat required for heating the solution and the broken ore.					

TABLE 1.7-3		ENERGY REQUIREMENTS				Level 2
INSITU LEACH PROCESS						
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER	
	Mining and Fracturing Explosives	LBS	143	.060125	8.6	
	Leaching Oxygen	LBS	13,160	.0018	23.7	
	SC-EW Reagents	LBS	24.92	.0172	0.4	
				TOTAL	32.7	

1.7.6 Conclusions

The in-situ extraction of copper from a deep seated sulfide copper deposit should be an attractive process from the view of energy consumption, since Mountain States Research and Development's study indicates that about 75 million Btu's are required to produce one ton of cathode copper. This consumption is in line with energy consumption by other hydrometallurgical methods. The major shortcoming of the process is the assumption that only 50 percent of the copper is recoverable in this process. If higher recoveries than 50 percent are achievable then the in-situ process would be truly an attractive approach. If the comparison is made with conventional mining and concentration of ore from a deep-seated deposit the in-situ method appears even more attractive.

1.7.7 Recommendations

Since the overall recovery of 50 percent makes the in-situ process little better than other hydrometallurgical processes in energy use, research efforts should concentrate on methods to increase the overall recovery of copper. Accordingly, an in-depth R&D program is necessary for improving the overall extraction of copper. This study should include a demonstration phase to determine the effectiveness of the process under operating conditions in-situ. Also the use of air instead of oxygen should be considered for certain conditions of ore depth and mineralization. An appreciable energy saving could be made using air and conditions permitting its use should be determined. Comparable tests in bench scale and large pilot scale research is needed to assess the following:

- 1) Actual oxygen consumption related to the type and extent of mineralization needs to be evaluated quantitatively.
- 2) Use of air compared to oxygen to determine the effect of oxygen partial pressure.
- 3) Recent developments (Coursen, 1979) in blasting stressed rock with flooded joints indicates the amount of explosive needed may be as low as that for open pit mining. This would reduce the total Level 2 energy by 4.8×10^6 Btu/ton copper. Explosive technology which will reduce the amount of explosive needed for uniform rubbleization should be tested under conditions approximately the specific in-situ mining plan.
- 4) In connection with 3) above, field tests on rubbleization should include up-flow flushing to remove fines produced by sliding joints during blasting. It appears such flushing can remove fines effectively, resulting in permeabilities of 2 or 3 Darcys.
- 5) The fanning or spreading effect of gases through open joints in a blasted ore body should be determined under conditions of two-phase flow.
- 6) Weathering and leaching characteristics of copper porphyry should be determined for extended periods of ore-solution contact time to improve model predictability.
- 7) Comparison of small scale and large scale tests should be correlated by a detailed model to test and improve scale up precision.
- 8) Solution chemistry capable of recovering precious metals concurrently or sequentially should be considered.
- 9) Reactions with host rock potentially capable of precipitating copper and consuming lixiviant should be quantified.

1.7.8 References

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1.8 COPPER CEMENTATION

1.8.1 Introduction

The recovery of copper from dilute leaching solutions by precipitation with iron, i.e., cementation, represents a significant source of recoverable copper representing approximately 10% of domestic mine output. The solutions obtained from in-situ, dump and heap leaching are dilute (15 kg/m³ copper). Cementation offers a simple and efficient means of recovering copper from such dilute solutions. The product of precipitate or cement copper is impure and requires further pyrometallurgical upgrading.

1.8.2 Process Description (Biswas and Davenport, 1976)

The cementation of copper from solution is described by the reaction

Other metals such as aluminum and zinc can be used. However, steel scrap is an economic cementation agent of choice. The pregnant leach solution is made to flow through a pile of scrap steel at which time the copper precipitates on the iron surfaces and is removed under the influence of solution flow as flake or powder. The copper is usually contaminated with iron (typical analysis 85-90% Cu, 0.2-2% Fe, 0.5% SiO₂ + Al₂O₃, remainder oxygen). Stoichiometrically, about 0.88 ton of iron is required to cement one ton of copper. In industrial practice the iron consumption is 1.5-2.5 tons per ton of copper cemented out due mainly to the following side reactions:

Atmospheric oxygen contributes to excess iron consumption oxidizing the iron or producing ferric ions that consume metallic iron. Some of the copper may also oxidize and redissolve requiring reprecipitation.

Thermodynamics indicate that the equilibrium ionic ratio $A_{\text{Fe}^{++}}/A_{\text{Cu}^{++}}$ is about 10^{28} at 25°C. This extremely large ratio indicates that reaction 1.8.1 can proceed until virtually all the copper ions are precipitated from solution. In industrial practice more than 90% of the copper is removed from the pregnant liquors before they are recycled to the leaching circuit. The kinetics of cementation have been studied extensively, and it is generally agreed that the rate controlling step is the diffusion of copper ions to the steel surface. Thus, the rate of copper precipitation

(Nadkarni and Wadsworth, 1968) is proportional to the concentration of copper, in solution, the exposed iron area and the specific rate constant 'k'

$$dC_{Cu^{+2}}/dt = - kA C_{Cu^{+2}} \quad (1.8.4)$$

The specific rate constant and hence the cementation rate increases with increasing temperature and degree of agitation. In addition, minimizing the concentration of Fe^{+3} ions and atmospheric oxygen lowers the effect of side reactions 1.8.2 and 1.8.3 leading to more efficient iron utilization. It has been shown that iron consumption approaches stoichiometric requirement when carried out in a nitrogen atmosphere (Biswas and Reid, 1972).

The flow sheet for the recovery of copper from dilute solutions by cementation is shown in Figure 1.8-1. The simplest and most common cementation system is the open launder in which the pregnant leach solutions flow by gravity down a wooden or concrete trough or series of troughs filled with steel scrap. The launders vary in dimensions and form — straight line or zigzag. Table 1.8-1 summarizes the operating parameters for launder precipitation plants. In more recent launder designs the scrap steel is held on wooden grids positioned above the launder bottom. This permits the cement copper to fall to the bottom of the launder where it can be recovered from the steel scrap. Open launder operations involve higher scrap steel usage with up to three times the stoichiometric requirement actually being used. It also requires considerable labor to handle steel scrap additions and to recover cement copper.

Several compact and dynamic cementation systems have been developed and used industrially (Spedden et al., 1966). The most successful is the Kennecott Cone precipitator in which the pregnant leach solution is forced upwards in a swirling motion through shredded steel scrap.

The Kennecott Cone system consists of a cylindrical tank, 6-7 m high, 4-5 m diameter, in which a 4-m high stainless-steel cone is fixed (apex down). The upper third of the cone is constructed of stainless-steel screen. The pregnant leach solution is swirled into the cone via two rings attached to the inside of the cone (one-third and half-way up) through laterally directed openings on the rings. The solution swirls upwards through the shredded steel scrap and the copper precipitates as contact is made.

The swirling action washes the copper from the iron surfaces and the particles become suspended in the solution. The copper particles are carried upward to near the top of the cone where, as the velocity decreases due to the widening of the cone, they sink through the screen part into the collection area at the bottom of the tank.

The Kennecott Cone is a high capacity unit ($10 \text{ m}^3\text{min}^{-1}$ of solution in a 7 m high, 4 m diameter vessel; Malouf, 1973). The system is flexible and two or more cones can be placed in a series (or series with a launder) to maximize copper recoveries and throughput or to handle solutions with high copper concentrations. In addition to the high throughput rate, the cone has the advantage of a low iron consumption, in the order of 1.6 times the stoichiometric requirement compared with 2.5 for equivalent launder techniques (Spedden et al., 1966). The Kennecott Cone has proven to be very efficient and it is now used extensively in association with large heap-leach operations.

STREAM LEGEND

SOLID

LIQUID (Non-molten)

FIGURE 1.8-1 COPPER CEMENTATION

TABLE 1.8-1 COMPARISON OF LAUNDER PRECIPITATION PLANTS (JACOBI, 1964)

	Inspiration copper	Ohio Cu, (Bingham Canyon)	Anaconda (Butte)	Andes Copper	Cananea
Laundry system	Zigzag	Straight line	Straight line	Zigzag	Zigzag
Daily production (tonnes)	11	9	8	8	22
Leach solution flow ($\text{m}^3 \text{min}^{-1}$)	9.5	3.2	19.0	2.2	5.1
Copper concentrations (kg m^{-3})					
Pregnant leach	0.85	2.04	0.31	2.41	3.30
Post cementation	0.02	0.06	0.02	0.07	0.36
Recovery of launders (%)	97	97	95	97	89
Number of laundry units	32	200	20	18	40
Dimensions of laundry units					
Length (m)	12	5	30	19	12
Width	0.5	0.8	3	3	1.5
Depth	1.5	0.8	0.9	1.8	0.9
Total laundry volume (m^3)	290	640	1620	1850	650
Velocity of leach solution (m min^{-1})	2.0	9.8	2.0	0.4	0.1
Contact time (min)	19.2	50	78	875	88
Ratio: $\frac{\text{Daily copper production}}{\text{Total laundry volume}}$ (tonnes day m^{-3})	0.04	0.014	0.005	0.004	0.03

Other dynamic precipitation techniques such as the tumbling of scrap in submerged drums have been tried but much of the copper precipitate produced was colloidal in size and difficult to recover.

1.8.3 Materials Balance

The principal material consumption is iron as scrap. Depending on the type of operation, the scrap iron consumption can range from 1.5 to 4 tons per ton of cement copper (Woodcock, 1967) and 1.5 to 2.5 tons (Biswas and Davenport, 1976).

1.8.4 Energy Requirements

Level 1 energy requirements in cementation consist principally of electrical energy in pumping solutions in precipitation cones and launders. The energy use is small and is estimated at 5 kWh per ton of cement copper or 0.05 million Btu per ton of cement copper.

The only materials consumption is the iron scrap used in cementation. Based on an iron use of 2.5 tons per ton of copper and an energy value of steel scrap of 18 million Btu per ton (Battelle, 1975), this results in an energy use of 45 million Btu per ton cement copper. Thus, the level 2 energy usage is 45.05 million Btu per net ton cement copper.

1.8.5 Utilization of Cement Copper

The most common method of treatment of cement copper is by melting it in smelting furnaces or converters. An alternate but rarely used method is to dissolve the cement copper in a basic aqueous solution followed by hydrogen reduction to yield copper powder ($<150\text{ }\mu\text{m}$) of 99.9% purity (EMJ, 1967). A German patent (Reid, 1972) according to which copper at 99.8% purity is produced by carrying out the cementation reaction under nitrogen followed by a sulfuric acid washing and a nitrogen atmosphere drying. This process will, if successful, produce a material suitable for powder metallurgy applications.

1.8.5.1 Disposition of Copper Precipitates

Table 1.8-2 shows the disposition of cement copper (precipitates) at U.S. copper smelters. It is seen that most of the precipitates used at smelters (88.5%) are added to the reverberatory roaster. It should also be noted that precipitates represented about 3.9% of the tonnage of copper concentrates charged at U.S. smelters.

1.8.5.2 Energy Requirements

Many smelting furnaces use precipitates as a portion of the charge. The energy requirements presented in subsequent sections represent actual operation energy use, i.e., for a mix of concentrates and cement copper. Based on the enthalpies of copper and iron sulfides and cement copper at their melting points, it is estimated that melting copper precipitates requires 15 percent of the energy used to melt on a per ton contained copper basis. If precipitates are charged to a converter, the excess heat can be used to melt the precipitates. However, this is rarely practiced because the moisture in the precipitates can cause hazards in converter operations and dust handling problems increase.

Table 1.8-2
DISPOSITION OF PRECIPITATES AT U.S. SMELTERS
(1971-73)

Smelter	Approximate Annual Tonnage			Precipitate Use (%)	
	Concentrates	Precipitates, Reverbs, Roasters	Converters	Reverb Roasters	Converters
Asarco, El Paso	295,600	3,000	9,000	25	75
Hayden	529,812	1,743	2,614	40	60
Tacoma	273,603	0	3,995	0	100
Phelps Dodge, Douglas	680,509	10,500	6,500	62	38
Morenci	810,000	16,000	1,200	93	7
New Cornelia	205,471	1,540	2,445	40	60
Kennecott, Garfield	780,542	52,650	2,211	96	4
Hayden	296,282	13,215	43	100	0
Hurley	265,442	36,700	405	99	1
McGill	283,196	16,435	0	100	0
Inspiration	282,200	28,500	0	100	0
Magma, San Manuel	798,500	0	0	0	0
Anaconda, Anaconda	647,870	37,840	0	100	0
Copper Range, White Pine	247,100	0	0	0	0
TOTAL	6,397,127	218,223	28,413	88.5	11.5

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2.0 PYROMETALLURGY

2.1 INTRODUCTION

This section deals with copper extraction processes that involve high temperature processing to produce a final blister copper product which is subsequently fire refined and electrorefined to the pure cathode product. Section 2.2 presents an analysis of the theoretical energies involved in the conversion of the standard concentrate to blister copper. The process is exothermic when pure oxygen is used to convert the concentrate to copper and produces surplus heat. If a mixture of air and oxygen is used, as the nitrogen in the gases increases, its heat content rapidly changes the surplus heat to a deficit. With pure air 4.2 million Btu per ton of cathode copper is necessary to overcome the energy deficit. It is evident from this analysis that oxygen enrichment of air blowing processes is energy efficient. If the heat liberated by the oxidation of sulfides in the charge can be recuperated or used efficiently in a given process, a low overall energy cost will result for the process.

The conventional roast, reverberatory matte smelting, converting process was treated in section 2.3 to provide a "yardstick" by which the other pyro-processes could be measured. The other processes chosen for study range from those that have had considerable commercial utilization such as the electric furnace (2.5), Oxy Fuel Reverb (2.15), the flash smelting processes (2.6, 2.7) and the Noranda process (2.9) to the Q-S process (2.11) presently under development by Dravo and the Thermo Electron Process (2.14) which has not been at the present time completely tested on a laboratory scale.

The Top Blown Rotary Converter Process (2.8) is an example of a process successful in the steel industry which has been adapted to nickel and copper sulfide smelting. It has only recently been used commercially in British Columbia for the first time on a copper ore concentrate. The Mitsubishi Process (2.10) is an example of a modern continuous smelting and converting process with a unique design. The AMAX Dead Roast Process (2.12) which utilizes a small blast furnace for final reduction of the copper oxide. The Segregation Process (2.13) is a novel process involving a combination chloridizing roast and coal reduction step which appears to be energy efficient.

Finally a section is included on impurity control in pyrometallurgical processes (2.4) since impurity elements play an important role in the nature of the subsequent smelting operations. Some elements may be valuable by-products while others are detrimental to the quality of the final cathode copper and are difficult and costly to remove. It is concluded that the single step smelting processes may retain more of the impurity elements in the final blister copper than the conventional smelting process and hence the continuous processes may have to either use more pure ores or be modified to include a separate converting or impurity removal step.

2.2 THE THEORETICAL ENERGY FOR SMELTING COPPER CONCENTRATES TO UNREFINED BLISTER COPPER

2.2.1 Introduction

As a base line for comparing real processes, an idealized theoretical energy for smelting is desired. Smelting is defined as the unit process of metallurgy in which the desired product, metal or matte, is separated from an undesired one, slag, by a gravity separation amongst the two liquid, condensed phases. Normally, a gas will also be present. A narrow interpretation of the definition would lead to the conclusion that no real copper smelting process meets these criteria, because the so-called slag phase is not liquid, it is itself a two-phase system of liquid slag and solid magnetite (Fe_3O_4) which can amount to as much as 30 percent of the slag weight. Magnetite causes bottom build-up in relatively quiescent furnaces, and is blamed for poor settling of matte out of slags, and therefore high slag losses. Consequently, the first step in making a material balance from which theoretical energy may be calculated is selection of a slag which should prevent magnetite formation by using available thermodynamic and activity data.

2.2.2 Selection of Slag Composition

Magnetite cannot form when conditions do not allow the following reaction, Eqn. 2.2.1, to proceed.

Thus the formation of magnetite requires the existence of FeO and a sufficient pressure of oxygen in the surroundings. FeO exists in the slag phase because FeS has been oxidized into it and into SO_2 in the gas phase. Thus the raw material for magnetite formation being present, what is the pressure of oxygen? The highest oxygen pressure encountered when going from concentrates to copper is where the oxidation of white metal, Cu_2S , occurs. The highest oxygen pressure will then result from the reaction of Eqn. 2.2.2.

This would correspond to an 80% Cu matte grade. Actual matte grades are generally lower, and those encountered in modern processes may be around 70% Cu. In this case, the oxygen pressure would be fixed by Eqn. 2.2.3.

The equilibrium constant of this reaction is readily calculated from thermodynamic data, and has the form shown in Eqn. 2.2.4.

$$K_3 = (\text{activity FeO} \times \text{pressure SO}_2) / [\text{activity FeS} \times (\text{pressure O}_2)^{1.5}] \quad (2.2.4)$$

Activity of FeO can be controlled by selecting a suitable slag, adding for example proper amounts of SiO_2 and CaO , known as "fluxes." Since the reaction uses up oxygen almost quantitatively, the pressure of SO_2 depends on oxygen content of the oxidant. If pure oxygen is used, then SO_2

pressure is approximately equal to atmospheric. If air is used, it will be about 15% as shown by equation 2.2.5 (based on 79% N₂, 21% O₂ in air):

For the more general case, one gets the result of Eqn. 2.2.6:

$$\text{pressure of SO}_2 \text{ (atm)} = \% \text{O}_2, \text{ blast} (150 - 0.5 \times \% \text{O}_2, \text{ blast}) \quad (2.2.6)$$

Since activity of FeS in matte is nearly equal to its molar fraction, one can estimate it from percent Cu in matte by Eqn. 2.2.7:

$$\text{activity FeS} = (1 - 0.006918 \times \% \text{Cu, matte}) / (1 - 0.005605 \times \% \text{Cu, matte}) \quad (2.2.7)$$

It appears that if activity of FeO is at about 0.35, then magnetite cannot form in the temperature range 1200-1300°C for oxygen contents in the blast up to 100%. Also, equilibrium copper in slag will be below 0.5%. (Yazawa, 1974).

By extrapolating activity data in the system CaO-FeO-SiO₂ (Timucin, 1970) down to 1300°C, it was found that a silica-saturated slag containing 10% CaO, and 45% each of FeO and SiO₂ had the desired activity. According to the work of Rontgen its viscosity was about 5 poises, and according to Henderson its density is 3.3, so that with a matte density of about 5, separation should be satisfactory.

In the slag, Al₂O₃ is considered chemically equivalent to SiO₂ on a weight basis in correcting the ideal slag composition to one made from gangue in the concentrates and fluxes. The fluxes are regarded as being pure SiO₂ and pure CaCO₃. The oxygen used is treated as pure O₂.

With these assumptions, the material balance is as shown in Table 2.2-1 and the energy balance as in Table 2.2-2. Thus the oxidation of green concentrates to blister copper is exothermic, with surplus energy of 1.9 million Btu per net ton of contained copper. Were one to use a lower SiO₂ slag, as is the common practice, the calculated energy surplus would be greater for two reasons, one being the formation of Fe₃O₄, with its higher heat of formation than FeO, and the other a decrease in the weight of slag. It is however felt that the actual energy surplus in this case would be decreased rather than increased because of the operating problems brought about by magnetite.

2.2.3 Effect of Air-Oxygen Mixtures

The effect of using a mixture of air and oxygen rather than pure oxygen is to add nitrogen gas and thereby increase the heat content of the gases, soon changing the heat surplus into a deficit. The heat content of nitrogen at 1250°C is 9.39 kcal/gm mol. Therefore the 528 kcal surplus would be consumed by the addition of 56.23 mols of N₂. Since the oxygen supplied is 1535 grams or 47.97 gm mols, it is seen that a blast containing less than 46% oxygen will change the surplus into a deficit. If air is used, heat in nitrogen will rise to 1695 kcal/kg Cu or 6.10 million Btu/ton Cu, changing the surplus to a deficit of 4.2 million Btu.

TABLE 2.2-1

Material Balance for the Production of Unrefined Blister Copper
from the Standard Concentrate under Idealized Conditions

Basis: 1000 net tons Cu in Blister

INPUT	tons	OUTPUT	tons
Green Concentrates	4500	Blister Copper	1020
Silica Flux	970	Slag	
Lime Flux	366	SiO ₂	1319
		Al ₂ O ₃	140
Oxygen	1535	FeO	1459
		CaO	289
		MgO	25
		Cu	13
		S	16
		Other Gas	12
			3283
		H ₂ O	450
		CO ₂	161
		SO ₂	2457
			<u>3068</u>
TOTAL INPUT	7371	TOTAL OUTPUT	7371

Table 2.2-2

Energy Balance for Production of Blister Copper from Standard Concentrates
Basis 1000 gm Cu or One Net Ton Cu in Unrefined Blister

<u>Input</u>	<u>kcal/kg Cu</u>	<u>Million Btu/net ton Copper</u>
Oxidation of sulfur	2743	9.88
Oxidation of iron	1215	4.37
Formation of slag	208	.75
Formation of alloy	<u>5</u>	<u>.02</u>
Total energy input	4171	15.02
<u>Output</u>		
Sensible heat at 1250°C		
Blister copper	188	.68
Slag	1255	4.41
Gas-SO ₂ 591		
CO ₂ 55		
H ₂ O 296	942	3.39
Decomposition		
sulfides 824		
CaCO ₃ 156	980	3.53
Evaporation of water	<u>308</u>	<u>1.11</u>
Total accounted for 3643		13.12
Surplus, by		
difference	<u>528</u>	<u>1.90</u>
Total energy output	4171	15.02

2.2.4 References

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2.3 CONVENTIONAL SMELTING

2.3.1 Introduction

Conventional pyrometallurgical practice for recovery of copper from its sulfide concentrates (reverberatory smelting) is fairly uniform from smelter to smelter and is adapted to treating fine grained sulfide concentrates consisting mainly of copper and iron sulfides and gangue.

Copper's strong affinity for sulfur and its weak affinity for oxygen as compared with that of iron and other base metals form the basis for the three major steps in producing copper metal from sulfide concentrates; roasting, smelting and converting. There are approximately 100 reverberatory furnaces in use worldwide (Biswas and Davenport, 1976).

2.3.2 Process Description

The process flowsheet is shown in Figure 2.3-1.

2.3.2.1 Raw Materials

Flotation concentrates containing from 15-30% copper constitute the bulk of the feed to the smelters. In addition, smelters will charge cement copper (produced by precipitation of copper in solution with iron) containing 70-85% copper.

2.3.2.2 Drying

The flotation concentrates can contain 10-15% moisture. Cement copper can contain as much as 30% moisture. The charge to a reverberatory furnace can be dried so that its overall moisture content is 4-8% without unduly increasing dusting problems in the reverb. The removal of moisture in drying reduces the fuel requirements in the reverb. Also the drier acts as a blender for homogenizing the charge. Rotary or multiple hearth driers are used for drying the feed materials.

FIGURE 2.3-1 REVERBERATORY SMELTING PROCESS

2.3.2.3 Roasting

About half the copper smelters in the U.S. roast their charge prior to smelting in the reverberatory furnace. The older smelters use multiple hearth roasters for this purpose while the new smelters use fluidized bed roasters.

The object of roasting is to regulate the amount of sulfur in the charge and to remove certain volatile impurities such as arsenic, antimony, and bismuth. In the case of custom or toll smelters, the composition of feed materials can vary widely. Hence, roasting in addition blends and homogenizes the charge. Smelters with access to high-grade, low-impurity concentrates eliminate roasting and smelt the concentrates directly.

Elimination of some of the sulfur in roasting results in a higher grade matte in the reverberatory furnace and hence decreases the oxidizing load on the converters. Sulfide roasting can be autogenous and additional fuel is not required. The charging of hot roasted calcines into the reverberatory furnace can decrease its fuel consumption per ton of charge by about 40% and consequently increase a reverb's unit capacity. The lower fuel requirement per ton of charge when using calcine smelting also reduces the volume of reverb off-gases. In addition, roasting also reduces the emissions of sulfur dioxide from the reverb by removing the loosely held or "labile" sulfur in the concentrates which would otherwise evolve in the reverb upon melting of the minerals.

Both types of roasters (multiple hearth and fluidized bed) usually operate around 1200°F. Sulfur dioxide concentration in the wet off-gas is usually 5-10% with new multiple hearth roasters and lower for old multiple hearth roasters (2-5% sulfur dioxide). With fluid bed roasters the wet off-gases can run 10-12% sulfur dioxide. Both types of roasters, therefore, can produce a steady stream of relatively rich off-gases suitable for sulfuric acid manufacture. Both types of roasters involve the handling and collecting of large quantities of hot abrasive dust which can lead to high maintenance costs.

2.3.2.4 Reverberatory Furnace Smelting

Roasted and unroasted materials, after mixing with suitable fluxes, are smelted in reverberatory furnaces. Liquid converter slag is also charged into the reverberatory furnace to recover its copper content. Heating of the charge is accomplished by burning fuel in the furnace cavity, the heat being transmitted to the charge primarily by radiation from the roof, walls and flame.

A reverb can use natural gas, fuel oil or pulverized coal as fuel. Most U.S. smelters have gas/oil capability and many are planning a switch to coal.

The maximum smelting capacity of a reverb is limited by the amount of fuel that can be burned (a function of reverb shape and size) and the quantity of heat required by a unit weight of charge. Reverb throughput can be increased by drying the charge, preheating the charge by roasting, and preheating and/or oxygen enrichment of the combustion air.

These other techniques rely on scrubbing of the reverb gases to absorb sulfur dioxide and then treating the scrubber liquor to either strip the sulfur dioxide (to produce a more concentrated stream suitable for acid manufacture) or to produce a disposable solid.

At the Ajo smelter in Arizona, Phelps Dodge installed an experimental system for absorbing sulfur dioxide in reverb and converter gases in dimethylaniline (DMA) and stripping the DMA to produce a more concentrated stream of sulfur dioxide. The system was operated intermittently by Phelps Dodge and is no longer in use. Other absorption-concentration systems have also been tried at other U.S. smelters, e.g., the citrate system at Magma Copper in Arizona and at Bunker Hill in Idaho. These systems are also no longer in operation. The DMA scrubbing system at Asarco's Tacoma, Washington smelter is the only absorption-concentration system in operation at a copper smelter in the U. S. This installation scrubs converter gas and not reverb gas. Asarco used the DMA system at their Selby, California lead smelter for many years.

The Smelter Control Research Association has studied several strategies for controlling reverb emissions and selected a dual-alkali scrubbing process as the most cost effective. In this process, the reverb gas is scrubbed with an ammonium hydroxide liquor and the absorbed sulfur oxides are precipitated as a calcium sulfite/sulfate sludge with lime (SCRA, 1977).

At the Onahama smelter in Japan, the reverb gases were ducted directly to an acid plant temporarily while the plant was being converted from conventional green charge smelting to the Mitsubishi process. The acid plant did not achieve autogenous operation (E&MJ, 1972).

2.3.2.5 Converting

Matte produced in the reverberatory furnace is transferred in ladles to the converters using overhead cranes. The converters used in copper smelting are of the cylindrical Peirce-Smith type, the most common size being 13' x 30'. Air is blown from the side through a series of openings called tuyeres. During the initial blowing period (the slag blow) iron sulfide in the matte is preferentially oxidized to iron oxide and magnetite and sulfur is removed with the off-gases as sulfur dioxide. Flux is added to the converter to combine with iron oxide and form a fluid iron silicate slag. When all the iron is oxidized, the slag is skimmed from the furnace leaving behind "white metal" or molten cuprous sulfide. Fresh matte is charged into the converter at this stage and the slag blowing continued until a sufficient quantity of white metal has accumulated. When this happens, the white metal is oxidized with air to blister copper during the "copper blow." The blister copper is removed from the converter and cast or subjected to additional fire refining prior to casting. Converter blowing rates can vary between 12,000 to 30,000 scfm of air. Also, the sulfur dioxide content of the off-gases is lower during the "slag blow" than during "copper blow."

Cooling of the hot converter gases is necessary in order to prevent thermal damage to the dry gas cleaning equipment. When this cooling is accomplished by adding dilution air, sulfur dioxide concentrations in the converter off-gases can vary from 1-7% and this gas is considered too dilute for sulfuric acid manufacture. When air dilution is prevented with close fitting hoods or with Hoboken converters, the off-gases average 5-10% sulfur dioxide. However, when dilution air is not used, cooling devices such as waste heat boilers, air/gas heat exchangers or water sprays are necessary to protect the dry gas cleaning equipment.

The converter gases pass via a balloon flue or individual high velocity flues to dry gas cleaning equipment such as cyclones and electrostatic precipitators. Thus, with proper hooding,

the converter off-gas is sufficiently high in sulfur dioxide so as to be suitable for sulfuric acid manufacture, but converting by its very nature is a batch operation and the off-gas flow rates vary widely. In the smaller copper smelters which use two or three converters, the scheduling of converter blows in order to obtain relatively steady flows to the acid plant is a difficult problem.

2.3.3 Material Balance

Table 2.3-1 shows the material balance for green charge smelting.

2.3.4 Energy Requirements

Table 2.3-2 presents the Level I energy requirements for green charge smelting, in million Btu per ton of blister copper.

The energy used in materials handling and general utility (material transport, blending and bedding of concentrate and flux, slag granulation and disposal, operation of control systems and plant lighting) is estimated at 15.5 kwh/ton concentrate smelted, or 147,000 Btu fuel equivalent.

Table 2.3-3 presents the Level II energy requirements for green charge smelting.

Tables 2.3-4 and 2.3-5 present the Level I and Level II energy requirements for calcine charge smelting. A multiple hearth roaster has been assumed for concentrate roasting. The sulfur distribution is as follows: roaster 50%, reverb 15%, converter 30% and fugitives 5%.

2.3.5 Conclusions

Conventional smelting (green charge reverb smelting or roast-reverb smelting) is characterized by the use of large quantities of hydrocarbon fuels because the process makes little use of the energy available from oxidation of the sulfide charge. The limited degree of oxidation in the reverb as well as the dilution of the resultant sulfur dioxide by combustion gases and leakage air results in a gas stream that cannot be economically treated for sulfur recovery.

The smelting of hot calcines requires less smelting fuel than that for wet charge smelting because the heat of oxidation of the sulfides is utilized in drying and preheating the charge. In many cases, the roasting can be carried out without an external source of fuel. The lower smelting fuel requirement also results in lower combustion air requirements and a smaller off-gas volume thereby requiring lesser energy for gas cleaning. The matte produced in the reverb has a higher matte grade resulting in further decrease in the energy requirements for converting and converter gas cleaning. Also, the recovery of sulfur as acid is also higher.

The recovery of sensible heat from reverberatory furnace off-gas through the use of waste heat boilers has been standard practice for many years. The recovery of waste heat from roaster gases is not practiced mainly because of lower off-gas temperatures and the high dust load has made the small amount of recoverable energy uneconomic. The temperature of operation of a fluid bed roaster is around 1500°F and there is a potential for waste-heat recovery by immersing heat transfer surfaces inside the fluidized bed. In a Dorr-Oliver slurry feeding type of design, the roaster is operated adiabatically so that excess heat is used to evaporate the water used in producing the slurry. In the Lurgi-type design waste heat is recovered via heat transfer surfaces immersed in the bed itself. To our knowledge, none of the fluid bed roasters at smelters in the United States recover waste heat. Spray cooling and dilution is used to cool the gas to a temperature suitable for feed to the acid plant.

In the reverberatory furnace, copper and sulfur form the stable copper sulfide. Excess sulfur unites with iron to form a stable ferrous sulfide. The combination of the two sulfides, known as matte, collects in the lower area of the furnace and is removed. Such mattes may contain from 15 to 65% copper, with a 40 to 45% copper content being most common. The matte also contains impurities such as antimony, arsenic, iron, and precious metals.

The remainder of the molten mass containing most of the other impurities known as slag, being of lower specific gravity, floats on top of the matte and is drawn off and discarded. Slags in copper smelting are ideally represented by fayalite, but contain alumina from the various charge materials and calcium oxide which is added for fluidity. Since reverb slags are discarded, the copper contained in the reverb slag is a major cause of copper loss in pyrometallurgical practice. The concentration of copper in the slag increases with increasing matte grade.

When using a reverb for green charge smelting, 20% to almost 45% of the sulfur in the feed is oxidized and is removed from the furnace with the off-gases. The wet off-gases can contain 1.5-3% sulfur dioxide. When using calcine smelting, sulfur dioxide evolution is lower and about 10-15% of the sulfur in the unroasted feed material is contained in the reverb off-gases. Sulfur dioxide concentration in the wet off-gases in this case can vary between 0.5 to 1%.

The hot gases from the reverb are cooled in waste heat boilers which extract a portion of the sensible heat in the gases. A considerable amount of dust is removed in the waste heat boiler and the gases are further cleaned in electrostatic precipitators before venting to the atmosphere.

Reverberatory furnaces can vary in width from about 22 feet to 38 feet and in length from about 100 feet to 132 feet. The roofs of the older reverberatory furnaces are sprung arch silica roofs, while almost all the newer furnaces have suspended roofs of basic refractory. Over the years, two types of reverberatory furnaces have evolved, each with its specific charging methods. The first and older is the deep bath reverberatory furnace which contains a large quantity of (in excess of 100 tons) molten slag and matte at all times. In modern deep bath reverberatory furnaces, the molten material is held in a refractory crucible with cooling water jackets along the sides which greatly diminishes the danger of a breakout of the liquid material. In deep bath smelting, several methods exist for charging. Wet concentrates can be charged using slinger belts (high speed conveyors) that spread the concentrates on the surface of the molten bath. Dry concentrates or calcines from the roaster can be charged through the roof or via a Wagstaff gun (an inclined tube). Roof charging (side charging) is rarely practiced in conjunction with deep bath smelting because of potential dusting problems with fine dry calcine and explosion problems with green charge.

The second type of reverberatory furnace is the dry hearth type in which a pool of matte exists mainly at the tapping end. The dry hearth type furnaces are charged with wet or partially dried concentrates (green feed smelting), or with calcines through the roof. In the latter case the dusting problem can be quite severe for fine concentrates.

As noted earlier, reverb gases are too dilute in sulfur dioxide to be suitable for autogeneous sulfuric acid manufacture. Several attempts have been made to control emissions from the reverb by other techniques but these have not been practiced for long on a commercial basis.

TABLE 2.3-1										REVERB SMELTING: GREEN CHARGE											
[TONS PER TON BLISTER COPPER]																					
STREAM NO.		(1)				(2)				(4)				(5)				(6)			
STREAM NAME		WET CONCENTRATE				SILICA FLUX				REVERB SLAG				REVERB OFF GAS				MATTE			
COMPOSITION		wt.		dry wt. %		wt.		dry wt. %		wt.		wt. %		wt.		wt. %		wt.		wt. %	
Cu		0.9932		25.0						0.0132		0.44						1.0416		42.0	
Fe		1.112		28.0		0.0072		1.40		01.124		37.33						.7648		30.82	
S		1.2316		31.0						0.0292		0.97						.6192		24.97	
O _{Fe} *		0.0188		0.47		0.0032		0.60		0.3192		10.60						.0552		2.21	
SiO ₂		0.3428		8.63		0.456		90.0		1.1844		39.34									
Al ₂ O ₃		0.1342		3.45		0.0208		4.0		0.1752		5.82									
CuO + MgO		0.1164		2.93		0.010		2.0		0.1348		4.48									
Others		0.0208		0.52		0.010		2.0		0.0308		1.02									
H ₂ O		0.39728												1.06211							
SO ₂														1.2392							
O ₂																					
CO														2.3656							
CO ₂														7.8110							
N ₂																					
TOTAL		4.37008		100.00		.5072		100.00		3.0108		100.00		11.2387				2.4808		100.00	
TEMP. (°F)				60				60		2250				2350				2150			
STATE				S				S				L				G				L	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.3-1 (cont.) REVERB SMELTING: GREEN CHARGE									
[TONS PER TON BLISTER COPPER]									
STREAM NO.	(7)		(8)		(9)		(10)		(11)
STREAM NAME	CONVERTER FLUX		CONVERTER SLAG		CONVERTER OFF GAS		CONVERTER AIR		BLISTER Cu
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. wt. %
Cu			.0616	4.08					.980 98.0
Fe	.006	1.40	.7696	50.93					.001 0.1
S			.0364	2.41					.009 0.9
O _{Fe} *	.0024	0.60	.2324	15.38					.0015 0.15
SiO ₂	.3856	90.00	.3856	25.50					
Al ₂ O ₃	.0172	4.00	.0172	1.14					
CuO + MgO	.0084	2.00	.0840	0.56					.0085 0.85
Others	.0085	2.00							
H ₂ O					1.148	31.36			
SO ₂							.7504	23	
O ₂									
CO									
CO ₂					2.51221	68.64	2.51221	77	
N ₂									
TOTAL	.4281	100.00	1.5112	100.00	3.66021	100.00	3.26261	100.00	1.0 100.00
TEMP. (°F)	60		2250		2300		60		2200
STATE		S		L		G		G	L

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.3-2

ENERGY REQUIREMENTS

Level 1

CONVENTIONAL SMELTING: GREEN CHARGE SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling and General Utility A) Electrical Energy	KWH	69.1	0.0105	0.726
2	Reverb. Smelting A) Fuel: Fuel Oil B) Electrical Energy C) Waste Heat Recovery: Steam	GAL KWH LBS	179.9 60.8 7140	0.139 0.0105 0.0014	25.006 0.638 -10.000
3	Converting A) Electrical Energy B) Fuel: Fuel Oil	KWH GAL	155 3.9	0.0105 0.139	1.628 0.542
4	Gas Cleaning A) Hot Gas Cleaning 1- Reverb (1.5% SO ₂) 2- Converters (7.0% SO ₂) B) Cold Gas Cleaning 1- Converters (7.0% SO ₂) 2- Fugitive Emissions Control	Thous. SCF Thous. SCF Thous. SCF KWH	1000.9 198.7 198.7 340	0.00336 0.00336 0.00126 0.0105	3.363 0.668 0.250 3.570
5	Acid Plant A) Converter Gas (7% SO ₂)	Thous. SCF	198.7	0.0114	2.265
6	Water Pollution Control A) Electrical	KWH	9.0	0.0105	0.095
6.7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	34.575

TABLE 2.3-3		ENERGY REQUIREMENTS			Level 2
CONVENTIONAL SMELTING: GREEN CHARGE SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Reverb. Smelting A) Silica Flux	TONS	0.518	0.042	0.022
3	Converting A) Silica Flux	TONS	0.437	0.042	0.018
4	Water Pollution Control A) Lime	LBS	30.0	0.0027	0.081
6,7	Anode Casting and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	0.589

*Not shown on flowsheet

TABLE 2.3-4 ENERGY REQUIREMENTS					
CONVENTIONAL SMELTING: CALCINE CHARGE SMELTING					
Level 1					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling				
*	A) Electrical Energy	KWH	69.1	0.0105	0.726
2	Roaster				
*	A) Electrical Energy	KWH	62.7	0.0105	0.658
2	Reverb. Smelting				
	A) Fuel: Fuel Oil	GAL	104.3	0.139	14.498
	B) Electrical Energy	KWH	60.8	0.0105	0.638
	C) Waste Heat Recovery: Steam	IBS	3107	0.0014	-4.350
3	Converting				
	A) Electrical Energy	KWH	120	0.0105	1.260
	B) Fuel: Fuel Oil	GAL	2.3	0.139	0.320
4	Gas Cleaning				
	A) Hot Gas Cleaning				
	1- Roaster (10% SO ₂)	Thous. SCF	149.2	0.00336	0.501
	2- Reverb (0.85% SO ₂)	Thous. SCF	525.	0.00336	1.764
	3- Converters (7% SO ₂)	Thous. SCF	167.3	0.00336	0.562
	B) Cold Gas Cleaning				
	1- Roaster (10% SO ₂)	Thous. SCF	149.2	0.00126	0.188
	2- Converter (7% SO ₂)	Thous. SCF	167.3	0.00126	0.211
	3- Fugitive Emissions Control	KWH	340.0	0.0105	3.570
5	Acid Plant				
	A) Roaster & Converter Gas (8.4% SO ₂)	Thous. SCF	316.5	0.01224	3.874
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095

TABLE 2.3-4 (Cont.)		ENERGY REQUIREMENTS			Level 1
CONVENTIONAL SMELTING: CALCINE CHARGE SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	30.339

*Not shown on flowsheet.

TABLE 2.3-5		ENERGY REQUIREMENTS				Level 2
CONVENTIONAL SMELTING: CALCINE CHARGE SMELTING						
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER	
2	Reverb. Smelting A) Silica flux	TON	0.375	0.042	0.016	
3	Converting A) Silica flux	TON	0.290	0.042	0.012	
*	Water Pollution Control A) Lime	LBS	30.0	0.0027	0.081	
6.7	Anode furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468	
				TOTAL	0.577	

*Not shown on flowsheet

Only three or four smelters in the United States are recovering heat from converter off-gases by using water-walled uptake hoods, the others use some form of dissipative cooling (dilution radiation or convection to reduce the temperature of the off-gas). The companies that have attempted to recover heat from the converter off-gases have had mixed success. To overcome acid condensation on the heat transfer surface, its temperature must be maintained above 400°F even when there is no off-gas from the converter. Thus, when a converter is not in operation, the working fluid (steam or water) heats the air leaking into the converter hood. Fuel must be burnt for keeping the working fluid warm. In some instances, this energy consumption can exceed the amount of waste heat recovered.

Little attempt has been made to recover waste heat from the anode furnaces and cathode melting furnaces. An exception is the Outokompu Harjavalta plant where anode furnace off gas is used to dry concentrates, reportedly decreasing fuel requirements for drying by approximately 25%. The anode furnaces only operate intermittently and are operated primarily as a holding furnace. Because of the low gas volume, the waste heat potential is limited. If anode refining is carried out along with scrap melting, as practiced in the secondary copper industry, the off-gas volume and the waste heat recovery potential would be higher. The ASARCO shaft furnace has the cathodes moving counter-current to the gas stream and is therefore an efficient heat exchanger by itself. Consequently, there is little additional potential for waste heat recovery in cathode melting in the ASARCO shaft furnace.

The principal developments with respect to decreasing energy requirements has been the oxygen enrichment of combustion air in the reverberatory furnace. The principal effect is decreasing the amount of nitrogen per unit of combusted fuel. This results in:

- An increased flame temperature and hence an increased rate of heat transfer to the charge.
- An increased residence time of the combustion gases (due to the lower volume per unit of fuel) and hence more complete transfer of their heat to the charge.
- A decreased carry off of sensible heat in the effluent gas.

These lead to increased smelting rates and decreased fuel consumption (Biswas and Davenport, 1976). Experiments on an INCO reverberatory furnace (Saddington, et al., 1967) indicates that oxygen enrichment of combustion air to 27% oxygen reduces fuel consumption by about 20%. Alternatively, if the fuel rate is kept constant production rate can be increased about 35% at a level of oxygen enrichment of 26% oxygen. Similar results have been obtained with Russian reverberatory furnaces (Kupriakov and Artemev, 1974). Oxygen enrichment to a level of 30% is used on a regular basis in five or six reverberatory furnace operations (Niimura, et al., 1973) (Kupriakov and Artemev, 1974). Enrichment above this level leads to excessively high temperatures and excessive refractory wear at the burner end. Industrial tests, as part of a program to increase enrichment to 40-50% oxygen, at the Almalyk smelter (Kupriakov and Artemev, 1974) demonstrate that this problem might be overcome by supplying the fuel with a shortage of oxygen and by supplying the remainder of the oxygen via vertical roof pipes spaced regularly down the length of the furnace.

At the Calteones smelter in Chile, oxy-fuel burners were tried in reverbs over a period of several years, finally getting to complete elimination of air-oil burners. A 50% decrease in fuel

usage and doubling of daily production rate are predicted based on an energy balance evaluation of air-oil versus an air fuel reverb. Although the refractory usage increased considerably with oxygen-fuel burners, as production was doubled the refractory usage per ton of copper produced did not increase as a result of switching from air-fuel to oxygen-fuel burners (Schwarze, 1977).

The converting of matte using air (low-to-medium matte grades) is autogenous. In fact, coolants such as scrap or cement copper must be added in most cases to prevent the converter from overheating. The enrichment of converter air lowers the quantity of nitrogen and thus permits the charging of larger quantities of coolant. An alternate coolant is copper concentrate which in addition to cooling the system melts to form matte and slag. Extensive tests in the United States and Japan have showed that with oxygen enrichment (30-40%), a significant proportion of the concentrates entering a smelter can be smelted in the converter (Tsuromoto, 1961; Messner and Kinneberg, 1969). Principal problems in the process are the high rate of refractory wear in the tuyere region due to overheating caused by the oxygen enriched blast, and excessive fugitive dust.

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2.4 IMPURITY CONTROL IN PYROMETALLURGICAL COPPER PROCESSES

2.4.1 Introduction

Copper sulfide concentrates are normally associated with a number of elements. These include: Au, Ag (noble metals); Co, Ni, Pt, Pd (Group VIII); Zn, Cd, Hg (Group II-B); Sn, Pb (Group IV-A); Mo (Group VI-B); Bi, Sb, As (Group V-A); Se, Te (chalcogens) and Cl (halogen), in addition to gangue. Of the elements listed above, some of the elements such as Mo and Zn are removed in the concentration process or occur in small enough quantities that they need not be removed. The principal elements of interest are (1) Au, Ag, Se, Te, representing valuable byproducts and (2) Zn, Pb, Sn, Bi, Sb, representing principal impurities. The following is a discussion of the impurity elimination characteristics of various processes, pyrometallurgical processes which produce blister copper and the further purification of blister copper to anode grade copper. Finally, impurity distributions in electrorefining are discussed. It should be emphasized that data on impurity distribution presented in this section although based on operating data are meant as a guide and are not to be considered typical of specific processes, operating on a specific concentrate.

2.4.2 Reverberatory Smelting and Converting

2.4.2.1 Reverberatory Smelting

Over many decades reverberatory smelting processes have been highly perfected with respect to minor element control. Reverberatory smelting provides a high recovery of valuable byproducts such as Au, Ag, Se, Te to copper while assuring an excellent elimination of detrimental elements such as Zn, Pb, Sn, Bi, Sb, and As. The two mechanisms for impurity removal are (1) oxidation and slagging, and (2) volatilization.

The elements removed by slagging are those whose oxides have a high negative free energy of formation. Besides iron, the elements removed to some degree by oxidation and slagging include Co, Ni, Zn, As, Sb, Bi, Ca, Mg^{*}, Al^{*}, Ba^{*}, Na^{*}, K^{*}, Mn^{*}, Li^{*}, Ti^{*}, V^{*}, and Sn. At the same time some of the highly deleterious impurities — As, Sb, Bi, Se, and Te — are removed either by volatilization either as sulfides or oxides or in the elemental form. About 99 percent of the Pb, 54 percent of the Bi, 50 percent of the Sb, 21 percent of the As, and 60 percent of the Se and Te are eliminated in the reverberatory furnace (Keller, 1902). The behavior of metals other than copper and iron in reverberatory smelting is estimated in Table 2.4-1.

These data serve only as a guide and the precise distribution of minor elements depends upon the smelting conditions and the type of process. The most important points are:

- Gold, silver, the platinum metals, cobalt and nickel enter the matte almost completely. These metals are carried forward to the converting operation and they are finally recovered as byproducts during the electrorefining of anode copper.
- Significant quantities of impurities harmful to copper also enter the matte: specifically antimony, arsenic, bismuth, lead, selenium and tellurium. Some of these are also recovered as byproducts during subsequent converting and refining operations.
- Much of the zinc reports in the slag from which it can be recovered by "slag fuming" (reduction) if it is present in sufficient quantities.

* Removal of these elements is complete in the smelting and subsequent converting operations.

TABLE 2.4-1
ESTIMATED DISTRIBUTION OF ELEMENTS
DURING MATTE SMELTING

Metal	Matte	Distribution	
		Slag	Volatized*
Alkali and alkaline earth metals aluminum, titanium		100	
Ag, Au, platinum metals	99	1	
Antimony	30	55	15
Arsenic	35	55	10
Bismuth	10	10	80
Cadmium	60	10	30
Cobalt	95	5	
Lead	30	10	60
Nickel	98	2	
Selenium	40		60
Tellurium	40		60
Tin	10	50	40
Zinc	40	50	10

*Not including solids blown from the furnace (dust losses).

Source: Ruddie, 1953, Yazawa and Azakami, 1969, Mackey, et al., 1975, published in Biswas and Davenport, 1976.

2.4.2.2 Converting

In the converter, due to the more strongly oxidizing conditions, and to the rapid passage of air, a great deal of impurity elimination takes place. Here the last traces of the less harmful impurities (Ca, Mg, Al, etc.) are removed and further amounts of the more tenaciously held impurities (As, Sb, Bi, Se, and Te) are eliminated. Converting may be expected to eliminate from ordinary mattes (low grade ~ 40 percent), 70 percent of Sb, 80 percent of the arsenic, 50 percent of the Se and Te, and 95 percent of the bismuth (Peters, 1907). Another source reports that 95-98 percent of the lead, 94-96 percent of the bismuth, 71-73 percent of antimony, 81-84 percent of arsenic, 19-52 percent of selenium and tellurium is removed during converting (Keller, 1899). Later experimental work indicates that little Se and Te is removed during converting (Baker and Hallows, 1950).

Table 2.4-2 summarizes the distribution of elements between blister copper, slag, and gas phase. Table 2.4-3 presents the composition of dusts from electrostatic precipitators operating on converter gases.

It is seen from Table 2.4-2 that As, Bi, Cd, Ge, Hg, Pb, Sb, and Sn are extensively removed as vapors during converting while most of the zinc is removed along with iron in the slag. Precious metals, and to a lesser degree, nickel and cobalt, proceed forward with the blister copper from which they are recovered during electrorefining.

There is also considerable entrainment of matte and slag droplets in the high-velocity converter waste gases. The solidified droplets are caught in the flue system (mostly in "ballon flues" but also in electrostatic precipitators) and are generally recycled within the smelter. The droplets have the approximate composition of the liquids at the time of ejection.

The dusts and vapors from converters contain sufficient copper for them to be recycled to the smelting furnace or to the converter itself. However, this procedure returns all of the impurities to the circuit and hence some smelters treat the dusts for impurity removal before they are recycled or these dusts are stockpiled. Bismuth in particular is recovered from converter dusts because: (a) it causes brittleness in the final copper anodes and (b) it is a valuable byproduct.

2.4.3 Flash Smelting

2.4.3.1 Outokumpu Flash Smelting (Harkki and Juusela, 1974)

The feed at the Harjavalta smelter usually contains only limited amounts of deleterious impurities such as As, Sb, Bi, Zn, etc. (Table 2.4-4) and hence no special treatment is needed. The flash smelting technique is flexible, i.e., copper content of the matte may vary from 40 to 80 percent, the flue dusts, or some part of them, may be taken out of circulation if they are enriched in some components. On account of this flexibility, different types of concentrates can be smelted. The distribution of elements can be affected even in the furnace by changing the process variables. The distribution of elements in the settler, flue dust, and gas phase, can be controlled and desired products from flash smelting achieved.

In the flash smelting furnace the impurity elements are distributed between slag, matte and flue dust. As the flue dust is normally circulating, the final distribution is between matte and slag. A small amount of the elements or compounds with a relatively high vapor pressure may be

TABLE 2.4-2
DISTRIBUTION (ESTIMATED) OF IMPURITY
ELEMENTS DURING CONVERTING

	Blister Copper	Gas ¹	Slag ²
Ag	90	0	10
Au	90	0	10
Pt metals	90	0	10
As	15	75	10
Bi	5	95	0
Cd	0	80	20
Co	80	0	20
Fe	0	0	100
Ge	0	100	0
Hg	10	90	0
Ni	75	0	25
Pb	5	85	10
Sb	20	60	20
Se	60	10	30
Sn	10	65	25
Te	60	10	30
Zn	0	30	70

¹Not including ejected droplets of matte and slag.

²Including entrained matte.

Source: Ruddle, 1953; Yazawa and Azakami, 1969; published in Biswas and Davenport, 1976.

TABLE 2.4-3

COMPOSITE CONVERTER COTTRELL DUST ANALYSES
FOR THE GASPE AND NORANDA SMELTERS

Smelter	Cu	Pb	Zn	Cd	Bi	Analysis (%)		SiO	Ag	Au	In
						Sb	S				
Gaspe	10.2	27.9	7.5	0.31	1.95	0.80	9.3	NR	NR	NR	NR
Noranda	11.0	22.1	13.9	0.82	--	0.18	10.2	6.5	0.04	0.0005	0.12

Source: Stanley, et al., 1972, published in Biswas and Davenport, 1976.

TABLE 2.4-4

COMPOSITION OF CONCENTRATE AT HARJAVALTA

Cu	Fe	S	Zn	Co	Ni (percent)	Pb	As	Sb	Bi	Se	Au (grams/10 ³ kg)	Ag
22.7	32.1	34.3	4.0	0.2	0.1	0.5	0.3	0.02	0.003	0.003	3.4	102

Source: Harkki and Juusela, 1974.

carried over to the gas phase through the electrostatic precipitator further to the sulfuric acid plant or the elemental sulfur producing units. If impurities are concentrated into the dusts, the dust circulation can be interrupted to prevent their accumulation in slag or matte from which their elimination may be difficult.

The distribution of elements between matte and slag is mainly controlled by the oxygen potential of the slag, which is characterized by the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio. When the oxygen potential increases, the slagging of components also increases. There seems to be a correlation between the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in slag and the copper content of matte. Figure 2.4-1 shows the mass distributions (i.e., the amount of the component in the slag divided by its amount in the slag and matte). Some of the lines are shown dashed because the results are strongly affected by factors other than matte grade such as content in feed, reaction shaft temperature, etc. The data in Figure 2.4-2 are based on the test runs carried out at the Harjavalta Smelter and in the pilot plant of Outokumpu Metallurgical Research Center in Pori.

The flue dust is formed from the components following the gas phase to the uptake shaft and further to the waste heat boiler and electrostatic precipitator, where the temperature decreases to about 300°C. At this lower temperature many of the volatile components can be collected as dust.

The amount of the so-called mechanical dust depends mainly on the concentrate, the formation of suspension in the reaction shaft, the shape of the furnace, the flow pattern in the furnace and on other physical factors. The amount of volatile components is controlled by the above mentioned factors as well as by the degree of oxidation and the reaction shaft temperature. The composition of the flue dust is affected by the gas composition in the boiler and electrostatic precipitator, which can be sulphidizing or oxidizing.

When the flue dust distributions are presented in the same way as the settler distributions, it is noted that some components are mainly in the mechanical dust (Cu, Ni, Co, Fe, and Au), other components being strongly affected by the degree of oxidation or by the reaction shaft temperature (Figures 2.4-2 and 2.4-3). The scatter in some flue dust distributions (dashed lines) is often due to the matte grade not being the only parameter affecting the results. The amount of feed, the percentage of elements in the feed, the reaction shaft temperature, gas volume and many other factors have their specific effects. The amount of the material going through the electrostatic precipitators is not calculated in these distributions.

The process parameters may be controlled to optimize the elimination of volatile components, e.g., Pb, Zn, Bi, As, and remove them from the circuit with part or all of the flue dust fraction. The removal of Bi is carried out by this method in the flash smelter of Peko-Wallsend Metals Limited in Tennant Creek, where the Bi content in the concentrate is about 0.7 percent. The pilot plant tests gave a Bi recovery in flue dust of over 90 percent. The Dowa Mining Company, Ltd. at their Kosaka Smelter in Japan reduces the circulating amount of Pb, Zn, As, Bi, and Cd by special treatment of flue dusts.

The distribution in gas phase is calculated from the amount of components collected after the electrostatic precipitators. Depending on the vapor pressure and temperature, some of the compounds (e.g., As, Hg, Se, Te) pass with the gas phase through the conventional dust separation, after which they can be recovered selectively (e.g. concentrated sulfuric acid scrubbing for Hg removal).

Source: Harkki and Juusela, 1974.

FIGURE 2.4-1 SLAG-MATTE DISTRIBUTION IN COPPER FLASH SMELTING

Source: Harkki and Juusela, 1974

FIGURE 2.4-2 FLUE DUST DISTRIBUTION IN COPPER FLASH SMELTING

Source: Harkki and Juusela, 1974.

FIGURE 2.4-3 EFFECT OF REACTION SHAFT TEMPERATURE ON FLUE DUST DISTRIBUTION OF Pb AND Zn

2.4.3.2 INCO Flash Smelting

The Copper Cliff concentrates are relatively free of impurities. The copper concentrates generally average less than 0.01 percent Bi + As + Se and less than 0.1 percent Pb. The off-gases from the flash furnace amount to 4300 scfm at an output of about 1200 tons per day of concentrates. The off-gases contain less than 3 percent of the feed as dust and between 5 to 70 percent of the bismuth, 20 to 50 percent of the lead and arsenic, and 5 to 15% of the selenium in the concentrates smelted depending on the type of concentrate and the oxygen potential. (Solar et al., March 1979).

There is also data on impurity distributions during oxygen flash smelting in a converter (Bell, et al., 1978). When flash smelting to about white metal composition with Cottrell dust additions to the feed, 13-16 percent of the input arsenic and bismuth reported to the matte with 15-30 percent reporting to the slag. On flotation of the slowly cooled slag about 90 percent of the lead and zinc are eliminated to the tailings, so that recycle of zinc and lead by the flotation concentrate is small.

2.4.4 Mitsubishi Continuous Copper Smelting and Converting Process

Table 2.4-5 shows the distribution ratios of impurities. Column "A" gives the values calculated by Yazawa. The values in column "B" are calculated from the analyses of matte and slag in the Mitsubishi Process smelting furnace. Column "C" shows the values calculated from the analyses of white metal and converter slag at the end point of a converter slag-making stage in conventional processes. Although the matte grade is 65 percent in case "B" and 76 percent in "C," there is a considerable difference in the distribution ratios of impurities. Such difference seems to indicate that the distribution ratios are affected by slag compositions.

In the Mitsubishi process, the sulfur content in blister is below 0.5 percent which is lower than that in blister which is in equilibrium with white metal. Further, there is no indication that a white metal layer exists as a separate phase in the converting furnace (Suzuki, 1973 and Suzuki and Nagano 1972). Such non-existence of a white metal layer seems to give the Mitsubishi process more favorable conditions for removal of impurities with slag. The favorable conditions in the Mitsubishi process are also pointed out by (Yazawa, 1967). The distribution ratios calculated from the analyses of converting furnace slag and blister copper in the Mitsubishi process are given in column "F."

The levels of antimony, arsenic and bismuth in Mitsubishi blister copper have been published but they have not been discussed in terms of the proportions retained from the original feed to the smelter. However, retention of Sb, As, and Bi in Mitsubishi blister copper is likely to be high because of the continuous contact between matte and metal in the converting furnace. For this reason some extra care will have to be taken with the electrorefining of Mitsubishi copper. The Mitsubishi process may produce impure blister when treating high impurity concentrates.

The distribution ratio of zinc (shown as ratio of weight percent) in the smelting furnace of the Mitsubishi process is plotted against matte grade in Figure 2.4-4. The line "A" in the figure represents data reported by (Okunev and Aglitskii, 1954). The normal matte grade in the Mitsubishi process is in the range of 60-65 percent and the distribution ratio under such

TABLE 2.4-5

DISTRIBUTION RATIOS OF IMPURITIES

Element	A aMO/aMS	B cM/cS	C cWM/cS	D cB/cWM	E cB/cS	F cB/cS
Pb	1.5×10^{-2}	1.6-5.0	0.9	15	13.5	2-6
Sb	37	0.25	1.0	13.6	13.6	0.1-0.3
As	--	2.1	1.0	9	9	6
Bi	0.68	--	--	8.1	--	--

Note: a: activity c: weight % MO: oxide MS: sulfide
WM: white metal S: slag B: blister

Source: Suzuki and Shibasaki, 1975

FIGURE 2.44 DISTRIBUTION OF LEAD AND ZINC BETWEEN MATTE AND SLAG

conditions is approximately, 2.5. If the slag fall (defined as weight of slag to weight of concentrate) is 80 percent and the matte fall is 40 percent (defined as weight of matte to weight of concentrate), the distribution of zinc into slag would be 85 percent. The ZnS content in matte is then oxidized in the converting furnace and distributed into slag. Since the converting furnace slag is returned to the smelting furnace, almost all zinc is distributed into the smelting furnace slag (discard slag) and removed from the system. This is also true of conventional practice where almost all the zinc is distributed in the slag and removed from the system.

The distribution of lead and zinc in the Mitsubishi process smelting furnace is shown in Figure 2.4-4. The major portion goes to the matte phase. PbS in matte is then partially oxidized to PbO in the converting furnace and distributed into slag. The distribution ratio of lead ($\frac{\% \text{ Pb in slag}}{\% \text{ Pb in blister}}$) is between 3 and 5. The average distribution ratio was experimentally determined to be 1.2 at the end point of a converter slag-making stage. A considerable amount of lead goes into blister copper. The separation of lead by the removal of flue dusts from the system therefore would become necessary when concentrate high in lead is treated.

Figure 2.4-5 gives the volatilization ratios of lead and zinc in the Mitsubishi process versus the lead and zinc contents in concentrate. When concentrate high in lead and zinc is treated, the volatilization ratio for zinc is in the range of 20-30 percent and that of lead is 60 percent.

The total carryover of mechanical dusts represents only 2-3 percent of the charged concentrate in the Mitsubishi process, comparable to that in the reverberatory furnace. Approximately one half of the dust is collected in the waste heat boiler and the other half in a precipitator. The volatile elements are concentrated into the flue dusts and can be removed out of the system.

2.4.5 TBRC Smelting

Full scale tests have demonstrated that 91.3% of the arsenic, 91.0% of lead, 89.7% of bismuth and 88.7% of selenium is eliminated in TBRC Smelting (Daniele, Jacquay, 1974).

2.4.6 Summary

The blister copper produced by single-step smelting processes such as the Noranda process will tend to contain more of the antimony, arsenic and bismuth from the original smelter charge than the blister copper produced by conventional smelting/converting operations (Mackey et al., 1975).

In conventional smelting/converting operations, these impurities are removed to a large extent by volatilization of their sulfides (Yazawa and Azakami, 1969) during the slag-forming stage of converting, i.e., before metallic copper is formed. In the case of single-step smelting, however, metallic copper is always present and a considerable fraction of the As, Bi and Sb dissolves in the copper before volatilization can occur. Once dissolved in the copper, these metals are difficult to remove pyrometallurgically because of their low chemical activities (Yazawa and Azakami, 1969).

Thus, the anodes prepared from single-step process blister copper tend to have a higher level of As, Bi and Sb than standard anodes. This necessitates more careful electrorefining, more extensive electrolyte purification, and it may, in fact, restrict the adoption of single-step smelting processes to the smelting of low impurity concentrates.

Source: Suzuki and Shibasaki, 1975.

FIGURE 2.4-5 RELATION BETWEEN RATES OF VOLATILIZATION AND CONTENTS IN CONCENTRATE

The other alternative is to break the continuous process, to include a converting option as has been done with the Noranda process by Kennecott in Utah. Another option would be to refine the crude copper obtained by the continuous process.

2.4.7 Fire Refining of Blister Copper to Anodes

Although the fire refining step can remove impurities such as As, Sb, Bi and Fe to some extent, these impurities are difficult to remove by oxidation from liquid copper (Yazawa and Azakami, 1969). Some operations, e.g., Tsumeb in S.W. Africa, have used sodium carbonate slags to reduce the As, Sb and Bi content of crude blister to acceptable levels.

2.4.8 Electrorefining

The purpose of electrorefining is to remove impurities and recover valuable byproducts. The principal impurities in copper anodes are As, Bi, Fe, Ni, Pb, Sb, Se and Te. These must be refined from the copper. In addition, Ag and Au are usually present in quantities large enough to be worth recovering. The behavior patterns of these impurities during electrorefining are as follows (Biswas and Davenport, 1976):

- Ag, Au and Platinum Metals — Gold and platinum metals do not dissolve in the electrolyte. Silver dissolves from the anode to a certain extent but it is precipitated from the electrolyte as AgCl by dissolving a small amount of NaCl or HCl in the electrolyte. Any appearance of these metals in the cathode is due to the mechanical entrapment of small quantities of anode slimes.
- S, Se and Te — Sulfur, selenium and tellurium are present in the anodes as compounds with copper or silver, i.e., Ag_2Se , Cu_2Se , Ag_2Te , or Cu_2S . These compounds mainly enter the anode residues (slimes) in a manner similar to the noble metals (Table 2.4-6).
- Pb and Sn — Lead and tin both form sulfates which are insoluble in the electrolyte [$PbSO_4$ and $Sn(OH)_2SO_4$] and hence they do not enter the electrolyte to any appreciable extent.
- As, Bi, Co, Fe, Ni and Sb — All of these metals tend to dissolve electrochemically from the anode along with (and even preferentially to) the copper of the anode. They tend, therefore, to build up in the electrolyte during electrorefining. These impurities must be removed from the electrolyte or they will eventually contaminate the cathode copper, mainly by occlusion of impure electrolyte in the growing cathode deposits. Removal of As and Ni is accomplished in a bleed stream in a purification section of the refinery. The composition limits of these impurities in refinery electrolyte is given in Table 2.4-6.
- Table 2.4-7 shows the distribution of impurities between the anode residues and electrolyte and it indicates that significant quantities of As and Sb report in the anode residues, most likely as the result of compound formation with copper in the anode. Bismuth behaves similarly. In addition, it is believed that to some extent As, Bi and Sb combine to form arsenate precipitates which also enter the anode residues.

TABLE 2.4-6
COMPOSITION RANGES OF ELECTROLYTES
IN MODERN COPPER REFINERIES

Metal	Proportion into Anode Residues (%)	Proportion into Electrolyte (%)
Au	99	<1
Ag	98	2
Se and Te	98	2
Pb	98	2
Sb	60	40
As	25	75
Ni	5	95
Fe		≈100

Source: Eichrodt and Schloen, 1954, published in Biswas and Davenport, 1976.

TABLE 2.4-7
PROPORTIONS OF ANODE IMPURITIES ENTERING
RESIDUES AND ELECTROLYTE AS ESTIMATED
BY EICHRODT AND SCHLOEN (1954)

Component	Concentration (kg m ⁻³)
Cu	40-50
H ₂ SO ₄ (free)	170-200
	Upper Limits
Ni	20 (Inco)
As	10
Fe	2
Sb	0.5
Cl	0.03
Specific gravity	1.25±0.03
Temperature	60-65°C

Source: Eichrodt and Schloen, 1954, published in
Biswas and Davenport, 1976.

2.4.8 References

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2.5 ELECTRIC FURNACE SMELTING

2.5.1 Introduction

This report includes material and energy requirements for copper smelting process using an electric furnace. Electrical furnace smelting is described in detail by (Biswas and Davenport, 1976).

The process described in this model is a modification of the Inspiration Consolidated Copper Company electric smelter at Miami, Arizona. The major modification is on the front end by adding a fluid bed roaster and deleting a rotary dryer. These modifications reduce power requirements and heat losses in the furnace by lowering the required operating temperature to produce 40 percent matte. The fluid bed roaster alone reduces the furnace fuel requirements by 3.03 million Btu's per ton cathode copper (Kellogg and Henderson, 1967).

The use of fluid bed roasting or rotary drying is highly dependent on the makeup of concentrates fed to the plant. High proportions of cement copper and chalcocite, as at Inspiration, would reduce the amount of sulfur in the feed to make it insufficient for the fluid bed roasting. In this model, one of the basic assumptions is the availability of concentrates bearing 31% S (dry basis), which is sufficient sulfur to justify the addition of a fluid bed roaster.

The first successful tests on smelting of sulfide ores in an electric furnace were made in Norway at the Sulitjelma Mine in 1911-1913. The first commercial furnace was completed in 1929 at this mine with a proven annual capacity of 5,000 tons of blister copper. The conversion to electric furnace smelting was very slow, restricted to areas where hydroelectrical energy competed favorably with fossil fuels. By 1970 there were only 25 electric copper furnaces operating, with a total capacity of 6 million tons of copper concentrate per year, and none of these were in the United States.

Due to increased environmental constraints on emissions from copper smelters, three electric furnaces have been constructed and have been operating in the United States since 1970. All three of these operations recover the sulfur dioxide from the electric furnace for sulfuric acid manufacturing.

The high equivalent fuel requirement of the electric furnace smelter is largely the result of low thermal efficiency in the production of electric power.

2.5.2 Process Description

2.5.2.1 Roasting and Furnace Charging

Copper sulfide concentrates containing 10 to 12 percent moisture are partially roasted in a fluid bed roaster and the bone-dry hot calcines are fed to the electric furnace as shown in the process flowsheet (see Figure 2.5-1). The amount of sulfur burned in the roaster is sufficient to produce a 40 percent copper matte. In a variation of this process, the copper concentrate is dried to 3 to 4 percent moisture before being fed to the electric furnace. This method, however, is practical only in cases of low sulfur content in the feed, and thus, will not be considered for a copper sulfide concentrate containing 31 percent sulfur. Heated calcine requires less fuel and so increases the furnace efficiency. Dry calcines are combined with dust collected from roaster, cyclones, and electrostatic precipitators and recycled converter slag to form the furnace feed. The feed is conditioned with limestone and silica flux to enhance proper slag formation. Furnace electrodes dip in the molten slag and the heat required to smelt the solid calcines is generated by the resistance of the slag to the high amperage electrical current. Solid furnace slag is a poor electrical conductor, but as the slag melts it dissociates into ionic form in the liquid state and becomes a relatively good electrolyte (Rosenkranz, 1976).

2.5.2.2 Electric Furnace Operation

Air is introduced under control to oxidize iron sulfides to iron oxides and sulfur dioxide. Molten slag, less than 0.5 percent copper, is continuously tapped and discarded. Matte is conveyed to converters for further processing and the gas from the electric furnace containing furnace dust, nitrogen, oxygen, carbon dioxide, sulfur dioxide, and a small amount of sulfur trioxide goes to gas cleaning.

Matte at a temperature of 2100 degrees Fahrenheit is blown with air or oxygen in the converter to produce blister copper. Air is injected under pressure to complete the oxidation of copper sulfide and any remaining iron sulfides to blister copper, iron oxide, and sulfur dioxide. Off-gas also goes to gas cleaning. Silica flux is added to aid formation of converter slag, which is recycled to the electric furnace. Blister copper is then treated in the anode furnace by first flowing with air to remove sulfur and then poled with reformed gas to remove oxygen. The slag which is skimmed from the anode furnace is returned to the converter. Anodes are cast and refined to electrolytic copper.

2.5.2.3 Acid Plant Operation

A double adsorption contact acid plant is incorporated in the process. The gases from roaster, furnace, and converter are combined and sent to final cleaning before entering the sulfuric acid plant. In the oxidation of sulfur dioxide to sulfur trioxide, the heat of the reaction is recovered to provide steam and to cool the sulfur dioxide gas.

2.5.3 Material and Energy Requirements

The material and energy requirements for electric furnace copper smelting are shown in Tables 2.5-1, 2.5-2 and 2.5-3. Table 2.5-2 includes Level 1 direct energy inputs. Table 2.5-3 contains Level 2 materials and their energy equivalents. Energy equivalent for electrical power and energy consumption values for fluid bed roasting, dust handling, converting, are taken from (Kellogg and Henderson, 1967).

FIGURE 2.5-1 ELECTRIC FURNACE

TABLE 2.5-1			ELECTRIC FURNACE PROCESS							
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CONCENTRATE		ROASTER AIR		ROASTER FUEL		ROASTER OFF GAS		CALCINE DUST	
COMPOSITION	wt.	dry wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	1.016	25.001					.762	10.257	.648	28.053
Fe	1.087	26.738					.652	8.776	.554	24.002
S	1.260	30.997					.567	7.626	.482	20.855
FeO	.428	.690					.231	3.106	.196	8.493
Fe ₂ O ₃	.042	1.040					.032	.427	.027	1.167
SiO ₂	.351	8.630					.263	3.541	.224	9.684
Al ₂ O ₃	.140	3.450					.105	1.415	.083	3.871
CaCO ₃	.048	1.183					.036	.485	.031	1.327
CaO	.092	2.271					.069	.932	.055	2.548
H ₂ O	.554						.606	8.159		
Fuel					.056	100.000				
O ₂			.842	23.000			.101	1.354		
N ₂			2.819	77.000			2.819	37.943		
SO ₂							1.011	13.611		
CO ₂							.176	2.369		
TOTAL	4.064	100.000	3.661	100.000	.056	100.000	7.429	100.000	2.309	100.000
TEMP. (F)	60		60		60		1200		1000	
STATE	S		G		L		G		S	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS									
(TONS PER TON CATHODE COPPER)									
STREAM NO.	(6)		(7)		(8)		(9)		(10)
STREAM NAME	ROASTER SO ₂ GAS		CALCINE		SILICA FLUX		LINE FLUX		RECYCLE DUST
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.
Cu	.114	2.232	.254	28.059					.178
Fe	.098	1.910	.217	24.002					.106
S	.085	1.660	.189	20.855					.093
FeO	.035	.676	.077	8.493					.035
Fe ₂ O ₃	.005	.093	.011	1.167	.003	2.000	.000	1.000	.008
SiO ₂	.039	.771	.088	9.684	.124	90.000	.001	2.000	.132
Al ₂ O ₃	.016	.308	.035	3.871	.006	4.000			.016
CaCO ₃	.005	.106	.012	1.327			.037	96.000	.005
CaO	.010	.203	.023	2.548	.006	4.000	.000	1.000	.010
H ₂ O	.606	11.838							
O ₂	.101	1.965							
H ₂	2.819	55.054							
SO ₂	1.011	19.749							
CO ₂	.176	3.437							
Cu ₂ O									.001
Fe ₂ SiO ₄									.158
Fe ₃ O ₄									.013
Al ₂ SiO ₅									.010
CaSiO ₃									.013
TOTAL	5.120	100.000	.905	100.000	.138	100.000	.038	100.000	.778
TEMP (F)	1100		1200		60		60		100
STATE	G		S		S		S		S

TABLE 2.5-1 (cont.)			ELECTRIC FURNACE PROCESS							
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	FURNACE FEED		FURNACE AIR		ELECTRODE		FURNACE OFF GAS		FURNACE SO ₂ GAS	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	1.079	25.895					.011	2.857	.011	2.857
Fe	.878	21.061					.009	2.248	.009	2.248
S	.763	18.303					.008	1.969	.008	1.969
FeO	.308	7.380								
Fe ₂ O ₃	.049	1.178					.001	.176	.001	.176
SiO ₂	.568	13.631					.006	1.454	.006	1.454
Al ₂ O ₃	.146	3.496								
CaCO ₃	.085	2.035								
CaO	.098	2.356								
Carbon					.010	100.000				
O ₂			.062	23.000			.015	3.870	.015	3.870
N ₂			.206	77.000			.206	54.018	.206	54.018
SO ₂							.019	4.990	.019	4.990
SO ₃							.006	1.559	.006	1.559
CO ₂							.075	19.793	.075	19.793
Cu ₂ O	.001	.019					.000	.002	.000	.002
Fe ₂ SiO ₄	.158	3.794					.019	4.930	.019	4.930
Fe ₃ O ₄	.013	.309					.001	.308	.001	.308
Al ₂ SiO ₅	.010	.236					.003	.793	.003	.793
CaSiO ₃	.013	.307					.004	1.033	.004	1.033
TOTAL	4.162	100.000	.268	100.000	.010	100.000	.381	100.000	.381	100.000
TEMP. (F)	811		350		60		1300		1100	
STATE	S		G		S		G		G	

TABLE 2.5-1 (cont.) ELECTRIC FURNACE PROCESS (TONS PER TON CATHODE COPPER)									
STREAM NO.	(16)		(17)		(18)		(19)		(20)
STREAM NAME	FURNACE SLAG		FURNACE MATTE		CONVERTER FLUX		CONVERTER AIR		CONVERTER FUEL
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. wt. %
Cu	.016	.491	1.161	40.966					
Fe	.013	.386	.836	29.500					
S	.011	.338	.809	28.546					
Fe ₂ O ₃	.066	2.000	.001	.038	.021	2.000			
SiO ₂	.544	16.517	.004	.154	.924	90.000			
Al ₂ O ₃					.041	4.000			
CaO					.041	4.000			
Fuel									.087 100.000
O ₂							1.787	23.000	
H ₂							5.981	77.000	
Cu ₂ O	.000	.000	.001	.038					
Fe ₂ SiO ₄	1.846	56.020	.015	.564					
Fe ₃ O ₄	.116	3.504	.001	.038					
Al ₂ SiO ₅	.297	9.006	.002	.075					
CaSiO ₃	.387	11.737	.003	.113					
TOTAL	3.296	100.000	2.834	100.000	1.026	100.000	2.768	100.000	.087 100.000
TEMP. (F)	2250		2100		60		60		60
STATE	L		L		S		G		L

TABLE 2.5-1 (cont.)										
ELECTRIC FURNACE PROCESS										
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	CONVERTER SLAG		CONVERTER OFFGAS		CONVERTER SO ₂ GAS		BLISTER COPPER		OXIDIZING AIR	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt.
Cu	0.109	5.280	.052	.607	.052	.607	1.000	97.561		
S	0.077	3.729	.000	.001	.000	.001	.001	.117		
Fe ₂ O ₃	0.018	.873	.003	.035	.003	.035	.000	.009		
SiO ₂	0.368	17.820	.007	1.009	.007	1.009	.002	.183		
H ₂ O			.002	.944	.002	.944				
O ₂			.458	5.300	.458	5.300			.014	23.000
N ₂			5.981	69.167	5.981	69.167			.048	77.000
SO ₂			1.173	13.563	1.173	13.563				
SO ₃			.366	4.238	.366	4.238				
CO ₂			.277	3.200	.277	3.200				
Cu ₂ O	0.000	.007	.001	.009	.001	.009	.015	1.469		
Fe ₂ SiO ₄	1.088	60.075	.139	1.611	.139	1.611	.005	.540		
Fe ₃ O ₄	0.105	5.072	.012	.135	.012	.135	.001	.052		
Al ₂ SiO ₅	0.061	2.946	.007	.079	.007	.079	.0005	.030		
CaSiO ₃	0.079	3.840	.009	.102	.009	.102	.0005	.039		
TOTAL	2.065	100.000	8.648	100.000	8.648	100.000	1.025	100.000	.062	100.000
TEMP. (F)	2250		2200		1100		2100		60	
STATE	L		G		G		L		G	

TABLE 2.5-1 (cont.)		ELECTRIC FURNACE PROCESS (TONS PER TON CATHODE COPPER)								
STREAM NO.	(26)		(27)		(28)		(29)		(30)	
STREAM NAME	ANODE FUEL		REDUCING AIR		ANODE OFF GAS		ANODE COPPER		CATHODE COPPER	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu							1.176	100.000	1.000	100.000
H ₂ O					.009	10.895				
Fuel	.000	100.000								
O ₂			.004	23.000	.002	2.270				
N ₂			.014	77.000	.062	70.731				
SO ₂					.002	2.725				
CO ₂					.012	13.379				
TOTAL	.000	100.000	.018	100.000	.087	100.000	1.176	100.000	1.000	100.000
TEMP. (F)	60		60		1800		1800		60	
STATE	L		G		G		L		S	

TABLE 2.5-1 (cont.)				ELECTRIC FURNACE PROCESS						
STREAM NO.	(31)		(32)		(33)		(34)		(35)	
STREAM NAME	DILUTION AIR		SO ₂ ACID GAS		ANODE SLAG		MAKEUP WATER		SULFURIC ACID	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Fe ₂ O ₃					.000	.959				
SiO ₂					.002	19.585				
H ₂ O			.688	4.391			.299	100.000	.287	7.000
H ₂ SO ₄									3.812	93.000
O ₂	.527	23.000	1.100	7.026						
N ₂	1.763	77.000	10.770	68.765						
SO ₂			2.203	14.067						
SO ₃			.372	2.378						
CO ₂			.528	3.372						
Fe ₂ SiO ₄					.006	66.422				
Fe ₃ O ₄					.001	5.575				
Al ₂ SiO ₅					.000	3.238				
CaSiO ₃					.000	4.221				
TOTAL	2.290	100.000	15.661	100.000	.009	100.000	.299	100.000	4.099	100.000
TEMP. (°F)	60		550		1800		60		100	
STATE	G		G		L		L		L	

TABLE 2.5-1 (cont.)		ELECTRIC FURNACE PROCESS			
		(TONS PER TON CATHODE COPPER)			
STREAM NO.	(36)				
STREAM NAME	SO ₂ TAIL GAS				
COMPOSITION	wt. %	wt. %			
O ₂	.553	4.662			
N ₂	10.770	90.793			
SO ₂	.011	.093			
CO ₂	.528	4.453			
TOTAL TEMP. (°F) STATE	11.862 100 G	100.000			

TABLE 2.5-2 ENERGY REQUIREMENTS Level 1					
ELECTRIC SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Flued Bed Roasting				
	A) Compressed Air	MILLION SCF	93.046	0.0042	.382
	B) Misc. Elec. Power	KWH	0.772	0.0105	.008
2	Hot Gas Handling				
	C) Fuel	GAL	15.484	0.1474	2.282
					2.672
3	Hot Gas Handling	MILLION SCF	112.864	0.00252	0.284
4	Electric Furnace				
	A) Direct Power	KWH	1381.1	0.0105	14.502
	B) Misc. Elec. Power	KWH	430.97	0.0105	4.525
5	Hot Gas Handling				
	C) Hot Gas Handling	MILLION SCF	7.105	0.00252	0.018
					19.045
6	Converters				
	A) Compressed Air	MILLION SCF	193.253	0.0147	2.841
	B) Hot Gas Handling	MILLION SCF	187.715	0.00252	.473
7	Hot Gas Handling				
	C) Hot Gas Handling Elec.	KWH	6.86	0.0105	.075
	D) Fuel	GAL	24.28	0.1474	3.579
					6.965
8	Dust Collecting				
9	A) Misc. Elec. Power	KWH	210	0.0105	2.205/Ton Anode
	Anode Refining and Casting				
	A) Fuel	GAL	0.01175	.1474	0.002/Ton Anode
10	B) Natural Gas	MILLION SCF	0.000188	1000	0.188/Ton Anode
	C) Misc. Elec. Power	KWH	13.94	0.0105	0.146/Ton Anode
	D) Hot Gas Handling	MILLION SCF	2.215	0.00252	0.006/Ton Anode
					0.342
11	Electrorefining				
	A) Direct Elec.	KWH	448	0.0105	4.704
	B) Misc. Elec. Power	KWH	5.0	0.0105	0.053
					4.757

TABLE 2.5-2 (Continued)					
ENERGY REQUIREMENTS					
ELECTRIC SMELTING					
Level 1					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Acid Plant				
	A) Elec. Power - Cold	MILLION	362.67	0.00137	0.429
	Gas	SCF			
	Elec. Power - Acid	MILLION	362.67	0.01176	4.265
	Plant	SCF			4.744
				TOTAL	41.014

TABLE 2.5-1		ENERGY REQUIREMENTS			Level 2
ELECTRIC SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
4	Furnace Feed				
	A) Silica Flux	LBS	275.4	0.00005	0.014
	B) Limestone	LBS	76.61	0.00005	0.004
	C) Electrodes	LBS	20.85	0.041000	0.855
6	Converters				
	A) Silica Flux	TON	1.026	0.100	0.103
	Utilities				
	A) Electric Energy	KWH	48.73	.0105	0.512
9	Anode Furnace and Electrorefining	TON	1.0	0.468	0.468
				TOTAL	1.956

2.5.4 Conclusions

Electric smelting is not as efficient in energy requirements as the conventional reverberatory smelting. The addition of fluid bed roasting, however, reduces the furnace fuel requirement by about three million Btu's per ton cathode copper. Gross energy requirement in electric smelting is 43.0 million Btu's per ton cathode copper versus 31.0 million Btu's per ton for conventional reverberatory smelting.

2.5.5 Recommendations

A roasting step should be incorporated into the electric smelting process, since this results in reducing the overall consumption of energy. Since electric smelting indicates the highest energy consumption of all the pyrometallurgical processes considered, further research and development efforts in electric smelting may not be justified.

2.5.6 References

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2.6 OUTOKUMPU FLASH SMELTING

2.6.1 Introduction

The Outokumpu Flash Smelting Process was developed in the years 1946-49. The first commercial Plant went into service in 1949 at Harjavalta Works, Finland.

There are currently 30 licensees of the Outokumpu process, with 23 plants in actual operation.

As an example, the process as used at Harjavalta is described, and variations are then described.

2.6.2 Process Description

The Outokumpu Flash Smelting Process is a pyrometallurgical process for the extraction of copper from sulfide ore concentrates. This process utilizes the heat generated by the exothermic oxidation reactions of iron and sulfur in the concentrate. The conventional operations of roasting, smelting, and partial converting are combined into a single unit operation of flash smelting. The major advantages of this method are a reduction in energy consumption and the production of a stream of gas high in sulfur dioxide which is suitable for sulfuric acid manufacture or the production of elemental sulfur.

Figure 2.6-1 is a flowsheet of the process at Harjavalta. After drying in a direct oil-fired kiln, the charge, consisting of concentrates and silica sand, is transported by means of a pneumatic conveying system to the flash furnace. The flash furnace is divided into three parts: the reaction shaft, the settler, and the uptake.

FIGURE 2.6-1 OUTOKUMPU FLASH SMELTING PROCESS

The concentrates together with the flux are smelted in the reaction shaft in suspension, which offers the most favorable conditions for rapid heat and mass transfer. The heat requirements for smelting are supplied almost entirely by the iron and sulfur oxidation. To balance heat requirements, additional fuel, preheated air and/or oxygen-enriched air can be used. Since 1971, preheated, oxygen-enriched air (200°C, 30-75% oxygen) has been used by Outokumpu. Under these conditions the reaction proceeds without additional fuel.

Molten particles are separated from the gas stream in the settler. Matte drops through the slag to the bottom of the settler. Matte grade is a function of the total oxygen/concentrate ratio and can be varied from 45-80%. One process in operation in Poland produces blister copper directly.

Because of high matte grade and incomplete settling action of matte particles, the slag has a relatively high copper content (0.8-2.5% copper), and slag cleaning is necessary. Slag cleaned at Harjavalta by froth flotation, which recovers the copper, mainly as sulfides from the slag. This concentrate is recycled back through the smelter. After cleaning, the slag copper concentration is about 0.4-0.6%, and this slag is sent for disposal.

To recover heat and dust, the smelter gases pass through the uptake to a waste heat boiler. Gases are then sent to an electrostatic precipitator. Flue dust is recycled to the smelter and the rich, clean sulfur dioxide gases are used for the production of sulfuric acid or elemental sulfur.

Saturated process steam from the waste heat boiler can be used to preheat the oxygen-enriched air that goes to the smelter, to generate power, to produce oxygen, for general heating purposes, and to drive rotating machines (pumps, blowers, etc.).

Matte is treated further in conventional converters to obtain blister copper. Due to the high matte grade and short blowing time, the converter capacity requirements are less than conventional. Converter slag is cleaned together with smelter slag. In considering the total plant complex, energy savings result from the operation of the converters in sequences which provide a steady gas stream to the acid plants. Also higher matte grades result in a lower total gas volume because of less infiltration (1-2%) of outside air in the flash smelting furnace.

Blister copper is transferred to an oil-fired rotating anode furnace, fire-refined, and cast into anodes.

A process for taking chalcocite and digenite concentrates directly to blister copper in one step has been developed at Outokumpu and is currently being used with 23% copper content chalcocite concentrates at a plant in Poland. The heat value of these compounds is low due to the low iron content, and high oxygen enrichment is necessary. Slag is cleaned to remove the relatively high copper content in the slag by electric furnace reduction. Total recovery of copper is up to 99% of the copper in the feed.

2.6.3 Material Balance

The material balance for the production of blister copper is shown in Table 2.6-1.

TABLE 2.6-1			OUTOKUMPU FLASH SMELTING							
[TONS PER TON BLISTER COPPER]										
STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET PRIM. CONCENTRATE		FLASH SILICA FLUX		DRY CHARGE (with slag concentrate)		DRYER OFF GAS		FLASH FURNACE AIR (dry)	
COMPOSITION	wt.	dry wt. %	wt.	dry wt. %	wt.	dry wt. %	wt.	wt. %	wt.	wt. %
Cu	0.9982	22.60			1.0484	24.34				
Fe	1.1180	25.20	0.0024	1.40	1.1613	26.96				
S	1.2378	27.90			1.2563	29.17				
O _{Fe}	0.0188	0.423	0.0010	0.60	0.0293	0.68				
SiO ₂	0.3444	7.767	0.1534	90.00	0.5140	11.93				
Al ₂ O ₃	0.1377	3.101	0.0068	4.00	0.1483	3.44				
CaO + MgO	0.1176	2.637	0.0034	2.00	0.1238	2.87				
Others	0.0208	0.468	0.0034	2.00	0.0257	0.59				
H ₂ O	0.4437	10.00					0.4690		0.0165	0.5
SO ₂									1.1781	36.5
O ₂										
CO										
CO ₂										
N ₂									2.0302	63.0
TOTAL	4.4366	100.00	0.1704	100.00	4.3067	100.00			3.2248	100.00
TEMP. (°F)	60		60		150		250		392	
STATE	S		S		S		G		G	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.6-1 (cont.)								
OUTOKUMPU FLASH SMELTING								
[TONS PER TON BLISTER COPPER]								
STREAM NO.	(6)		(7)		(8)		(9)	
STREAM NAME	FLASH FURNACE MATTE		FLASH FURNACE OFF GAS		FLASH FURNACE SLAG		CONVERTER AIR	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wet wt. %	wt.	wt. %
Cu	1.0078	65.00			0.0407	1.9		0.0178
Fe	0.1879	12.12			0.9735	45.45		0.1861
S	0.3402	21.94			0.0193	0.9		0.0045
O _{Fe*}	0.0146	0.94			0.2971	13.87		0.0594
SiO ₂					0.5140	24.00		0.0836
Al ₂ O ₃					0.1416	6.61		0.0019
CaO + MgO					0.1238	5.78		0.0019
Others					0.0306	1.43		0.0035
H ₂ O			0.0165					
SO ₂			1.8162				0.4253	26.00
O ₂								
CO								
CO ₂								
N ₂			2.0302				1.2106	74.00
TOTAL	1.5504	100.00	3.8629		2.1418	100.00	1.6359	100.00
TEMP. (°F)	2200		2400		2300		60	2250
STATE	L		G		L		G	L

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.6-1 (cont.)										
OUTOKUMPU FLASH SMELTING										
(TONS PER TON BLISTER COPPER)										
STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	BLISTER CU		SILICA FLUX		CONVERTER OFF GAS		FLOT. CONC.		FLOT. TAILINGS	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wet wt. %	wt. dry wt. %	
Cu	0.990	99.0					0.0502	35.00	0.0082	0.35
Fe	0.003	0.3	0.0013	1.40			0.0409	28.53	1.1187	47.46
S	0.003	0.3					0.0185	12.92	0.0052	0.22
O _{Fe} *	0.0005	0.05	0.0006	0.60			0.0096	6.67	0.3470	14.72
SiO ₂			0.0834	90.00					0.5815	24.67
Al ₂ O ₃			0.0037	4.00					0.1377	5.84
CaO + MgO			0.0019	2.00					0.1223	5.19
Others	0.035	0.035	0.0019	2.00			0.242	16.88	0.03654	1.55
H ₂ O						0.6708				
SO ₂										
O ₂										
CO										
CO ₂						1.2106				
N ₂										
TOTAL	1.0	100.00	0.0927	100.00			0.1434	100.00	2.3571	100.00
TEMP (°F)	2200		60		2300		60		60	
STATE	L		F		G		S		S	

*Oxygen associated with FeO and Fe₃O₄

2.6.4 Energy Requirements

Table 2.6-2 and Table 2.6-3 present the Level I and Level II energy requirements for Outokumpu flash smelting.

2.6.5 Discussion

The most economical and practical way of flash smelting for a particular plant largely depends on local circumstances such as price of energy, need for scrap melting, treatment of process gases, and prices and recoveries of other metals in the concentrates. The following discussion examines the variables in using the flash smelting method developed by Outokumpu.

2.6.5.1 Matte Grade

Matte grade depends on the oxygen-concentrate feed ratios, the furnace temperature, and the amount of impurities in the concentrate. In R&D work at Outokumpu and in connection with operating industrial plants, the flash smelting furnace product has ranged from low grade matte, containing 35% copper to white metal and further to blister copper. Slags have varied from 0.6-15% depending on oxygen-concentrate feed ratios and furnace temperature. Raising the matte grade decreases the need for additional fuel in flash smelting because of a fairly large portion of the latent heat value of the concentrate itself is used at the smelting stage (Haarki, 1976) but also increases the amount of copper in the slag.

2.6.5.2 Heat Requirements in Smelting

To balance heat requirements not met by the exothermic reactions in smelting, additional fuel, preheated air and/or oxygen-enriched air can be used.

By using oxygen-enriched air (consequently, reduced gas volume), the capacity of the smelter can be considerably increased, and fuel consumption is significantly reduced. Present practice also enables the unit to operate without fuel addition. Preheating of process air reduces the smelting furnace gas volume and offers savings in the capital costs of the equipment on the gas side. Preheating the process air can offer energy savings in reduced fuel consumption in the smelter and by utilizing process steam from a waste heat boiler.

2.6.5.3 Waste Heat

The Outokumpu process uses a waste heat boiler as part of its gas treatment cycle. The steam recovered from the boiler can be used for preheating process air, producing oxygen-enriched air (Juusela, 1974), or generating electric power, although the latter is generally too expensive to be practical.

2.6.5.4 Flue Dust

Flue dust is usually recycled but can also be treated separately to recover valuable metals or to eliminate harmful elements.

2.6.5.5 Treatment of Sulfur Dioxide in Off Gases

In development work, Outokumpu used two methods for handling the sulfur dioxide produced. Originally, the gases from the converter and smelter were combined, and the sulfur dioxide was treated to produce sulfuric acid. This is common practice.

TABLE 2.6-2

ENERGY REQUIREMENTS
OUTOXUMPU FLASH SMELTING

Level 1

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling A) Electrical Energy	KWH	54.4	0.0105	0.571
2	Drying A) Fuel Oil	Gal	7.7	0.139	1.06
	B) Electric Energy	KWH	16.3	0.0105	0.171
3	Flash Smelting A) Electrical Energy	KWH	76.1	0.0105	0.799
	B) Waste Heat Recovery	LB%	-1807	0.0014	-2.529
4	Converting A) Electrical Energy (mate- rial handling & blowing)	KWH	60.7	0.0105	0.637
	B) Waste Heat Recovery	LB%	-648	0.0014	-0.907
5	Slag Flotation A) Electrical Energy	KWH	142.3	0.0105	1.494
6	Gas Cleaning A) Hot Gas Cleaning	Thous. SCF	165.2	0.00252	0.416
	B) Cold Gas Cleaning	Thous. SCF	165.2	0.00126	0.208
	C) Fugitive Emission Control	KWH	340	0.0105	3.570
7	Acid Plant A) Smelter and Converter Gas (10" 50%)	Thous. SCF	306.7	0.0126	3.864
8	Water Pollution Control A) Electric Energy	KWH	9.0	0.0105	0.095
9, 9	Anode Furnace and Electrorefining	TONS OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	15.279

TABLE 2.6-3		ENERGY REQUIREMENTS			Level 2
OUTOKUMPU FLASH SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Flash Smelting				
	A) Oxygen	TON	0.593	4.41	2.615
	B) Silica Flux	TON	0.249	0.042	0.010
4	Converting				
	A) Oxygen	TON	0.096	4.41	0.423
	B) Silica Flux	TON	0.101	0.042	0.004
5	Slag Flotation				
	A) Flotation Reagents	LBS	2.0	0.02	0.040
x	Water Pollution Control				
	A) Lime	LBS	30.00	0.0027	0.081
8,9	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	3.641

In 1962, a method for recovering elemental sulfur by high temperature reduction from the gases was developed by Outokumpu. If no market for sulfuric acid exists near the smelter, this can be a favorable alternative. This method involves the reduction of sulfur dioxide in the uptake of the furnace by using pulverized coal, or gaseous or liquid hydrocarbon reductants. The design and operation of the flash furnace is modified to produce a high sulfur dioxide, low oxygen stream suitable for this reduction step. Since various side reactions occur during the reduction, leading to the formation of sulfur compounds such as COS, the gases, after passing through the waste heat boiler and electrostatic precipitator, are catalyzed to convert the sulfur compounds into sulfur vapor. The vapor is condensed to produce elemental sulfur.

2.6.5.6 Slag Cleaning

Since the flash smelting process produces slags containing sufficient amounts of copper to make its recovery feasible, slag cleaning is normally used. Two methods are used with this process: flotation and electric furnace slag cleaning.

Flotation involves slow cooling of the slag to permit precipitation/agglomeration of copper sulfides and metallic copper. The slag is then crushed and ground, and copper is recovered via froth flotation. The concentrate recovered is then fed back to the smelter, usually mixed with the ore concentrate and flue dust.

In electric furnace slag cleaning, a reducing environment is provided which decreases the solubility of copper in the slag. Also, the slag is kept molten and fluid for an extended period of time to allow for entrained matte particles to coalesce, settle, and form a matte pool at the bottom of the furnace. Coke or coal is used as the reducing agent.

The matte phase from this furnace also goes to the converter.

A few smelters utilize both techniques, i.e., flotation for converter slag and electric furnace for flash furnace slag.

2.6.5.7 Blister Copper Production

As noted in the process description for Harjavalta, copper concentrates can be taken directly to blister copper in one stage. This is advantageous especially for concentrates containing less iron than normal. The copper content in the slag is high compared to processes producing matte and the slag must be treated separately.

2.6.6 Conclusions

Flash smelting utilizes the heat evolved from oxidizing part of the sulfide charge to produce much or all of the energy required for smelting. The recovery of waste heat from the flash furnace off-gas is standard practice. The amount of fuel required for smelting can be reduced by increasing the preheat temperature of flash furnace air, oxygen enrichment of flash furnace air and the degree to which the charge is oxidized in the furnace, i.e., the matte grade. The lowered fuel consumption also results in reduced off-gas volume. Present practice enables the flash furnace to operate without fuel addition with oxygen enrichment in the range of 30-75% oxygen and a preheat temperature of 200°C.

Increasing the matte grade decreases the need for additional fuel in flash smelting because a fairly large portion of the fuel value of the concentrate is used at the smelting stage. In addition, production of high grade matte leads to energy savings in converting.

2.6.7 References

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2.7 INCO FLASH SMELTING

2.7.1 Introduction

The INCO Metals Company (INCO), Copper Cliff, Ontario, Canada, is among the pioneers of the commercial use of oxygen in liquid-phase pyrometallurgy. In the years 1945 to 1949 the company developed a process for direct flash smelting of copper sulfide concentrates with oxygen. In 1952, the first commercial scale oxygen flash smelting furnace was brought into service at Copper Cliff. There are currently two copper processing plants, the other the Almalyk Smelter in the USSR using the oxygen flash smelting method for recovery of copper, and the following is a general description of the process as used at Copper Cliff.

2.7.2 Process Description

The INCO Oxygen Flash Smelting Process is a pyrometallurgical process for the extraction of copper from sulfide concentrates. Characteristic of this process is autogenous flash smelting, utilization of high purity 95-99.5% oxygen, and production of gases with a high content of sulfur dioxide (80%) that can be further processed to produce liquid sulfur dioxide or reduced to elemental sulfur or to sulfuric acid using converter gases, smelter secondary emissions or air as diluent.

Figure 2.7-1 is a general flowsheet for the oxygen flash smelting process. The procedure as shown is followed by INCO with the exception that only 50% of the converter slag is currently returned to the smelting furnace because nickel contained in the feed concentrate (typically about 1%) must be rejected with at least a portion of the copper converter slag. INCO reprocesses the remainder of the converter slag through the nickel reverberatory furnace for recovery of nickel and copper. In this paper, recycle of converter slag through the flash furnace has been considered for purposes of material and energy balances, since the content of copper in the slag is appreciable (4%).

Copper concentrates are received at the dryers in the form of filter cake containing 8% moisture. Each dryer unit consists of a blower, natural gas-fired heater, fluidized bed dryer, and collection baghouse. Since 1971, two fluidized bed dryers have been used at INCO for preparing a proportioned concentrate/sand mixture.

High purity tonnage oxygen is received at the furnace at 23 psig, and a reduction in pressure to 15 psig is made for piping to the burners.

The flash furnace has opposed pairs of burners and a central gas uptake. The proportioned feed mixture is gravity-fed through the burners where it combines with oxygen and then enters the furnace. Ignition is instantaneous, and the smelting temperature is maintained solely by the oxidation of the iron sulfides while the concentrates are in suspension. The iron oxides produced are fluxed by the sand to generate an iron silicate slag. The remaining copper, iron, and sulfur collect as matte below the slag layer.

Slag at 2250°F is skimmed manually and then discarded. Prior to 1964, pyrrhotite cleaning of the slag was carried out, but this practice has been discontinued at INCO (Merla, 1972) because overall copper losses were not decreased significantly.

Gases, containing about 80% sulfur dioxide, leave the flash furnace at 2300°F and are led to a settling chamber where particulate solids are removed, and the gases are cooled to 1300°F. Further cooling is achieved with water in a splash tower after which the gases are passed through three venturi scrubbers in series and a Cottrell precipitator. The clean sulfur dioxide gases are then sent for liquefaction, which is done by cooling and compressing. If sulfuric acid were to be produced the settling chamber would be followed by a spray cooler and electrostatic precipitator.

Matte, containing about 47% copper, is removed from the furnace at 2150°F and is transferred to Peirce-Smith converters for processing to blister copper. Operating practice for converting at INCO is standard except that about 50% of the converter slag is recycled through the nickel side of the plant for recovery of nickel and copper and about 50% is returned to the flash furnace. Offgases from the converter contain about 4-5% sulfur dioxide after dilution with cooling air and are exhausted through a stack.

Blister copper from the converter is further processed by anode refining and casting and electrorefining.

As the off-gas volume is typically less than 5,000 SCFM, in most cases a waste heat boiler cannot be justified either from an energy savings, or economic operational integrity standpoint.

2.7.3 Material Balance

Table 2.7-1 presents the material balance for the INCO flash smelting process.

2.7.4 Energy Requirements

Tables 2.7-2 and 2.7-3 present Level I and Level II energy requirements for the INCO flash smelting process.

2.7.5 Conclusions

INCO Flash Smelting under autogenous conditions, using tonnage oxygen (95-99.0% O₂) and a 29-30% Cu 30-31% Fe & 33-34% S feed concentrate, will typically yield matte grades in the 40-45% range, though excursions as low as 35% Cu or as high as 55% Cu have been experienced due to changes in operating conditions. Throughout this range the furnace partition coefficient (%Cu in matte/%Cu in slag) has remained at about 70. Return of molten (or cold) converter slag to the furnace will increase this autogenous matte grade by as much as 5 percentage points of copper, depending on the quantity recycled. It should be understood that for all typical copper concentrates being processed through an INCO type flash furnace at a specific feed rate that there is a specific autogenous matte grade. This autogenous matte grade can however be varied in a number of proven ways. Increasing the furnace feed rate will decrease matte grades while increases in furnace slag silica content by the use of higher furnace flux additions will increase matte grades. Additions of "inert" materials such as smelter dusts, converter slags, limestone or water will also increase the autogenous matte grade. Decreasing additions of these inert materials will of course decrease the matte grade. In certain cases very minor additions (less than 1% of concentrate feed rate) of fuel (i.e., pulverized coal) will decrease the matte grade very substantially (up to 10 percentage points of copper). In almost 30 years of operation no magnetite buildup on the furnace bottom has been experienced and the original bottom installed in the

TABLE 2.7-1										INCO OXYGEN FLASH SMELTING											
[TONS PER TON BLISTER COPPER]																					
STREAM NO.		(1)				(2)				(3)				(4)				(5)			
STREAM NAME		WET CONCENTRATE				FLASH SILICA FLUX				DRY FURNACE CHARGE				DRYERS OFF GAS				FLASH FURNACE OXYGEN			
COMPOSITION		wt.		wet wt. %		wt.		dry wt. %		wt.		dry wt. %		wt.		wet wt. %		wt.		wt. %	
Cu		0.9995		22.50						0.9995		23.19									
Fe		1.1194		25.20		0.0044		1.40		1.1238		26.08									
S		1.2383		27.87						1.2383		28.73									
O _{Fe} *		0.0186		0.42		0.0019		0.60		0.0205		0.48									
SiO ₂		0.3450		7.77		0.2807		90.00		0.6257		14.52									
Al ₂ O ₃		0.1379		3.11		0.0125		4.00		0.1504		3.49									
CaO + MgO		0.1171		2.63		0.0062		2.00		0.1233		2.86									
Others		0.0220		0.50		0.0062		2.00		0.0282		0.65									
H ₂ O		0.4442		10.00		0.0064				0.0086				0.5213		8.17					
SO ₂																					
O ₂														1.2142		19.03		0.8917		95.60	
CO																					
CO ₂														0.1133		1.78					
N ₂														4.5309		71.02		0.0411		4.40	
TOTAL WET		4.4420				0.3183				4.3183				6.3796							
TOTAL DRY		3.9978		100.00		0.3119		100.00		4.3097		100.00		5.8583		100.00		0.9328		100.00	
TEMP. (°F)		60				60				77				225				77			
STATE		S				S				S				G				G			

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.7-1 (cont.)			INCO OXYGEN FLASH SMELTING							
[TONS PER TON BLISTER COPPER]										
STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	FLASH FURNACE OFF-GAS		FLASH FURNACE MATTE		FLASH FURNACE SLAG		CONVERTER SLAG		AIR TO CONVERTER	
COMPOSITION	wt.	wet wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu			1.0273	50.45	0.0195	0.72	0.0373	3.96		
Fe			0.4816	23.65	1.1266	41.80	0.4771	50.55		
S			0.4854	23.83	0.0387	1.44	0.0218	2.31		
O _{Fe} *			0.0336	1.65	0.3282	12.18	0.1471	15.59		
SiO ₂					0.8675	32.18	0.2389	25.31		
Al ₂ O ₃					0.1612	5.98	0.0108	1.14		
CuO + MgO					0.1207	4.77	0.0054	0.57		
Others			0.0085	0.42	0.0251	0.93	0.0054	0.57		
H ₂ O	0.0086	0.52								
SO ₂	1.4851	90.16							0.5683	23.20
O ₂										
CO										
CO ₂										
N ₂	0.1535	9.32							1.8814	76.80
TOTAL WET	1.6472									
TOTAL DRY	1.6386	100.00	2.0364	100.00	2.6955	100.00	0.9438	100.00	2.4497	100.00
TEMP. (°F)	2241		2151		2241		2241		60	
STATE	G		L		L		L		G	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.7-1 (cont.)			INCO OXYGEN FLASH SMELTING					
[TONS PER TON BLISTER COPPER]								
STREAM NO.	(11)		(12)		(13)			
STREAM NAME	CONVERTER SILICA FLUX		CONVERTER OFF-GAS		BLISTER COPPER			
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %		
Cu					0.9800	98.00		
Fe	0.0038	1.40			0.0010	0.1		
S					0.0090	0.90		
O _{Fe} *	0.0016	0.60			0.0015	0.15		
SiO ₂	0.2418	90.00						
Al ₂ O ₃	0.0108	4.00						
CaO + MgO	0.0054	2.00						
Others	0.0054	2.00			0.0085	0.85		
H ₂ O								
SO ₂			0.9047	32.47				
O ₂								
CO								
CO ₂								
N ₂			1.8814	67.53				
TOTAL DRY	0.2688	100.00	2.7861	100.00	1.0000	100.00		
TEMP. (°F)	60		60		2200			
STATE	S		S		L			

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.7-2		ENERGY REQUIREMENTS			LEVEL 1
INCO FLASH SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling A) Electrical Energy	KWH	69.1	0.0105	0.726
2	Drying A) Fuel: Natural Gas B) Electrical Energy	SCF KWH	1750 10.0	0.001 0.0105	1.750 0.105
3	Flash Smelting A) Electrical Energy	KWH	4.5	0.0105	0.047
4	Converting A) Electrical Energy	KWH	89.8	0.0105	0.943
5	Gas Cleaning A) Hot Furnace Gas Cleaning (81% SO ₂ -Dry Basis) B) Hot Converter Gas Cleaning (7% SO ₂ -Dry Basis) C) Cold Furnace Gas Cleaning (75% SO ₂ -Dry Basis) D) Cold Converter Gas Cleaning (5% SO ₂ -Dry Basis) E) Fugitive Emission Control	THOUS. SCF THOUS. SCF THOUS. SCF THOUS. SCF KWH	22.1 153.0 32.6 213.6 340.0	0.00336 0.00336 0.00126 0.00126 0.0105	0.074 0.514 0.041 0.269 3.570
6	Acid Plant A) Smelter and Converter Gas (11.1% SO ₂ -Dry Basis)	THOUS.	253.5	0.0126	3.194
*	Water Pollution Control A) Electrical Energy	KWH	9.0	0.0105	0.095

*Not Shown on Flowsheet

TABLE 2.7-2 (cont.)		ENERGY REQUIREMENTS			LEVEL 1
INCO FLASH SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
7,8	<u>Anode Furnace and Electrorefining</u>	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	17.152

TABLE 2.7-3		ENERGY REQUIREMENTS		LEVEL 2	
INCO FLASH SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Flash Smelting				
	A) Oxygen	TON	.933	3.78	3.526
	B) Silica Flux	TON	.312	0.042	0.013
4	Converting				
	A) Silica Flux	TON	.269	0.042	0.011
*	Water Pollution Control				
	A) Lime	LBS	30.0	0.0027	0.081
7,8	Anode Furnace and Electrorefining	TON	1.0	0.468	0.468
				TOTAL	4.099

*Not shown on flowsheet

second production furnace which commenced operation in 1953 is still in use. The recycle of converter slag first tested in 1978 has been incorporated as a regular operating practice and is currently being held at a rate of about 50% of total converter slag generated, with the limitation being the nickel content of the feed rather than the furnace operation. This reversion has not decreased the furnace matte/slag partition coefficient. The INCO furnace produces a low off gas volume, typically about 5,000 SCFM with a high sulfur dioxide content (80% SO_2). As a result, dusting rates are low and typically run in the range of 2-3% of the feed rate. Generally it is not considered economic to install a waste heat boiler on the furnace because of the exceptionally low off gas volume. The high SO_2 gas strength is ideally suited to the production of liquid SO_2 or as a sweetener for other smelter gases in the production of sulfuric acid.

2.7.6 References

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2.8 THE TOP BLOWN ROTARY CONVERTER (TBRC) SMELTING

2.8.1 Introduction

The Kaldo Process was first used commercially in 1957, in Sweden, to produce steel from high phosphorus iron ore. INCO Limited adapted the converter employed in the Kaldo Process to nonferrous smelting in 1959 in a three-ton pilot plant furnace in Sweden for the blowing of nickel sulfide to metallic nickel. In 1965, INCO installed a ten-ton converter of this type in a smelter (naming it TBRC) at its research facilities in Port Colborne, Ontario, to convert nickel sulfide into nickel metal and to convert copper, nickel sulfides and copper sulfides to metal. As a result of successful pilot plant testing, two 14-foot diameter furnaces were installed at INCO's Copper Cliff nickel refinery at Sudbury, Ontario and three in Sovako, Indonesia.

In 1971, INCO gave Dravo a worldwide exclusive license to design, engineer and construct copper smelters using the TBRC process. Through a joint venture by Dravo and INCO, in 1973, the TBRC smelter for nickel conversion was applied to production scale tests of copper smelting at INCO's Copper Cliff refinery. Successful pilot tests were made with an ore concentrate containing 29% copper, 30% iron and 30% sulfur plus silica and trace elements.

The first commercial scale introduction of the TBRC technique to copper metallurgy occurred within the secondary copper industry. La Metallo-Chimique S.A., Belgium (with

secondary copper smelters at Beerse, Belgium, and Alton, Illinois) has, since the mid-sixties, developed techniques for TBRC smelting and refining of copper-bearing secondary raw materials including techniques for slag refining and extraction of valuable byproducts. One of the features of the development is a jacketed furnace shell.

At Tennant Creek in Australia, two 25-ton TBRC type top blown, rotary converters were installed by Peko-Wallsend and brought on stream in January 1974 and operated for 14 months. These units were installed at less than a 5° angle. The TBRCs were used for treating high grade mattes (65% Cu) containing 0.2% Bi. With the TBRC's ability to provide heat and control atmosphere, it was possible to eliminate bismuth by volatilization from 0.2% to 0.04% Bi. This was achievable by prolonged converting times, at a high expense in fuel oil and lining life.

The first commercial copper smelter designed and engineered by Dravo using the TBRC smelter technology is operated by Alton Mines Ltd. in Kanloops, British Columbia. The Alton ore body is principally native copper with some bornite, chalcocite and chalcopyrite and is concentrated to a metallic concentrate that averages 82% copper and a flotation concentrate containing 51% copper and 7.1% sulfur.

2.8.2 Process Description

The TBRC vessel is similar to the basic vessel used in the Kaldo process for steel production. Thrust rollers secure the vessel longitudinally, and motor-driven support rollers support the vessel in its frame and rotate it at variable operating speeds from 0-40 RPM. Different speeds are used in different process stages, e.g., low RPM while charging and high RPM at the end of the white metal blow and during the anode refining stage. High RPM increases process reaction rates and efficiencies, but also increases refractory wear. The furnace can be tilted through 360° for filling, blowing, and pouring. The process flow-sheet is shown in Figure 2.8-1.

A movable, tight-fitting hood covers the open end of the converter. This hood carries the process lance, charging chute, and INCO flash burner, all of which are water-cooled. The process lance utilizes oxygen, fuel and air in various combinations to act as either a burner or blowing lance. The hood is closed over the vessel mouth whenever processing takes place. The hood can be swung away from the vessel mouth, the TBRC rotated, and molten material or scrap that is too large for the chute can be added. The vessel is inclined between 15°-20° during operation. The angle is selected to obtain an optimum balance between degree of fill and agitation (Daniele and Jaquay, 1972).

The smelting of copper concentrates is essentially an autogenous operation in the TBRC. The charge consisting of concentrate and flux is prepared and dried. Smelting would be accomplished by the flash smelting technique as demonstrated by INCO in their continuing development efforts (Bell, 1978).

Dravo no longer considers multiple TBRCs to be the best way to go on a new large tonnage smelting facility (Daniele, Jaquay, 1972 and 1974). Today, Dravo's approach is that although multiple TBRCs are a technically feasible approach, it is doubtful that they can compete on a capital cost basis with a large primary smelting unit producing continuous high strength off-gases for use in a sulfuric acid plant. However, the TBRC can be considered as a viable alternative to Peirce-Smith converters where the primary unit produces high grade matte.

The TBRC™ Process represents a complete process — smelting, converting, and refining. The overall capital competitiveness of the process, however, lies in a range up to 700-800 TPD copper concentrate. As capital cost was not a criterion in these studies, the following energy consumption information is based on a TBRC™ copper smelter producing copper from approximately 1200 TPD chalcopyrite concentrate. Such a smelter would require four (4) operating TBRC vessels.

A typical cycle would include the following process steps:

1. Flash smelting of a pre-fluxed concentrate with oxygen.
2. Cleaning of flash smelting slag.
3. Pouring slag from vessel.
4. Begin converting step by adding silica flux and blowing with oxygen enriched air.
5. Cleaning of converting slag and pouring from vessel.
6. Begin finish blow to produce blister copper.
7. Further de-sulfurize and then de-oxidize to produce anode or fire-refined copper.

In a 1200 TPD smelter each TBRC converter would not perform all seven (7) steps. A typical utilization would be two (2) smelting and slag cleaning, one (1) converting, and one (1) finish blow and refining.

Cycle Descriptions:

The concentrate smelting TBRCs are preheated to operating temperatures. Pre-fluxed and dried ($<1\%$ H_2O) concentrate is charged through an INCO flash smelting burner. Temperature control is maintained by adjusting the O_2 :Concentrate ratio. This ratio varies with different concentrate grades. Once the available volume is filled, a slag cleaning step is performed, then the slag is poured from the TBRC vessel. The sequence is repeated until an optimum volume of matte has been accumulated for the converting stage. More than 50% of the slag is removed during the smelting cycle stage.

The converting cycle begins when sufficient 55-60% copper matte has been accumulated. This can be accomplished by either building up the matte level in one TBRC or transferring matte from another TBRC to the converting vessel. Should the matte contain impurities, e.g., arsenic, antimony, bismuth, lead, etc., an impurity volatilization step would be performed prior to blowing commencing. Once the converting cycle is begun, silica flux is added via the charging chute. The process lance is set for an oxygen-air mixture, approximately 30% O_2 by volume, and blowing proceeds. Once sufficient slag is produced it is either subjected to a slag cleaning step or transferred to another TBRC for cleaning.

The complexity introduced by matte, slag, and white metal transfers in a large tonnage smelter is the reason that a single primary smelting unit may be preferable. Another choice to minimize transfers is slow cooling and milling of the converting stage slags. This could also enhance overall copper recovery, e.g., Afton Mines Ltd., recycles slag to their concentrator and achieves 99%+ copper recovery.

Once all the iron is slagged and the slag removed from the TBRC, the finish blow, white metal to copper, begins. Again, blowing utilizes a mixture of oxygen and air. Once oxygen levels of

0.15-0.20% are achieved (0.1% sulfur or less), reduction can begin by adding carbon to the bath. Here one of the advantages of the high speed rotary vessel comes into play. Further desulfurization takes place during de-oxidation due to the forced mixing of copper sulfides and oxides. This permits the TBRC to perform the anode furnace or fire refining furnace function. The copper is removed from the furnace by tilting the TBRC downward and pouring the copper into ladles beneath the furnace.

The exhaust gases from the furnace are collected in the hood which is connected to gas cooling and cleaning equipment. The clearance between the hood and the rotating furnace is held to as little as 2 inches to limit the amount of ambient air entering the exhaust system at this point. The negative pressure in the hood is controlled to the minimum value which will prevent the escape of exhaust gas. Sulfur dioxide concentration in the exhaust gases is generally high enough for economic recovery of the sulfur as sulfuric acid or as elemental sulfur (Jaquay). An exception to this is at the Afton mines smelter where the concentrate has low sulfur content. The sulfur dioxide in the gases at this operation are removed by a Dravo designed dual alkali scrubbing system (Pazour, 1978).

Close control of the furnace atmosphere, the turbulence of the bath, the oxygen/air mixture, and the temperature of the melt is necessary for useful operation of the TBRC. Computer control, utilizing a heat and material balance (Jaquay), can be used to determine the amounts of raw material, flux, oxygen, and air that are required to reach a desired melt condition of temperature, composition, or volume. To supplement this and provide for necessary adjustments, slag and matte samples are sent to a lab for a check on chemical composition and the temperature is measured by an immersion thermocouple or optical pyrometer.

The turbulence in the bath is controlled by varying the rotational speeds. Constant vessel rotation enhances gas/solid/liquid contact and heat distribution. High oxygen efficiency can be maintained by adjustment of the rotational speed and lance angle. Tests done by INCO indicated that oxygen efficiency can be maintained above 90% (Daniele and Jaquay, 1972) (Bell, 1978).

The lance is used to control the smelting atmosphere by the injection of different combinations of fuel, air, and oxygen to obtain neutral, oxidizing, or reducing conditions as required. The temperature of the charge can be raised by injecting oxygen and fuel through the lance which will burn and mix the two gases at the nozzle. Alternatively, temperature can be lowered by adding scrap or low iron concentrates, by introducing water into the converter to use up the excess heat or by a greater air to oxygen ratio (Bell et al., 1978).

2.8.3 Material Balance

Table 2.8-1 shows the material balance for smelting of concentrates by the top blown rotary converter process.

2.8.4 Energy Requirements

Table 2.8-2 presents the Level I energy requirements for TBRC smelting, in million Btu per ton of blister copper.

The energy used in materials handling and general utility is estimated at 15.5 kWh per ton concentrate smelted, or 147,000 Btu fuel equivalent.

Table 2.8-3 presents the Level II energy requirements for TBRC smelting.

TABLE 2.8-1

TTRC™ PROCESS

[TONS PER TON BLISTER COPPER]

STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET CONCENTRATE		SMELTING SILICA FLUX		DRYERS OFF GAS		DRY FURNACE CHARGE		SMELTING OXYGEN	
COMPOSITION	wt.	wet wt. %	wt.	wet wt. %	wt.	wet wt. %	wt.	wet wt. %	wt.	wet wt. %
Cu	0.9995	22.50					0.9995	23.19		
Fe	1.1194	25.20	0.0044	1.40			1.1238	26.08		
S	1.2383	27.87					1.2383	28.73		
O _{Fe} *	0.0186	0.42	0.0019	0.60			0.0205	0.48		
SiO ₂	0.3450	7.77	0.2807	90.00			0.6257	14.52		
Al ₂ O ₃	0.1379	3.11	0.0125	4.00			0.1504	3.49		
CaO + MgO	0.1171	2.63	0.0062	2.00			0.1233	2.86		
Others	0.0220	0.50	0.0062	2.00			0.0282	0.65		
H ₂ O	0.4442	10.00	0.0064		0.5213	8.17	0.0086			
SO ₂										
O ₂					1.2142	19.03			1.000	95.60
CO					0.1133	1.78				
CO ₂					4.5309	71.02			0.046	4.40
N ₂										
TOTAL WET	4.4420		0.3183		6.3796		4.3183			
TOTAL DRY	3.9978	100.00	0.3119	100.00	5.8583	100.00	4.3097	100.00	1.046	100.00
TEMP. (°F)	60		60		225		77		60	
STATE	S		S		G		S		G	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.8-1 (cont.)			TBRC™ PROCESS							
[TONS PER TON BLISTER COPPER]										
STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	SMELTING OFF-GAS		SMELTING MATTE		SMELTING SLAG		CONVERTING FLUX		CONVERTING BLOW	
COMPOSITION	wt.	wet wt. %	wt.	wet wt. %	wt.	wt. %	wt.	wet wt. %	wt.	wet wt. %
Cu			0.9893	56.83	0.0107	0.60				
Fe			0.2763	15.87	0.8475	47.46	0.0028	1.40		
S			0.4056	23.30			0.0011	0.60		
O _{Fe*}										
SiO ₂					0.6257	35.04	0.1781	90.00		
Al ₂ O ₃					0.1504	8.42	0.0079	4.00		
CaO + MgO					0.1233	6.90	0.0040	2.00		
Others			0.0696	4.00	0.0282	1.58	0.0040	2.00		
H ₂ O	0.0086						0.0040			
SO ₂	1.660	44.1							0.2667	32.86
O ₂	0.472	12.6								
CO										
CO ₂										
N ₂	1.626	44.1							0.5449	67.14
TOTAL WET							0.2010			
TOTAL DRY	3.758	100.00	1.7408	100.00	1.7858	100.00	0.1979	100.00	0.8166	100.00
TEMP. (°F)	1800-2000		2250		2300		60		60	
STATE	G		L		L		S		G	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.8-1 (cont.)			TBRC™ PROCESS							
[TONS PER TON BLISTER COPPER]										
STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	CONVERTING SLAG		CONVERTING OFF-GAS		FINISH BLOW		FINISH OFF-GAS		BLISTER COPPER	
COMPOSITION	wt.	wet wt. %	wt.	wet wt. %	wt.	wet wt. %	wt.	wet wt. %	wt.	wet wt. %
Cu	0.0083	1.31							0.98	98
Fe	0.2791	44.03							0.001	0.10
S									0.009	0.90
O _{Fe} *	0.0829	13.08							0.0015	0.15
SiO ₂	0.1781	28.10								
Al ₂ O ₃	0.0079	1.24								
CuO + MgO	0.0040	0.63								
Others	0.0736	11.61							0.0085	0.85
H ₂ O										
SO ₂			0.3166	22.49			0.4904	26.08		
O ₂			0.1256	8.92	0.3065	32.86	0.1952	10.38		
CO										
CO ₂										
N ₂			0.9656	68.59	0.6262	67.14	1.1950	63.54		
TOTAL WET										
TOTAL DRY	0.6339	100.00	1.4078	100.00	0.9327	100.00	1.8806	100.00	1.0	100.00
TEMP. (°F)	2300		1800-2000		60		1800-2000		2200	
STATE	L		G		G		G		L	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.8-2		ENERGY REQUIREMENTS			LEVEL 1
TBRC™ PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials handling				
	A) Electrical Energy	KWH	69.1	0.0105	0.726
2	Drying				
	A) Fuel: Natural Gas	SCF	1750	0.001	1.750
	B) Electrical Energy	KWH	10	0.0105	0.105
3-6	TBRC TOTAL				
	A) Fuel: Natural Gas	SCF	400	0.001	0.400
	B) Electrical Energy	KWH	110.9	0.0105	1.164
7	Gas Cleaning				
	A) Hot Gas Cleaning				
	Smelting	SCF x 10 ³	74.9	0.00336	0.252
	Converting	SCF x 10 ³	32.9	0.00336	0.110
	Finish	SCF x 10 ³	42.8	0.00336	0.144
	B) Cold Gas Cleaning (10.8% SO ₂)	SCF x 10 ³	270.5	0.00126	0.341
	C) Fugitive Emission Control	KWH	340.0	0.0105	3.570
8	Acid Plant				
	A) AIT Process Off-Gases (9% SO ₂)	SCF x 10 ³	324.5	0.0126	4.089
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095
9,10	Anode Furnace & Electrorefining	TON CATHODE	1.0	5.824	5.824
					18.570

*Not on Flowsheet

TABLE 2.8-3		ENERGY REQUIREMENTS			LEVEL 2
TBRC TM PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	TBRC - Smelting				
	A) Oxygen	TON	1.000	3.78	3.780
	B) Silica Flux	TON	0.312	0.042	0.013
	C) Coke	TON	0.004	31.50	0.126
4	TBRC - Converting				
	A) Oxygen	TON	0.1026	3.78	0.388
	B) Silica Flux	TON	0.198	0.042	0.008
5	TBRC - Finish				
	A) Oxygen	TON	0.1179	3.78	0.446
6	TBRC - Preheat, Hold & Temp. Adjust				
	A) Oxygen	TON	0.0338	3.78	0.128
7	Water Pollution Control				
	A) Lime	LB	30	0.0027	0.081
9,10	Anode Furnace and Electrorefining	TON OF CATHODE	1.0	0.016	0.016
					4.986

*Not on Flowsheet

2.8.5 Conclusions

TBRC copper smelting process allows for the control of vessel atmosphere, bath temperature and turbulence that result in control of oxidation potential, improved gas/solid/liquid contact and improved thermal efficiency. As pure oxygen is used, the fuel used in smelting is small for heating the converters and adjusting temperature. The principal fuel use is in drying. The off-gas volume is small and rich in sulfur dioxide, maximum 50%.

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2.9 NORANDA CONTINUOUS SMELTING

2.9.1 Introduction

The estimated energy requirement of the Noranda continuous smelting process to produce an equivalent 100,000 tons per year of cathode copper is 23.03×10^{11} Btu. The process configuration upon which this estimate was based is the new three continuous-smelting vessel operation at Kennecott's Garfield Smelter. This smelter was chosen because it is the only example of the Noranda system in the United States, and it is the only smelter designed from the beginning for the Noranda system. However, due to the newness of this facility, there is not significant operating data available upon which to base an energy evaluation; consequently, the energy calculations were based on data obtained from Noranda Mines Ltd.'s Horne Smelter at Noranda, Quebec. In addition to the calculated primary energy requirements, amounts of consumables (i.e., oxygen, fluxes, etc.) required to produce 100,000 tons of cathode equivalents were compiled, from which energy requirements were calculated.

The development of the Noranda continuous smelting process began in 1964 (Themelis, et al., 1972). The process is based on the thesis that the operating and capital cost of smelting and converting could be reduced by combining the conventional reverberatory smelting furnace and the batch-operated copper converting furnaces into a single vessel, performing both functions in a continuous operation. The heat from converting (oxidation of sulfur and iron) would be used in smelting the copper concentration and producing a high sulfur blister copper that would be "finished" in a converter or an anode furnace fitted with additional tuyeres. Based on this concept and laboratory experiments, a semi-commercial scale pilot plant was constructed in the latter part of 1967 and early 1968. The 35 ft. long x 9½ ft. diameter vessel was designed to smelt 100 tons per day of concentrate. Based upon the successful results of the pilot plant, an 800 tpd continuous smelting vessel, which is 17 ft. in diameter by 70 ft. long, was built at Noranda in 1973. (Hallett, 1976) Figure 2.9-1.

Since the conception of the Noranda continuous smelting process, substantial concern has been expressed as to the impact of SO_2 and particulate emissions from copper smelters upon air quality. These concerns were first formalized in the Clean Air Act and its amendments of 1970, which limit the concentration of sulfur oxides and particulates in the atmosphere and required those industries contributing to the general level of pollution to affect any changes necessary to comply with the newly enacted "Ambient Standards."

Conventional copper reverberatory-converter systems required substantial modification to meet these requirements. In fact, some felt that air quality standards could not be met with a modified reverberatory smelting system due to the substantial volumes of reverberatory gases containing about 1% to 2% SO_2 , which were difficult to treat economically. With both the

FIGURE 2.9-1 NORANDA CONTINUOUS SMELTING VESSEL WITH CONVERTER

Courtesy Kennecott Copper Corporation

smelting and converting being performed in a single vessel, the Noranda off-gases at the vessel mouth contained 16% to 20% SO_2 that could be readily treated in a single or double contact acid plants.

In 1973, Kennecott committed itself to using the Noranda continuous smelting system. (Dayton, 1979) During subsequent testing by Kennecott and Noranda, the originally conceived process producing blister was modified to produce a high-copper matte. The matte (70%-75% Cu, 5% Fe, 21% S) would then be blown to blister in a finishing converter using oxygen-enriched air to suit Kennecott concentrate. Kennecott chose the matte smelting option due to the fact that impurities in their copper concentrates, i.e., arsenic, antimony and bismuth, would be concentrated in the blister phase if the matte and metal were held in a single vessel.

Metallurgical modeling of the Noranda smelting system and the Kennecott tankhouse provided some interesting considerations. Tankhouse investigations revealed that arsenic, antimony, and bismuth, or their compounds can detrimentally affect electrolyte composition, anode slime fall, and cathode quality. In addition, the total impact of these elements might not be apparent for years since the achievement of a steady-state electrolyte composition and electrowinning operation at a large refinery can take years.

Anode and cathode copper of acceptable quality could not be assured if blister copper were to be produced directly in the smelting vessel, so it was decided to make use of a two-step matte-making and converting process.

2.9.2 Process Description

Kennecott Copper Corporation's smelter at Garfield, Utah, consists of three continuous smelting vessels and four Peirce-Smith converters. Each smelting vessel is a horizontal brick-lined cylinder 70 ft. long by 17 ft. in diameter. Feed materials (concentrates, precipitate and fluxes) are introduced into the smelting vessel through an end wall via a slinger belt onto the molten bath. Oxygen enriched air (up to 35% O_2) is injected into the bath through 63 tuyeres. At higher oxygen enrichment percentages, the heat of reaction of the oxidation of iron and sulfur is almost sufficient to melt the input materials and sustain an autogenous process. The required supplementary heat is supplied at the feed end of the reactor by a gas/oil oxygen-enriched air burner and by an oxyfuel burner at the slag end.

The predetermined matte grade in the smelting vessel is maintained by controlling the ratio of feed material to oxygen input. Control of the reactor is achieved by metering the quantities of materials fed from the bins on belt scales and metering of the oxygen and air flows. The ratio of these inputs (O_2 /concentrate) required to obtain the desired matte grade is determined by computer and displayed on a cathode ray tube. The variable speed belts and valves are then set to achieve the calculated ratio and resulting matte grade. Flux is added at a precalculated rate to maintain the desired iron to silica ratio in the slag.

Feeding is continuous resulting in a steady increase in liquid levels within the reactor. As the control of matte and slag levels is an important aspect of reactor control, these levels are periodically determined by "dip stick" measurement. Slag and matte are tapped off periodically to maintain levels within desired limits.

Matte is tapped into 260 cu. ft. ladles positioned on matte carriers. These carriers are moved into the converter aisle by a capstan winch controlled by the smelting vessel operator. The ladles are then transported to the converters by overhead crane.

Slag is tapped into 400 cu. ft. ladles and transported with Kress haulers to a slag cooling area. As reactor slag contains high copper values varying from 3% to 9%, it is slowly cooled and treated by milling and floating to recover the copper. The tailings from the slag flotation operation contain 0.3% to 0.4% copper resulting in an overall smelter recovery of about 92%.

Of the four standard 13' x 30' Peirce-Smith converters, only two converters are required for normal operations, with the third on standby and the fourth undergoing routine overhaul. Blast air is controlled on a constant volume basis at about 25,000 CFM which permits high production rates and the stabilization of gas flows to the acid plants. With a matte grade of 70% to 75% copper and the high blowing rates, converter cycle times are on the order of 2-4 hours. Fluxes and secondaries are conveyed to portable hoppers, which are transported by the converter aisle cranes, to pedestals adjacent to each converter. From here, flux is fed via a short conveyor and chute into the mouth of the converter. The converters are equipped with primary and secondary hoods, the latter being used to collect fugitive gases during out-of-stack periods and pouring operations.

A new system of hot metal haulage from the converters to the anode furnaces has been developed to cut energy requirements. Blister was formerly transported some thousand yards in open pots on tractor haulers. In the new system, the molten metal is transported in insulated torpedo cars mounted on rails. Each car has a conning tower structure to admit and empty molten metal, eliminating the shell encountered in the open pots, which required remelting. The blister copper in the anode furnace is fire refined and cast as anodes to be electro-refined at the refinery.

Process gases from continuous smelting vessels are directed via a water-cooled hood to a waste heat boiler where some heat and a portion of the particulates are removed. The stream is further cleaned in hot cyclones before entering dry electrostatic precipitators. The gas effluent of the electrostatic precipitators is sent to the acid plants.

Converter gases are also channeled through water-cooled hoods to particulate dropout chambers. The gases are next passed through three shot coolers (air-to-gas heat exchangers) for further cooling of gases and removal of particulates before reaching the dry electrostatic precipitators. Dust reclaimed upstream from the electrostatic precipitators is recycled into the smelting vessels. The electrostatic precipitator dropout is pelletized and stockpiled on a concrete pad.

Fugitive emissions are captured with secondary hooding systems on the furnaces and at tapping locations. These dilute emissions are drawn into a pair of large flues on top of the smelter building through ducts fitted with large fans. This gas flows into a single downcomer and into the mixing chamber upstream from the stack.

Control of gas flow to the 1,200 ft. stack is complex. If gases are too hot, they will burn the fiberglass liner; if they are too cold, plume buoyancy is reduced. Tailgases from the acid plants, normally less than 0.4% SO_2 , are mixed with the fugitive emissions, with waste heat from the three direct-fire boilers at the smelter power plant and the two direct-fired steam superheaters, and with hot air from the shot coolers. The entire system must be balanced to function safely and efficiently.

2.9.3 Material Balance

The estimates for material and energy requirements are based on energy models developed by Noranda Mines Ltd. for the continuous smelting vessel and converters for the matte mode with two levels of oxygen enrichment. A flowsheet for the process is presented in Figure 2.9-2. This flowsheet designates the process steps and material streams, which are summarized as a material balance in Table 2.9-1.

2.9.4 Energy Requirements

The energy requirements (Level 1) for each process step are presented in Table 2.9-2. The level 2 energy requirements based on consumables usage are presented in Table 2.9-3.

2.9.5 Discussion

The energy requirements for Noranda Continuous Smelting can be reduced by raising the oxygen enrichment level in the tuyere and burner air, by raising the matte grade in the bath and by preheating the tuyere and burner air. Perhaps the most practical of these methods of reducing the energy requirements is increasing oxygen enrichment of the tuyere and burner air. Two Noranda Simulations indicate that the fuel requirement for the reactor decreases from 3.96×10^6 Btu for an oxygen enrichment of 30% to 2.65×10^6 Btu per ton of cathode copper for an oxygen enrichment of 36%. Of course, this decrease in fuel results from an increase of oxygen usage of approximately 3100 Scf per ton of copper. Since the extra oxygen required about 5×10^6 Btu to produce, the net energy savings is about 8×10^6 Btu per ton of copper. While some studies have been performed on oxygen enrichment a definitive optimization of oxygen enrichment in the Noranda reactor has not been accomplished.

The possibility of decreasing the fuel requirements by raising the matte grade is limited due to the impurity levels in the copper concentrate as discussed earlier. In the Kennecott flow scheme the matte transferred from the reactor contains 70% copper. This level may be raised to 75% to 78% without significant impurity pick up; however, at the present time, this grade increase reduces operating flexibility without commensurate decreases in operating costs and does not appear justified.

Preheating the tuyere and burner air can reduce the energy requirements of the reactor by about 160,000 to 170,000 Btu per ton of copper produced for every 100°F the air temperature is raised. This method of reducing fuel usage may require changes in the blowers and piping at high preheat temperatures. One of the advantages of this energy saving technique is that it can use waste heat recovered from the reactor off-gas.

Another possible use of recovered waste heat is the drying and preheating of concentrates. However, if this technique is to be used to full advantage, another method of feeding the concentrates into the bath should be developed. Presently, reactor feed is dried to 7-8% moisture and then charged through the end of the vessel on the bath. If the reactor feed were dried and preheated further, the dust loading of the reactor off-gas would be increased. Consequently, if dried and preheated reactor feed is anticipated to reduce energy consumption, a method of impinging the feed into the bath (e.g., lances), or using other methods of feeding to minimize the dust loading in the off-gas must be developed.

TABLE 2.9-1			NORANDA CONTINUOUS SMELTING							
(TONS PER TON BLISTER COPPER)										
STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	WET CONCENTRATE		SLAG CONCENTRATE		RECYCLED DUST		REACTOR FLUX		DRYER CONCENTRATE	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	0.990	22.49	0.245	32.32	0.049	26.34			1.235	24.73
Fe	1.108	25.18	0.157	20.71	0.011	5.38	0.024	6.38	1.265	25.34
S	1.225	27.83	0.059	7.78	0.029	15.59			1.284	25.72
O _{Fe} *	0.020	0.45	0.049	6.46	0.003	1.61	0.002	2.12	0.069	1.38
SiO ₂	0.343	7.79	0.088	11.61	0.01	5.38	0.286	76.06	0.431	8.63
Al ₂ O ₃										
CuO + MgO										
Others	0.275	6.24	0.081	10.69	0.084	45.16	0.032	8.50	0.356	7.13
H ₂ O	0.441	10.02	0.079	10.42			0.026	6.91	0.353	7.07
SO ₂										
O ₂										
CO										
CO ₂										
N ₂										
TOTAL	4.402	100.00	0.758	100.00	0.186	100.00	0.376	100.00	4.993	100.00
TEMP. (°F)	77°		77°		77°		77°		77°	
STATE	S		S		S		S		S	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.5-1 (cont.)										
NORANDA CONTINUOUS SMELTING										
[TONS PER TON BLISTER COPPER]										
STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	REACTOR FEED		REACTOR AIR		REACTOR OFFGAS		REACTOR MATTE		REACTOR SLAG	
COMPOSITION	WT.	WT. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	1.284	22.82					1.00	69.88	0.245	8.26
Fe	1.299	23.09					0.098	6.85	1.191	40.17
S	1.313	23.34					0.294	20.54	0.059	1.99
O _{Fe} *	0.08	1.42					0.01	0.70	0.397	13.39
SiO ₂	0.727	12.92							0.717	24.18
Al ₂ O ₃										
CaO + MgO										
Others	0.472	8.39					0.029	2.03	0.356	12.01
H ₂ O	0.451	8.02			0.638	10.70				
SO ₂					1.860	31.21				
O ₂			1.392	32.95	0.111	1.86				
CO										
CO ₂					0.228	3.83				
N ₂			2.833	67.05	3.123	52.40				
TOTAL	5.626	100.00	4.225	100.00	5.960	100.00	1.431	100.00	2.965	100.00
TEMP. (°F)	770		770		2400 ⁰		2200 ⁰		2200 ⁰	
STATE	S		G		G		L		L/S	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.9-1 (cont.)

NORANDA CONTINUOUS SMELTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	REACTOR DUST		CONVERTER AIR		CONVERTER OFFGAS		CONVERTER DUST		CONVERTER FLUX	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	0.039	23.78					0.010	45.95		
Fe	0.01	6.10					0.001	4.55	0.003	4.0
S	0.026	15.85					0.003	13.64		
O _{Fe} *	0.003	1.83							0.001	1.0
SiO ₂	0.01	6.10							0.058	73.0
Al ₂ O ₃										
CuO + MgO										
Others	0.076	46.34					0.008	36.36	0.012	15.0
H ₂ O									0.005	7.0
SO ₂					0.569	43.63				
O ₂			0.343	32.70	0.029	2.23				
CO										
CO ₂										
N ₂			0.706	67.30	0.706	54.14				
TOTAL	0.164	100.00	1.049	100.00	1.304	100.00	0.022	100.00	0.079	100.00
TEMP. (°F)	2200 ^o				2300 ^o		2250 ^o		77 ^o	
STATE	L/S				G		L/S		S	

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.9-1 (cont.) NORANDA CONTINUOUS SMELTING									
[TONS. PER TON BLISTER COPPER]									
STREAM NO.	(16)		(17)		(18)		(19)		(20)
STREAM NAME	BLISTER		CONVERTER SLAG		FEED TO SLAG CLEANING		SLAG TAILS		FEED TO ACID**
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. wt. %
Cu	0.980	98.00	0.010	4.74	0.255	8.02	0.010	0.40	
Fe	0.001	0.10	0.097	45.97	1.288	40.56	1.131	45.29	
S	0.009	0.90	0.001	.47	0.060	1.89	0.001	0.04	
O _{Fe} *	0.002	0.20	0.032	15.17	0.429	13.51	0.380	15.22	
SiO ₂			0.058	27.49	0.775	24.40	0.687	27.51	
Al ₂ O ₃									
CaO + MgO									
Others	0.008	0.80	0.013	6.16	0.369	11.62	0.288	11.54	
H ₂ O									0.961 4.28
SO ₂									3.735 16.62
O ₂									2.667 11.87
CO									
CO ₂									0.324 1.44
N ₂									14.784 65.79
TOTAL	1.000	100.00	0.211	100.00	3.176	100.00	2.497	100.00	22.471 100.00
TEMP. (°F)	2250°		2250°		77°		77°		500°
STATE	L		L/S		S		S		G

*Oxygen associated with FeO and Fe₃O₄

**Including dilution air

TABLE 2.9-1 (cont.)		NORANDA CONTINUOUS SMELTING			
[TONS PER TON BLISTER COPPER]					
STREAM NO.	(21)				
STREAM NAME	COPPER ANODES				
COMPOSITION	wt.	wt. %			
Cu	0.980	99.80			
Fe					
S					
O _{Fe} *					
SiO ₂					
Al ₂ O ₃					
CaO + MgO					
Others	0.002	0.02			
H ₂ O					
SO ₂					
O ₂					
CO					
CO ₂					
N ₂					
TOTAL	0.982	100.00			
TEMP. (°F)	776				
STATE	S				

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.9-2		ENERGY REQUIREMENTS			LEVEL 1
NORANDA CONTINUOUS SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Charge Drying A) Natural Gas	SCF	800	0.001	0.800
2	Continuous Smelting A) Fuel (Natural Gas)	SCF	3,717	0.001	3.717
	B) Compress tuyere air	million SCF	0.08555	14.7	1.258
	C) Compress burner air	million SCF	0.009417	0.63	0.006
	D) Steam credit	LBS	1900	0.000955	-1.815
3	Converting A) Fuel (Natural Gas)	SCF	90	0.001	0.09
	B) Compress Tuyere air	million SCF	0.024934	14.7	0.366
4	Gas Handling A) Reactor and con- verter (75% dilution)	million SCF	0.274	2.520	0.690
	B) Fugitive gas	million SCF	10.5	0.34	3.570
5	Anode Furnace and Electrorefining	KWH	1.00	5.824	5.824
6	Slag Concentrator	KWH	124.2	0.0105	1.307
7	Material Handling	KWH	75	0.0105	0.790
8	Acid Manufacture	KWH	295	0.0105	3.096
				TOTAL	19.699

TABLE 2.9-3		ENERGY REQUIREMENTS			LEVEL 2
NORANDA CONTINUOUS SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Continuous Smelting				
	A) Silica Flux	LBS	715	0.000021	0.015
	B) Oxygen	Million SCF	0.0166	159.2	2.643
3	Converting				
	A) Silica Flux	LBS	151	0.000021	0.003
	B) Oxygen	Million SCF	0.003276	159.2	0.522
5	Anode furnace				
	A) Anode Furnace and Electrorefining	TON	1.0	0.468	0.468
6	Slag Concentrator				
	A) Reagents	LBS	1.9	0.0200	0.038
	B) Balls and liners	LBS	34.0	0.0180	0.612
				TOTAL	4.301

Another area that might result in energy savings as well as decreased use of potentially scarce natural gas or fuel oil is the mixing of coal with the reactor feed. This practice has been demonstrated in the Noranda Reactor; however, the use of coal has not been optimized nor has it totally eliminated the use of fuel oil or natural gas. In addition to the reduced use of natural gas and fuel oil, the coal igniting directly on the bath appears to improve the heat transfer characteristics.

Two other areas in which energy conservation may be accomplished are the utilization of the waste heat in the off-gas from the converters and utilizing the heat available in the reactor slags. Presently neither of these heat sources are considered sufficiently practical to be utilized in the present Kennecott operation.

2.9.6 Conclusions and Recommendations

The Noranda process is a proven pyrometallurgical process requiring about 23×10^6 Btu per ton of cathode copper for Level 1 plus Level 2 energy requirements. The energy requirements for Noranda continuous smelting can be reduced by raising the oxygen enrichment level in the tuyere and burner air, by raising the matte grade and by preheating the tuyere and burner air. Computer simulations indicate that the fuel requirement for the reactor can be decreased by about 8×10^6 Btu per ton of cathode copper for an oxygen enrichment of 36 percent. Reducing fuel requirement by raising the matte grade is limited by increased impurity levels in the copper concentrate. Preheating tuyere and burner air may reduce the energy requirements by 1.6×10^6 Btu per ton of cathode copper for every 100°F the air is heated. Waste heat could also be used to dry and preheat the concentrate. Recommendations for areas of useful research are as follows.

- Perform tests to determine the optimum oxygen enrichment to be used in the Noranda Reactor reflecting total operating costs including fuel, labor, refractories, etc.
- Demonstrate the practicality of preheating tuyere and burner air in the Noranda Reactor. Develop methods to charge dried and preheated reactor feed to the Noranda Reactor without increasing the reactor off-gas dust load.
- Perform tests to determine the optimum coal usage and to minimize the use of fuel oil and natural gas.

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2.10 MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

2.10.1 Introduction

The Mitsubishi Continuous Copper Smelting and Converting Process was developed by the Mitsubishi Metal Corporation with development work starting in 1961. The first commercial plant using this process was put into operation in 1974 at Naoshima smelter. A second plant has been built for Texas Gulf at Timmins, Ontario.

Following is a description of the process as used at Naoshima.

2.10.2 Process Description

The Mitsubishi process is a continuous process for copper smelting and converting. The major advantages of the process are production of a high grade matte (65% copper) with low level copper loss in the discard slag, low fuel requirement for the smelter, and production of relatively high sulfur dioxide strength (14-15%) gases that permits efficient sulfur recovery. All furnaces are of the stationary type, and molten products are transferred by gravity through sealed launders, which prevents spill gases and the sulfur dioxide emissions that normally accompany these transfers.

Figure 2.10-1 is a flowsheet of the process.

Naoshima uses a concentrate bedding system to produce a uniform composition of the concentrates to be smelted. The concentrate mixture is dried in a dryer unit combining a rotary and a flash dryer to a moisture content of less than 1%.

Charge materials consisting of the dry concentrates, silica flux, limestone flux, recycled converter slag, and dusts are fed into the smelter through feeding lances which inject the materials directly into the matte layer. The lances are designed so that the charge materials are provided with enough speed to be caught effectively in the molten bath in the smelter.

FIGURE 2.10-1 MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

In the furnace the charge is smelted to produce matte and slag. The slag layer is extremely thin, and the molten bath consists mostly of matte containing 60-65% copper, thus making possible a high oxygen efficiency, top blowing operation with relatively low pressure blast (Nagano, 1976). Oxygen enrichment of the air to the smelter is about 33%, and the fuel requirement for the smelter is low. Air can also be preheated for further efficiency, although this is not currently done at Naoshima.

The smelted mixture continuously overflows through an outlet hole and is transferred to the slag cleaning furnace, which is an electric furnace that separates the mixture into slag and matte. Small amounts of reducing agents, pyrites, and/or coke breeze are added to reduce further the copper content in the slag. At Naoshima, only coke breeze is added at present in order to minimize the sulfur emissions.

The slag, containing 0.5-0.6% copper, is continuously tapped through a slag overflow hole, granulated with water and discarded.

The matte is gravity-fed to the converting furnace where it is continuously converted into blister copper by blowing oxygen-enriched (23%) air and limestone flux (and cement copper as a cooling material when required), through lances.

Blister copper is siphoned out of the converting furnace, completely separated from the slag, to a holding furnace from which it is then tapped and sent to an anode furnace.

The converter slag, containing 10-20% copper, is tapped from the converter, water-granulated, dried, and then returned to the smelting furnace.

Gases from the smelting and converting furnaces contain 14-15% sulfur dioxide and are cooled to approximately 350°C through respective waste heat boilers. The gases from the boilers are combined, sent to a Cottrell precipitator for removal of dusts, and then sent to an acid plant.

Dusts can be treated in two ways, depending on the amount of impurities in the concentrates. When treating concentrates with a low content of impurities, dusts from the furnaces and precipitator are recycled back to the smelting furnace. When concentrates contain a high amount of impurities, economical recovery of dusts from the system for subsequent recovery of lead and zinc is possible (Suzuki, 1973).

Naoshima uses computer control of the process for sampling and analyzing feed materials, for adjustment of the flux and air ratios as necessary, and for adjustment of the firing rate for temperature control in the furnace.

2.10.3 Material Balance

Table 2.10-1 shows the material balance for the continuous Mitsubishi smelting and converting process.

2.10.4 Energy Requirements

Table 2.10-2 and 2.10-3 show the level I and level II energy requirements for the Mitsubishi continuous smelting and converting process.

TABLE 2.10-1 MITSUBISHI CONTINUOUS SMELTING AND CONVERTING									
[TONS PER TON BLISTER COPPER]									
STREAM NO.	(1)		(2)		(3)		(4)		(5)
STREAM NAME	WET CONCENTRATE		DRY CONCENTRATE		SILICA FLUX		LIMESTONE FLUX		SMELTER GASES
COMPOSITION	wt.	wet wt. %	wt.	dry wt. %	wt.	wt. %	wt.	wt. %	wt. wt. %
Cu	0.9944	22.5	0.9944	24.9					
Fe	1.1139	25.2	1.1139	27.8	0.0093	1.4	0.000	0.8	
S	1.233	27.9	1.233	30.8					
O _{Fe} *	0.0186	0.4	0.0186	0.5	0.004	0.6	0.0003	0.3	
SiO ₂	0.3433	7.8	0.3433	8.6	0.600	90.0	0.0022	2.1	
Al ₂ O ₃	0.1372	3.1	0.1372	3.4	0.0267	4.0			
CaO + MgO	0.1165	2.6	0.1165	2.9	0.0133	2.0	0.0575	54.9	
Others	0.0207	0.5	0.0207	0.5	0.0133	2.0			
H ₂ O	0.4419	10.0	0.0221	0.6					0.0736 1.4
SO ₂									1.777 33.7
O ₂									0.0173 0.3
CO									
CO ₂							0.0439	41.9	0.4386 8.3
N ₂									2.9648 56.3
TOTAL	4.4195	100.00	3.9997	100.00	0.6666	100.00	0.1047	100.00	5.2713 100.00
TEMP. (°F)	60		190		60		60		2200
STATE		S		S		S		S	G

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.10-1 (cont.) MITSUBISHI CONTINUOUS SMELTING AND CONVERTING

[TONS PER TON BLISTER COPPER]

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	MATTE-SLAG		COKE		DISPOSAL SLAG		MATTE		REVERT. SLAG	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	1.0484	23.5			0.0144	0.5	1.034	64.1	0.054	14.2
Fe	1.2705	28.5	0.0014	7.0	1.1256	39.2	0.1463	9.1	0.1466	38.3
S	0.3568	8.0	0.0002	1.0	0.0087	0.3	0.3528	21.9	0.0046	1.2
O _{Fe*}	0.3392	7.6	0.0003	1.5	0.3187	11.1	0.0207	1.3	0.0593	15.6
SiO ₂	0.9483	21.3	0.0008	4.0	0.9490	33.0			0.0029	0.8
Al ₂ O ₃	0.1639	3.7			0.1639	5.7				
CaO + MgO	0.2685	6.0			0.2686	9.3			0.0811	21.3
Others	0.0669	1.5	0.0172	86.5	0.0255	0.9	0.0586	3.6	0.0328	8.6
H ₂ O										
SO ₂										
O ₂										
CO										
CO ₂										
N ₂										
TOTAL	4.4625	100.00	0.0199	100.00	2.8744	100.00	1.6124	100.00	0.2813	100.00
TEMP. (°F)	2200		60		2200		2200		2372/60	
STATE		L		S		L		L		L/S

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.10-1 (cont.) MITSUBISHI CONTINUOUS SMELTING AND CONVERTING									
[TONS PER TON BLISTER COPPER]									
STREAM NO.	(11)		(12)		(13)		(14)		(15)
STREAM NAME	CONV. OFF GAS		LIMESTONE FLUX		BLISTER COPPER		SMELTER AIR		CONVERTER AIR
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. %
Cu			0.0011	0.70	0.980	98.0			
Fe					0.001	0.1			
S					0.009	0.9			
O _{Fe}			0.0004	0.30	0.0015	0.2			
S ₂ O ₂			0.0029	2.0	0.0085	0.8			
Al ₂ O ₃									
CaO + MgO			0.812	55.0					
Others									
H ₂ O									
SO ₂	0.6778	29.3					0.9306	40.9	0.5523
O ₂	0.1279	5.5							28.6
CO									
CO ₂	0.1255	5.4	0.062	42.0			1.3427	51.1	1.3807
N ₂	1.3807	59.8							71.4
TOTAL	2.3119	100.00	0.1476	100.00	1.000	100.00	2.2733	100.00	1.933
TEMP. (°F)	2100		60		2372		60		60
STATE	G		S		L		G		G

*Oxygen associated with FeO and Fe₃O₄

**Includes carbon from coke

TABLE 2.10-2 ENERGY REQUIREMENTS Level 1					
MITSUBISHI CONTINUOUS SMELTING AND CONVERTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling A) Electrical Energy	KWH	63.1	0.0105	0.663
2	Drying A) Fuel Oil	GAL	9.271	0.139	1.289
3	Smelting A) Fuel Oil B) Electrical Energy	GAL KWH	39.9 150.0	0.139 0.0105	5.546 1.575
4	Electric Slag Cleaning A) Electrical Energy	KWH	128.1	0.0105	1.345
5	Converting A) Fuel Oil B) Electrical Energy	GAL KWH	1.8 135.0	0.139 0.0105	0.250 1.418
*	Waste Heat Recovery A) Steam	LB	5213	0.0014	-7.998
*	Heating Launderers A) Natural Gas	SCF	918.0	0.001	0.918
6	Gas Cleaning A) Hot Gas Cleaning (11.4% SO ₂) B) Cold Gas Cleaning (11.4% SO ₂) C) Fugitive Emissions Control	Thous. SCF Thous. SCF KWH	256.1 256.3 85	0.00336 0.00126 0.0105	0.861 0.323 0.893
7	Acid Plant A) Smelter and Con- verter (9.0% SO ₂)	Thous. SCF	323.9	0.0126	4.081
*	Water Pollution Control A) Electrical Energy	KWH	9.0	0.0105	0.095
8,9	Anode Furnace and Electrorefining	TONS OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	17.083

* Not shown on flowsheet

TABLE 2.10-3		ENERGY REQUIREMENTS		Level 2	
MITSUBISHI CONTINUOUS SMELTING AND CONVERTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Smelting				
	A) Silica Flux	TON	0.691	0.042	0.029
	B) Limestone Flux	TON	0.106	0.104	0.011
	C) Oxygen	TON	0.201	3.78	0.760
4	Electric Slag Cleaning				
	A) Coke	TON	0.020	31.5	0.630
	B) Electrodes	TON	0.001	160	0.160
5	Converting				
	A) Oxygen	KWH	0.138	3.78	0.522
	B) Limestone Flux	TON	0.151	0.104	0.016
•	Water Pollution Control				
	A) Lime	LBS	30	0.0027	0.081
	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	2.677

*Not shown on flowsheet

2.10.5 Effect of Oxygen Enrichment on Energy Consumption

Table 2.10-4 shows the effect of oxygen enrichment on energy consumption. Increased utilization of tonnage oxygen in smelting process increases smelting rate, decreases fuel consumption and decreases off gas volume and consequently size of gas treatment facilities. The effect of oxygen enrichment to 50% has been tested (Suzuki, 1979).

2.10.6 Conclusions

The oxidant in the smelting and converting furnaces is oxygen-enriched air (30-36% oxygen in smelting and 25-28% in converting). The fuel requirement could be lowered by increasing the level of oxygen enrichment. Waste heat boilers are used to recover heat from both the smelter and converter off-gas. In the Mitsubishi process, the intermediate products, i.e., matte and slag, are transferred through sealed launders, thus eliminating the fugitive emissions that accompany matte tapping, charging of converter, and slag skimming, which are all inevitable in conventional converter operation. Consequently, the fugitive emissions problem is considerably reduced.

2.10.7 References

Kellogg, H.H. and J.M. Henderson, "Energy Use in Sulfide Smelting," Extractive Metallurgy of Copper. International Symposium on Copper Extraction and Refining, Las Vegas, Nevada, February 22-26, 1976.

"Mitsubishi Develops New Copper Smelting Process," *American Metal Market*, November 16, 1971, pp. 1-5.

"MI Process for Continuous Copper Smelting and Converting," Mitsubishi Metal Corporation publication.

"Mitsubishi Metal Builds New Copper Smelter on Tidewater," *World Mining*, Vol. 16(12), 2963, p. 60.

Nagano, T. and T. Suzuki, "Commercial Operation of Mitsubishi Continuous Copper Smelting and Converting Process," paper presented at the 105th AIME Annual Meeting, Las Vegas, Nevada, February 1976.

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Suzuki, T., I. Oyama, and T. Shibasaki, "Computer Control in Mitsubishi Continuous Copper Smelting and Converting Process," the 103rd AIME Annual Meeting, Dallas, Texas, February 1974.

Suzuki, T. and M. Goto, "Recent Improvements in Mitsubishi Process Operation," Annual Meeting of Metallurgical Society of AIME, Tucson, Arizona, December, 1979.

TABLE 2.10-4

**EFFECT OF OXYGEN ENRICHMENT ON FUEL USE IN
MITSUBISHI CONTINUOUS SMELTING AND CONVERTING**

	This Study	Mitsubishi
Smelting Furnace		
Matte Grade (%)	64.1	65
Oxygen Enrichment of Lance Blast (wt %)	40.9	58.3
Fuel Requirements (10^6 Btu/Ton Cathode Cu)	5.546	0.866
Tonnage Oxygen (Tons/Ton Cathode Cu)	0.201	0.838
Converting Furnace		
Oxygen Enrichment of Lance Blast (wt %)	28.6	32.9
Fuel Requirements (10^6 Btu/Ton Cathode Cu)	0.25	0.015
Tonnage Oxygen (Tons/Ton Cathode Cu)	0.135	0.193

Sources: Arthur D. Little, Inc., and Mitsubishi Metal Corp.

2.11 QUENEAU-SCHUHMANN CONTINUOUS SMELTING

2.11.1 Introduction

The Queneau-Schuhmann (Q-S) oxygen process was proposed by Dr. Paul E. Queneau and Dr. R. Schuhmann, Jr. Their invention covers a process and apparatus which provide continuous, autogenous conversion of sulfide ore concentrates to metal in a single reactor (Queneau and Schuhmann, 1976). Dravo has the worldwide rights to the process and apparatus for copper, nickel and cobalt concentrates. For the treatment of lead concentrates, this concept is further along the path of commercialization. Its pilot plant development has been completed at the Berzelius Works in Duisburg, Germany by Lurgi as the Q-S-L (Queneau, Schuhmann, Lurgi) process for the direct production of lead (Queneau, 1977). This pilot plant was operated in the batch mode (as countercurrent continuous flow was not possible) and the results obtained are reported to be promising (Journal of Metals, 1978). A decision was made to build a Q-S-L demonstration plant of 50,000 tons per year bullion capacity (Schwartz et al., 1980) and is now under construction.

2.11.2 Process Description

The following description is for a *conceptual* copper plant and is based on the literature and discussions with Dr. Queneau. Figure 2.11-1 is a flowsheet of the process.

The Q-S converter is a long, gently sloped vessel of circular cross section with blister copper discharge at one end and slag and gas discharge at the other. Autogenous converting is carried out by staged bottom blowing with oxygen in one main section of the furnace toward the blister copper discharge end. Slag cleaning is carried out in the other main section towards the slag discharge end by bottom blowing with a coal-sulfur dioxide-oxygen mixture, which the inventors term 'deconverting.' The vessel is mounted for slow oscillation about its horizontal axis and is tiltable for access to and maintenance of the submerged oxygen injectors. Under operating conditions the molten bath layers separate out into matte, slag, and a pool of crude copper. The vessel is sloped and stepped longitudinally for the disposition of matte and metal and to inhibit their back flow towards the slag cleaning region.

The reactor geometry, the feeding arrangement for solids and fluids and the location of the submerged injectors are designed to establish a multi-stage sequence of progressive oxidation along the length of the reactor with the highest oxygen activity at the copper discharge end and the lowest oxygen activity at the slag discharge end. To achieve this lengthwise staging, matte and slag flow countercurrently. Low grade matte from the slag cleaning region of the furnace joins fresh matte from incoming feed and the stream is progressively desulfurized to white metal and finally to crude copper, as it flows down slope towards discharge. Copper-rich slag from the metal discharge end with its magnetite load moves in the opposite direction, is progressively reduced and finally cleansed of copper by agitation with a mixture of sulfur dioxide, coal and oxygen followed by settling.

The several oxygen injectors extend through the refractory lining of the vessel and introduce oxygen below the matte-slag interface. Fluid shielding with hydrocarbon fluid is analogous to that used in oxygen steelmaking by Eisenwerk Maximilianshuette. In the Q-S process a non-combustible, protective fluid such as nitrogen or sulfur dioxide is used instead of a hydrocarbon fluid. The sulfur dioxide is obtained by recirculating cooled off-gas from the reactor and nitrogen from the oxygen plant tail gas. The use of sulfur dioxide-protected oxygen injection makes

possible the production of an off-gas analyzing up to 90% sulfur dioxide by volume if liquid sulfur dioxide is a marketable product.

Copper concentrates and necessary fluxes that have been dried down to less than 1% or less moisture are introduced over the bath through appropriate feeders. A substantial fraction, usually more than two-thirds, of total oxygen input usually accompanies the concentrates. The addition of concentrates is staged in the converting section, to assist in maintaining the desired chemical gradients along the length of the reactor. A relatively high ratio of oxygen to concentrate is used towards the metal discharge end, in contrast to lower oxygen ratios towards the slag cleaning end. Iron sulfide may be added without oxygen in the slag cleaning region.

Slow oscillation of the reactor increases the effective contact area between the reactants, by distributing incoming solid feed materials over the surface of the bath and by causing injected gases to sweep back and forth through it. Shell displacement is also conducive to increased refractory life in the submerged injector and slag line zones.

Slag cleaning is achieved by a controlled reversal of the converting reaction to achieve slag cleaning (termed deconverting) and is achieved by injecting powdered coal, sulfur dioxide and oxygen. The mixture lowers the ferric/ferrous ratio and the equivalent oxygen potential of the slag substantially and causes formation of low grade matte in situ by deconverting reactions such as

It is claimed that a slag containing 0.2% Cu can be obtained which can be discarded.

An optional feature carried out in a separate apparatus utilizes deconverting for off-gas sulfur fixation as FeS. The sulfur dioxide, together with a carbonaceous reducing agent and oxygen, is injected into molten converter slag to produce liquid iron sulfide which is cast into pigs for sale or stockpile. However, in order to fix all the sulfur in this form an additional source of iron is normally needed with most U.S. chalcopyrite concentrates.

The Q-S converter will require relatively sophisticated control instrumentation to permit close approach to steady state operation with optimum chemical and thermal conditions in all sections. Primary stoichiometric control is based on accurately metering, analyzing, and proportioning concentrates, fluxes, carbonaceous reducing agent, and gases to yield the desired products. Short term fluctuations are accommodated by accumulation or depletion of matte and metal in the converter.

A convenient criterion for this purpose is the ratio of ferric iron to total iron in the slag determined by slag sampling and analysis. The ferric iron to total iron is expected to vary from above about 0.2 at the metal discharge end, down to about 0.05 at the slag discharge end (converting copper sulfide concentrates at 1300°C). Other control means include monitoring of product weights, chemical analysis and temperatures. The temperature can be controlled by varying the quantity of recirculated sulfur dioxide, nitrogen content of oxygen, by water injection and in some cases by feeding the concentrate or flux as a slurry.

The excess heat could be more effectively used to melt cement copper or copper scrap. The reactor is designed to operate at a relatively high temperature level, under standard cooling means for refractory protection.

The high operating temperatures, which are characteristic of this process, allow the use of slags high in magnetite and silica during converting and high in silica during deconverting while maintaining the required fluidity needed for rapid reaction and clean phase separation.

A Q-S reactor capable of processing at least 1200 metric tons per day of chalcopyrite concentrate to crude copper is 20 feet in diameter and 150 feet long and has a 1% slope (Queneau, 1977). As most of the oxygen is used for flash oxidation above the bath, the independently regulatable injectors can be spaced six feet or more apart (compared to six inches between Peirce-Smith tuyeres). The gas flow rate through the individual Q-S injector can be half the usual flow rate through a Peirce-Smith tuyere. This results in the formation with minimum splash of an orderly series of moderately turbulent reaction pools separated by calmer settling zones (similar in concept to a mixer-settler configuration). In addition, ample settling basins are provided at both ends of the reactor and between the converting and deconverting operations.

2.11.3 Material Balance

Table 2.11-1 presents the material balance for the Q-S oxygen process. It is based on limited data available in literature and discussions with Dr. Queneau. In comparison to some of the other material balances presented for other pyrometallurgical processes, this material balance is more speculative and would have to be revised, if necessary, when more data become available.

2.11.4 Energy Requirements

Table 2.11-2 and Table 2.11-3 present the Level I and Level II energy requirements for the Q-S process.

2.11.5 Conclusions

The Q-S process for copper smelting is conceptual. However, laboratory scale work on phase separations is underway at United States universities. The Q-S process is perhaps a decade from commercial utilization.

As the smelting is carried out in a single reactor eliminating the need for transfer of molten intermediate products, the fugitive emissions problem is considerably reduced.

2.11.6 References

"Environmentally Clean Lead Bullion Production," *Journal of Metals*, Vol. 12, December 1978, pp. 11-12.

Queneau, P.E. and R. Schuhmann, Jr., "The Q-S Oxygen Process," *Journal of Metals*, Vol. 26(8), August 1974, p. 14.

Queneau, P.E., "Oxygen Technology and Conservation," *Metallurgical Transactions B*, Vol. 8B(3), September 1977, pp. 357-369.

TABLE 2.11-1										QUENEAU-SCHUMMANN CONTINUOUS SMELTING											
[TONS PER TON BLISTER COPPER]																					
STREAM NO.		(1)				(2)				(3)				(4)				(5)			
STREAM NAME		WFT CONCENTRATES				SILICA FLUX				DRYER OFFGAS				DRY CHARGE				OFFGAS RECYCLE			
COMPOSITION		wt.	dry wt. %			wt.	wt. %			wt.	wt. %			wt.	dry wt. %			wt.	wt. %		
Cu		0.9899	25.00											0.9899	19.53						
Fe		1.1087	28.00			0.0155	1.4							1.1242	22.18						
S		1.2275	31.00											1.2275	24.22						
O _{Fe} *		0.0186	0.47			0.0067	0.6							0.0253	0.50						
SiO ₂		0.3417	8.63			0.998	90.00							1.3397	26.43						
Al ₂ O ₃		0.1366	3.45			0.0444	4.0							0.181	3.57						
CaO + MgO		0.116	2.93			0.0222	2.0							0.1382	2.73						
Others		0.0206	0.52			0.0222	2.0							0.0428	0.84						
H ₂ O		0.440								0.4748	44.7			0.0044							
SO ₂																		0.088	88.0		
O ₂																					
CO																					
CO ₂										0.1367	12.9							0.0103	10.3		
N ₂ + Ar										0.4515	42.5							0.0017	1.7		
TOTAL		4.3996	100.00			1.1089	100.00			1.063	100.00			5.073	100.00			0.100	100.00		
TEMP. (°F)																					
STATE																					

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.11-1 (cont.) QUENEAU-SCHUHMANN CONTINUOUS SMELTING									
[TONS PER TON BLISTER COPPER]									
STREAM NO.	(6)		(7)		(8)		(9)		(10)
STREAM NAME	OXYGEN		PYRITE (FeS_2)		COAL		DISCARD SLAG		OFFGAS
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. %
Cu							0.0099	0.3	
Fe			0.0513	46.6	0.0022	2.0	1.1766	35.0	
S			0.0587	53.4	0.0029	2.6	0.0134	0.4	
O_{Fe}					0.0107	9.7	0.3639	10.8	
SiO_2					0.004	3.6	1.3437	40.0	
Al_2O_3					0.003	2.7	0.1840	5.5	
$\text{CuO} + \text{MgO}$					C 0.0804	73.1	0.1382	4.1	
Others					H 0.0014	1.5	0.0428	1.3	
H_2O					N 0.0053	4.8			0.0521 1.8
SO_2									2.5334 86.9
O_2	1.7018	98.0							
CO									
CO_2									0.2948 10.1
$\text{N}_2 + \text{Ar}$	0.0347	2.0							0.0364 1.2
TOTAL	1.7365	100.00	0.110	100.00	0.1102	100.00	3.3591	100.00	2.9167 100.00
TEMP. ($^{\circ}\text{F}$)									
STATE									

*Oxygen associated with FeO and Fe_3O_4

TABLE 2.11-1 (cont.) QUENEAU-SCHUMMANN CONTINUOUS SMELTING					
[TONS PER TON BLISTER COPPER]					
STREAM NO.	(11)				
STREAM NAME	BLISTER COPPER				
COMPOSITION	wt.	wt. %			
Cu	0.980	98.00			
Fe	0.001	1.10			
S	0.009	0.90			
O _{Fe} *	0.0015	0.15			
SiO ₂					
Al ₂ O ₃					
CaO + MgO					
Others	0.0085	0.85			
H ₂ O					
SO ₂					
O ₂					
CO					
CO ₂					
N ₂ + Ar					
TOTAL	1.000	100.00			
TEMP. (°F)					
STATE					

*Oxygen associated with FeO and Fe₃O₄

TABLE 2.11-2 ENERGY REQUIREMENTS LEVEL 1					
QUENEAU - SCHUHMAN CONTINUOUS SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Materials Handling A) Electrical Energy	KWH	63.1	0.0105	0.662
2	Drying A) Fuel Oil	GAL	10.6	0.139	1.473
4	Gas Cleaning A) Hot Gas Cleaning (78.3% SO ₂)	Thous. SCF	39.2	0.00336	0.132
	B) Cold Gas Cleaning	Thous. SCF	39.2	0.00126	0.049
5	Acid Plant A) Smelter Off Gas (9% SO ₂)	Thous. SCF	341.0	0.0126	4.297
*	Water Pollution Control A) Electrical Energy	KWH	9.0	0.0105	0.095
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	12.532

*Not shown on Flowsheet

TABLE 2.11-3

ENERGY REQUIREMENTS

LEVEL 2

QUENEAU - SCHUHMAN CONTINUOUS SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Q-S Oxygen Smelting				
	A) Oxygen	TON	1.7719	3.78	6.698
	B) Silica Flux	TON	1.131	0.042	0.048
	C) Coal	TON	0.112	25.00	2.800
•	Water Pollution Control				
	A) Lime	LBS	30.0	0.0027	0.081
6.7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	10.095

Queneau, P.E. and R. Schuhmann, Jr., "Metallurgical Process Using Oxygen," U.S. Patents: 3,941,587, March 2, 1976; 3,988,148, October 26, 1976; 3,988,149, October 26, 1976; 3,990,889, November 9, 1976.

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2.12 AMAX DEAD ROAST-BLAST FURNACE SMELTING

This section is based on analysis provided by AMAX Base Metals Research & Development, Inc.

2.12.1 Summary

The energy requirements of the AMAX Dead Roast-Blast Furnace Process were estimated to be 19.58 million Btu's per ton of cathode copper based on a proposed 30,000 ton per year of cathode copper flow sheet.

2.12.2 Introduction

In the early production of copper using a blast furnace, the smelting of calcine or ores containing both iron and copper was discouraged because a substantial proportion of the iron would tend to be reduced with the copper and a large amount of copper would be lost in the slag. In the AMAX Dead Roast-Blast Furnace Process (Rajcevic, 1977; Opie, 1979), the dead roasting of concentrates is carried out at a temperature high enough to form a calcine containing a preponderance of ferric iron oxide as evidenced by the formation of substantial amounts of copper ferrite. During smelting, the copper oxide is reduced to copper while the iron oxide is reduced only to ferrous oxide due to the short residence time in the low column shaft of the blast furnace. The ferrous oxide reacts with silica and other gangue minerals to form the slag. A good grade blister copper is produced directly and no matte is formed as long as the concentrate is roasted to less than 1.5% sulfur.

The Dead Roast-Blast Furnace Process as shown in Figure 2.12-1 consists of the following steps:

1. The sulfide concentrate is dead-roasted in a fluid bed to remove more than 97% of the sulfur in a continuous operation similar to that employed for roasting pyrite or zinc sulfide concentrates. The SO₂ gas produced (10-14%) is consistent in composition and in rate of production.
2. The roasted calcine is briquetted or pelletized with a small flux addition.

3. The agglomerates are smelted at a rapid rate in a blast furnace with a very low charge-column to produce a high-grade blister copper and a low-grade copper slag. Copper is selectively reduced from the copper-iron oxide calcine to form blister while substantially all of the iron reports in the slag.

2.12.3 Advantages of the Process

2.12.3.1 Excellent Sulfur Control

About 97% of the sulfur input to the plant is oxidized to a rich SO_2 gas of constant composition which can be converted to sulfuric acid in a relatively low cost acid plant. No matte or converter slag, saturated in SO_2 , are formed, thus the fugitive emissions resulting from transfer of these materials need not be contended with. The sulfur in the calcine feed to the blast furnace, amounting to about 3% of the sulfur in the concentrate, distributes between slag, blister and furnace gases. Sulfur can be forced into the furnace gases by enriching the blast with oxygen. However, a major portion of the sulfur in the furnace gases reacts with volatile metal oxides forming sulfates which are collectable as solids in a baghouse resulting in furnace emissions which meet current SO_2 standards.

2.12.3.2 Low Capital Costs

Compared to commercially proven matte smelting processes, capital costs have been estimated to be lower by 20 to 40 percent depending on scale. The smaller the scale, the greater the savings. These lower costs result from:

1. A simplified SO_2 gas collection system.
2. A smaller acid plant because SO_2 -containing gases from the roaster are highly concentrated, smaller in volume, and continuously generated.
3. A water-jacketed furnace design requiring no refractories in the shaft. Because of the rapid smelting rate, the furnace is small compared to other smelting furnaces.
4. Simplified plant layout because no conventional crane aisle is needed for ladle transfer. Converters are not required.
5. No need for slag cleaning if a 96% copper recovery is economically acceptable.

2.12.3.3 High Metal Recoveries

Recovery of copper and precious metals in a good grade blister is as high as 96% without slag cleaning. By cleaning the slag in either an electric furnace, or by grinding and flotation, recoveries can exceed 98%. It is believed that a simple two-stage settler with the second stage operating with a reducing gas or carbonaceous cover will result in a throwaway slag with copper losses competitive with those from conventional matte smelters. Table 2.12-1 summarizes materials balance data.

2.12.3.4 Energy Conservation

The fluid-bed roaster with a properly designed waste-heat boiler has the potential of producing enough electricity or steam to supply the major power requirements of the plant (Opie, 1979). Furthermore, because of the low charge column in the blast furnace, low-grade coke or mixtures of coke and other solid carbonaceous fuels can be used. Additional energy if needed could be recovered from the high temperature furnace off-gases. Tables 2.12-2 and 2.12-3 show an energy balance, following the procedure used by H.H. Kellogg (Kellogg, 1976).

TABLE 2.12-1 DEAD ROAST - BLAST FURNACE						
(TONS PER TON BLISTER COPPER)						
STREAM NO.	(1)		(2)		(3)	
STREAM NAME	CHALCOPYRITE CONCENTRATE		CALCINE		PELLETS	
COMPOSITION	wt.	dry wt. %	wt.	wt. %	wt.	wt. %
Cu	1.020		1.020		1.020	98.00
Fe	0.902		0.092		0.902	1.00
S	1.078		0.010		0.010	1.00
SiO ₂	0.275		0.275		0.422	
Al ₂ O ₃						
CaO + MgO						
Others	0.186		0.823		0.823	
H ₂ O						
SO ₂						
SO ₃						
CO ₂						
O ₂						
N ₂						
CO						
R						
TOTAL	3.461		3.030		3.177	
Temp (°F)	77		1562		77	
STATE	S		S		S	
					1.000	100.00
					2552	
					L	
					0.980	77
					S	100.00

TABLE 2.12-1 (cont.)		DEAD ROAST - BLAST FURNACE							
(TONS PER TON BLISTER COPPER)									
STREAM NO.	(6)		(7)		(8)		(9)		
STREAM NAME	CATHODES		ROASTER GAS		TOP GAS		SLAG		
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	
Cu	0.980	100.00					0.04		
Fe							0.892		
S							0.422		
SiO ₂									
Al ₂ O ₃									
CaO + MgO									
Others							0.578		
H ₂ O			1.892	17.69	0.01	0.30			
SO ₂			2.039	19.06					
SO ₃			0.137	1.28					
CO ₂			0.068	0.64	1.265	37.83			
O ₂			0.137	1.28					
N ₂			6.314	59.04	1.863	55.71			
CO					0.206	6.16			
AR			0.108	1.01					
TOTAL	0.980	100.00	10.695	100.00	3.344	100.00	1.732	100.00	
TEMP (°F)	77		1562		2552		2552		
STATE	S		G		G		S		

TABLE 2.12-2		ENERGY REQUIREMENTS			Level 1
AMAX DEAD ROAST - BLAST FURNACE					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Roasting				
	A) Air Compressor	Kg	8402	0.000102	0.857
	B) Fuel, Start Up Only	MILLION BTU	0.200	1.00	0.200
	C) Waste Heat Recovery	MILLION BTU	4.728	1.00	4.728
2	Pelletizing	KWH	50	0.0105	0.525
3	Smelting				
	A) Core-Coal Blend	LBS	880	0.01236	10.876
	B) Blast Compressor (Air)	Kg	2186	0.000579	1.266
	C) Top Gas Heat Recov- ery	Kg	2.14	0.23271	-0.498
4	Gas Handling				
	A) Roasted and Smelter	MILLION SCI	0.3341	2.52	0.842
5	Acid Manufacture	KWH	398.48	0.0105	4.184
6	Anode Casting	TON	1.00	1.346	1.346
7	Electrorefining				
	A) Electrical	KWH	272.35	0.0105	2.86
	B) Process Heating	LBS	1300	0.0014	1.82
TOTAL					19.54

<div>TABLE 2.12-3</div> <div>ENERGY REQUIREMENTS</div> <div>Level 2</div> <div>AMAX DEAD ROAST - BLAST FURNACE</div>					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
3	Smelting				
	A) Flux	TON	0.15	0.10	0.015
6	Melting and Refining				
	A) Flux	TON	0.10	0.10	0.010
7	Electrorefining				
	A) Acid and Reagents	TON	0.0165	0.83	0.014
				TOTAL	0.039

2.12.3.5 Flexibility

Although it is prudent to operate all units of the plant together, if desired the roaster-acid plant and briquetting or pelletizing facility could still be operated when the blast furnace is shut down and vice versa as long as some storage of furnace charge is allowed for. This makes possible the alternative of locating the roaster-acid plant-agglomerating facilities near a mine site where acid could be used for treating oxide ore. The blast furnace, in turn, could be located near a copper refinery or a cheap source of coal. The calcine agglomerates could also serve as feed for a secondary smelter.

2.12.3.6 References

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2.13 SEGREGATION PROCESS

2.13.1 Introduction

This report contains estimates of the material and energy requirements for a copper extraction process. The process is commonly called and is referred to in this report as the "segregation" process. The technique employed for copper extraction is similar to that of the TORCO process used for processing refractory oxide ores (Mackay and Gibson, 1969; Heath, 1970; Pinkney, 1969). These ores are not amenable to conventional froth flotation or to acid leaching. The segregation process considered herein, however, is modified for treatment of chalcopyrite concentrates. A detailed description of such a modified process is given in Opie, Coffin and Cusanelli (1977).

2.13.2 Process Description

The main processing features are (1) a roasting of the concentrates to oxidize the copper and iron sulfide minerals and (2) a segregation step in which the calcine from the roast is reacted with a mixture of coal and salt (NaCl) at 370°C (see Figure 2.13-1). Enough excess heat is produced

FIGURE 2.13-1 SEGREGATION PROCESS

from the roasting reactions to allow significant waste heat recovery. The roaster and segregator equipment is advantageously designed so that the temperature of the calcine can be maintained during the segregation step by heat loss from the roaster. The product from the segregation step is a carbonous material with the copper in the form of discrete particles of up to 1-mm diameter. This segregate is amenable to froth flotation. Further processing consists of segregate division, a gangue and an impure copper stream, by flotation and of electrorefining the impure copper to a wire-grade or cathode-grade product.

The major stoichiometric relationships for the processing reactions are as follows:

Roaster Operation, Process Step 1

a. Chalcopyrite combustion

b. Pyrite combustion

Copper Segregation, Process Step 2

Sodium chloride, reacting with water vapor and with the acid constituents of the gangue, produces hydrogen chloride which reacts with the copper minerals. Copper is volatilized as cuprous chloride, diffuses to the surface of the coal, and is immediately reduced by hydrogen produced from the volatile fraction of the coal or by the water-gas reaction. Hydrogen chloride is regenerated, and a new cycle of reaction begins. In this way, a small amount of sodium chloride is used to transfer the copper from the gangue and copper minerals to the surface of the coal particles (Rey, 1967).

Reaction Sequence

2.13.3 Material Requirements Evaluation

Estimates of material and energy requirements for a modified segregation process appropriate for the treatment of chalcopyrite concentrates are summarized by process step and totaled in Tables 2.13-1, 2.13-2, and 2.13-3. The process considered is based on descriptions provided by (Opie, et al., 1977) and by (Rampacek, et al., 1959). For a modern application of the segregation technique for the extraction of copper from chalcopyrite concentrates, a 98% recovery of copper is feasible (Opie, et al., 1977). Flotation, electrorefining, gas scrubbing, and sulfuric acid recovery steps are added as would constitute a complete process flowsheet. Figure 2.13-1 depicts the process steps with designators for each process element. The summary of calculated material flows is listed in Table 2.13-1.

TABLE 2.13-1		SEGREGATION PROCESS									
[TONS PER TON BLISTER COPPER]											
STREAM NO.	(1)		(2)		(3)		(4)		(5)		
STREAM NAME	CHALCOPYRITE CONCENTRATE		ROASTER FEED		CALCINE		SEGREGATE		IMPURE COPPER		
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	
Cu	1.00	25.00	1.176	24.09	1.176	26.77	1.176	27.52	0.980	83.97	
Fe	1.118	27.95	1.559	31.93	1.559	35.50	1.559	36.48	0.01	0.86	
S	1.245	31.13	1.245	25.50	0.010	0.23	0.010	0.23	0.01	0.86	
C			0.020	0.41			0.186	4.35	0.167	14.31	
SiO ₂											
Al ₂ O ₃											
CaO + MgO											
Others	0.637	15.92	0.882	18.07	1.647	37.50	1.343	31.42			
H ₂ O											
SO ₂											
SO ₃											
O ₂											
CO											
CO ₂											
N ₂											
TOTAL	4.00	100.00	4.882	100.00	4.392	100.00	4.274	100.00	1.167	100.00	
TEMP. (°F)	70°		70°		1600°		1600°		70°		
STATE	S		S		S		S		S		

TABLE 2.13-1 (cont.) SEGREGATION PROCESS									
[TONS PER TON BLISTER COPPER]									
STREAM NO.	(6)		(7)		(8)		(9)		(10)
STREAM NAME	ANODES		CATHODES		ROASTER GAS		TAILINGS		MIDDINGS
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	
Cu	0.980	100.00	0.980	100.00			0.020	0.89	19.73
Fe							1.118	50.00	49.44
S									
C									0.02
SiO ₂									
Al ₂ O ₃									
CaO + MgO									
Others							1.098	49.11	0.255
H ₂ O					0.667	21.95			28.59
SO ₂					2.412	0.89			
SO ₃					0.098	6.07			
O ₂					0.225	0.62			
CO									
CO ₂					0.069	2.05			
N ₂					7.520	68.42			
TOTAL	0.980	100.00	0.980	100.00	10.991	100.00	2.236	100.00	0.892
TEMP. (°F)	70°		70°		1600°		70°		70°
STATE	S		S		G		S		S

TABLE 2.13-2		ENERGY REQUIREMENTS			Level 1
SEGREGATION PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Roaster				
	A) Waste Heat Recovery	BTU	-4.58	1.00	-4.58
	B) Fuel (start up only)	BTU	0.2	1.00	0.20
2	Segregator				
	A) Coal	TON	0.33	25.00	8.25
3	Flotation				
	A) Electrical	KWH	72.5	0.0105	0.736
4	Melting, Refining and Anode Casting				
	A) Heating and Melting (Fuel Oil)	GAL	19.5	0.150	2.925
	B) Polling Gas	SCF	225	0.0010	0.225
5	Electrorefining				
	A) Electrical	KWH	272	0.0105	2.856
	B) Process Heating (Steam)	LBS	1300	0.0014	1.820
6,7	Gas Scrubbers				
	A) Electrical	KWH	62	0.0105	0.651
	Ancillary Loads				
	A) Electrical	KWH	50	0.0105	0.525
8	Acid Plant	KWH	398.48	0.0105	4.184
*	Fugitive Emissions Control	KWH	340.00	0.0105	3.570
				TOTAL	20.862

TABLE 2.13-3

ENERGY REQUIREMENTS

Level 2

SEGREGATION PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Segregator A) NaCl	TON	0.022	0.49	0.011
3	Flotation A) Reagents	LBS	3.26	0.02	0.065
4	Melting, Refining and Anode Casting A) Flux	TON	0.1	0.76	0.076
5	Electrorefining A) Acid and Reagents	TON	0.0165	0.83	0.014
	B) Glue	TON	0.00003	40.00	0.0012
	C) Thiourea	TON	0.00003	40.00	0.0012
	D) Hydrochloric Acid	TON	0.000002	9.25	0.00002
				TOTAL	0.168

2.13.4 Energy Requirements Evaluation

A summary for the energy requirements for the process is listed in Tables 2.13-2 and 2.13-3. The energy evaluation is based on the material summary presented above. Table 2.13-2 is a listing of "Level-1" requirements. The listing is on a modular basis in sequential processing order. At "Level 1," the chemicals and other consumables in the process are not included except for the fuel used. Table 2.13-3 is a listing of "Level 2" energy requirements — chemicals, fluxes, refractories and other consumables used on a continuous basis in association with the process. Energy equivalent estimates are included in the tables and the equivalent fuel requirements are calculated and summed. This information supports all values given in the tables, but is too extensive for inclusion as footnotes.

The energy requirements presented in Tables 2.13-2 and 2.13-3 are evaluated with the consideration that the process is operated in a conventional manner. The totals are termed "operational" in the above summary table. The operational estimate does not include special processing features for economizing to reduce energy consumption. For an estimate that does consider special features for energy reduction (a "theoretical" estimate), the recovery of coal may be considered. Since less than half of the coal fed to the segregator is consumed in the copper recovery reactions (37%), a significant energy reduction would occur by the recovery and recycle of unreacted coal. The potential for Level-1 energy requirement reduction is 5.43 million Btu/ton product (calculated from energy equivalent values given in Table 2.13-2). The resulting Level-1 theoretical energy requirement is 8.03 million Btu/ton product.

2.13.5 Discussion

Historically, the segregation step was discovered in 1923 during experimental work in which oxide ores of copper were being treated with coal to reduce the copper to the metallic state prior to ammoniacal leaching (Moulden and Tapin, 1928; Rey, 1935 and 1936). By 1931, the technique had been further developed by the construction of two plants in Africa for treating oxide ores. One plant was built at Southern Rhodesia by the Minerals Separation Company (50 tons of ore/day). The other plant was built at Katanga in the Belgian Congo by the Union Miniere de Haut Katanga (350 tons of ore/day). Recovery was reported as about 87% on the Minerals Separation Company plant. No data is available on the Union Miniere de Haut Katanga plant. Both plants closed after a short period of operation because of mechanical and economical difficulties (Rampacek, et al, 1959; Rey, June 1967 and March 1968).

Since the early development of the segregation technique, many investigators have been interested in the perfection of methods and equipment (Rey, 1935, 1936, 1967) evaluated the treatment of low-grade oxide ores and mixed sulfide-oxide ores. Sutulov (1963) has evaluated the factors of time, temperature, and coke and salt percentages. His results show that the segregation process could be an alternative to beneficiation. McKinney and Evans (1963) have demonstrated that it is technically feasible to apply the process to oxide ores in a direct-fired rotary kiln; thus, rendering the method more attractive for commercial application. The effects of different salts and various additions of salts on the volatilization of copper was investigated by McKinney and Waddleton (1962) and Marcuson (1978). Pollard and Pease (September 1960, March 1961) report on a 1-ton/hour pilot plant constructed by the Lampa Mining Co., Ltd. at the Berenguela Mine, Peru. Silver was also extracted, and the plant development was considered as generally suitable for any ore that may be segregated. Pinkney and Plint (1967, 1968), Pinkney (1969), Mackay and Gibson (March 1968, December 1968 and September 1969), and Heath (1970) report on the treatment of refractory ores with the TORCO segregation process developed in South Africa. Freeman (1960, 1961) reports on the processing of silicate ores at the Hecla Mining Co. and El Paso Natural Gas Co., Lakeshore Copper Property, Arizona.

Highly significant aspects in the evaluation of energy requirements for the segregation process are the recovery of waste heat from the roaster, the consumption of coal in the segregator, the melting-refining-anode-casting energies, and the energy for electrorefining. The first two items, heat recovery and coal consumption, are sensitive to chalcopyrite concentrate composition and, to some extent, on process design considerations. The latter two items are mainly dependent on the production rate of cathodes. The sensitivity of the processing energy requirements is such that a concentrate composition change resulting in a 10% reduction of waste heat recovery increased the energy requirements by 6%.

2.13.6 Conclusions and Recommendations

As evidenced by the process report by Opie, et al (1977), the Opie and Coffin patent (1974) on roasting and solid state segregation reduction of sulfide concentrates, and the many other researchers referenced, a segregation process for the recovery of copper from chalcopyrite concentrates is discernible. The processing scheme and material flows are well defined from past research efforts. Based on this earlier information, the evaluation presented in this study clearly defines the process energy requirements. A presentation of a breakdown of the energy assessment and an evaluation of a "theoretical" energy total provides an indication of the extent of possible variances in energy requirements.

The total energy requirements for an operational process that includes no special features for economizing is 21.64 million Btu/ton product with 21.47 million Btu/ton product provided in the form of direct fuels, steam and electrical power consumption. A "theoretical" estimate considering the recovery and recycle of unreacted coal indicates the process has the potential for total energy requirements of 16.21 million Btu/ton product. The process energy requirements are sensitive to chalcopyrite concentrate composition in that changes in composition would affect the waste heat recovery from the roaster (e.g., lower sulfur levels) or increase coal consumption (e.g., greater fraction of gangue or reactions with constituents of the gangue).

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2.14 THERMO ELECTRON CHLORINATION PROCESS

2.14.1 Introduction

The following is a brief description and evaluation of the chalcopyrite chlorination process reported by Thermo Electron Corporation to U.S. Department of Energy (Thermo Electron, 1978).

2.14.2 Process Description

Chalcopyrite concentrates are reacted with chlorine gas, forming cuprous chloride, ferric chloride, and elemental sulfur. The cuprous chloride is drawn off the lower part of the reactor in molten form and electrolyzed to copper metal and chlorine gas for recycle. Ferric chloride and elemental sulfur vapors pass out the top of the reactor and are condensed to liquids and separated by decantation. The ferric chloride is then burned with oxygen to Fe_2O_3 , chlorine again being recycled to the main reactor. Principal reactions are as follows:

2.14.3 Material Balance

A schematic flowsheet of the process is presented in Figure 2.14-1 and a material balance in Table 2.14-1. The material balance differs somewhat from the Thermo Electron report, as it is based on 1,000 tons of copper cathodes from feed assaying 25 percent copper, 29 percent iron, and 31 percent sulfur. Their flowsheet is based on 1,442 tons of concentrate assaying 24 percent copper, 21 percent iron, and 24 percent sulfur. Another difference is that the flowsheet given here omits a step where trace amounts of cupric chloride (CuCl_2) are water-leached from the gangue leaving the reactor. This step is shown in the Thermo Electron report but is not included in their material or energy balances. Note that 100 percent recovery of all products and 100 percent utilization of all reagents is assumed. The process is mostly conceptual at this time and is in a very early stage of development.

STREAM LEGEND

SOLIDS	
LIQUID	
MOLTEN	
GAS	
MINOR	

FIGURE 2.14-1 THERMO-ELECTRON CORP. PROCESS

TABLE 2.14-1
IDEAL MATERIAL BALANCE FOR 1000 TONS COPPER

<u>Stream No.</u>	<u>Description</u>	<u>Tons/1000 Tons Copper</u>
1	Feed 25% Cu, 29% Fe, 31% S, 15% gangue	4000
2	Gangue from reactor to waste	600
3	Chlorine gas recycled from oxidizer (17)	2210
4	Molten CuCl ₂ , feed to electrolysis	1560
5	Chlorine from cell, recycled to reactor	560
6	Copper cathodes	1000
7	Offgas containing ferric chloride and sulfur vapors	8350
8	Liquid FeCl ₃ and S° recycled to reactor	3740
9	Liquid FeCl ₃ and S° to decanter	4610
10	Offgas to scrubber	-
11	Offgas to atmosphere	-
12	Water to scrubber	-
13	Scrubber underflow to waste	-
14	Molten sulfur product	1240
15	Liquid FeCl ₃ to oxidizer	3370
16	Oxygen gas to FeCl ₃ oxidizer	440
17	Chlorine from oxidizer, recycled to reactor (3)	2210
18	Fe ₃ O ₄ product	1600

2.14.4 Energy Requirements

Theoretically, the only energy inputs to the process are for electrolysis of cuprous chloride and for manufacture of oxygen to burn the ferric chloride. Thermo Electron reports that 11.0 megawatts is used for electrolytic production of 346 tons per day copper metal at 50 percent cell efficiency and 1.4 megawatts for manufacture of 116 tons per day separated oxygen. This is 763 kilowatt hours per ton of copper and 290 kilowatt hours per ton of oxygen. MSRD's analysis shows 774 kilowatt hours per ton of copper in electrolysis (a good check) but 405 kilowatt hours per ton of oxygen. The 405 figure was given to us by AIRCO and is for a new plant producing 150 tons per day oxygen gas at 95.5 percent purity, 200 pounds per square inch. Bringing everything to the consistent basis of the flowsheet in Figure 2.14-1 and using a conversion factor of 10,000 Btu's per kilowatt hour, the theoretical energy requirements are as follows:

TABLE 2.14-2

THERMO ELECTRON CHLORINATION PROCESS

LEVEL 1 — THEORETICAL ENERGY REQUIREMENT

	Btu per Ton Copper Thermo Electron	MSRD
Electrolysis	7.6×10^6	7.7×10^6

TABLE 2.14-3

THERMO ELECTRON CHLORINATION PROCESS

LEVEL 2 — THEORETICAL ENERGY REQUIREMENT

	Btu per Ton Copper Thermo Electron	MSRD
Oxygen Manufacture	1.3×10^6	1.8×10^6

This discrepancy is not major. However, since the chlorination process is being compared to actual operating processes, some practical assumptions will be made which will increase the real energy requirements. These assumptions are 90 percent recovery of copper, 10 percent makeup of chlorine, and 10 percent excess oxygen. In addition, 10 percent of the total energy will be assumed for operation of the scrubber and miscellaneous equipment.

Chlorine is manufactured in diaphragm cells at an energy cost of about 2.440 kilowatt hours per ton. At 10 percent excess and 90 percent copper recovery (see Figure 2.14-1 and Table 2.14-1), about 0.31 tons of chlorine will have to be made up per ton of copper recovered. This requires 756 kilowatt hours (7.6×10^6 Btu) per ton of copper recovered.

Energy requirements are now estimated as follows:

TABLE 2.14-4

THERMO ELECTRON CHLORINATION PROCESS

LEVEL 1 — ASSUMED OPERATIONAL ENERGY REQUIREMENTS

	Btu per Ton Copper
Electrolysis	8.6×10^6
Miscellaneous	1.8×10^6
Total	10.4×10^6

TABLE 2.14-5

THERMO ELECTRON CHLORINATION PROCESS

LEVEL 2 — ASSUMED OPERATIONAL ENERGY REQUIREMENTS

	Btu per Ton Copper
Oxygen Manufacture	2.2×10^6
Chlorine Manufacture	7.6×10^6
Total	9.8×10^6

Hypothesized in the Thermo Electron report is an energy recovery of 347 kilowatt hours per ton of copper by converting the heat from the ferric chloride-sulfur condenser to electric power. MSRD does not believe this to be feasible. It is difficult to evaluate the amount of ideal heat available, because it is not certain if sulfur is condensing from S^0 , S^0 , S^1 , S^2 , etc. Also, some of the specific heats are uncertain. Our judgment is that at most 3.0×10^6 Btu's per ton of copper might be available on an ideal basis (see Reactions 1 and 2 and Energy Balance Item No. 6). But conversion of this heat to electric power would be very inefficient due to the low temperature. A factor of 10,000 Btu's per kilowatt hour is reasonable for fossil-fuel steam power plants but unrealistic for utilization of waste heat at only 585 degrees Kelvin. A better figure would be about 24,000 Btu's per kilowatt hour, giving only 14 percent heat recovery efficiency or 0.4×10^6 Btu's per ton of copper. This is negligible in the energy balance.

No heat recovery at all should be assumed for this process in its present stage of development.

2.14.5 Discussion

Although 20 million Btu's per ton of copper is a relatively low energy requirement, the chlorination process may not be a practical approach. Most of the key steps have apparently not been demonstrated even in the laboratory. Of particular concern are the flow of solids and gas through the chlorination reactor, the drawoff of molten cuprous chloride ($CuCl$) from the reactor, molten salt electrolysis of cuprous chloride, separation of ferric chloride ($FeCl_3$) from sulfur (S).

scrubbing of the offgas, and production of iron oxide (Fe_2O_3) by burning ferric chloride with oxygen. It is not known if all these steps, although theoretically interesting, will work with acceptable efficiencies, purities, etc. Dealing with the corrosive environments presented by chlorine gas and metal chlorides at elevated temperatures will also be challenging from the practical standpoint.

2.14.6 Reference

Dean T. Morgan, James Schad, Alexandra Zakak and Dae Sik Kim (Consultant). Thermo Electron Corporation. "Chlorine Extraction Processes for Energy-Conserving Recovery of Non-ferrous Metals." 101 First Avenue, Waltham, Mass. 02154. Contract No. EC-77-C-02-4532, U.S. Department of Energy, Director for Industrial Conservation, 20 Massachusetts Avenue, Washington, D.C. 20545, December 1978. Report Number TE4228-97-79.

2.15 OXY-FUEL REVERBERATORY SMELTING

2.15.1 Introduction

This variant on the matte smelting process was developed in Chile during the years after the Kennecott Calteones smelter had been nationalized, and is well described in papers presented at AIME meetings in New York and Atlanta (Schwarze, March 1977; Schwarze et al. March 1977 and Achurra et al March 1977).

Kennecott had built an oxygen plant at the smelter before relinquishing their facilities and the new management sought to utilize this to increase productivity of the plant. Over a period of several years they gradually replaced air-oil burners by oxygen-oil burners, until finally the reverberatory furnaces operated on oxygen-oil exclusively. Production rate doubled, oil consumption fell to half the old figure and while roof life decreased, its life per ton of product remained constant. Due to the large decrease in dilution by nitrogen, SO_2 content of the reverb gases was in the 8-10% range, ample for acid manufacture. Therefore the process is presented here as offering another option for a plant trying to meet environmental standards with minimum capital expenditure.

2.15.2 Process Description

The process outlined on the attached flow sheet, Figure 2.15-1, is almost identical to the standard reverb smelting process in that converter slags are returned to the reverb for cleaning, eliminating the costly slag cleaning methods needed by other new processes. While this is perhaps not essential, the concentrates were dried separately at Calteones, since they had been doing this before. It is doubtless a more efficient way to use energy since the waste gases from this operation leave at a lower temperature than from the reverb.

Referring to the tabulation of streams in the Reverberatory Furnace Smelting Section, Stream (1) has had the H_2O eliminated in the dryer. Stream (2) Silica flux, remains unchanged, as do (4) Reverb slag; (6) Matte; (7) Converter flux; (8) Converter slag; (9) Converter off-gas; (10) Converter air; and (11) Blister copper.

It is only streams (3) NG & Air and (5) Reverb off-gas that change significantly, and are shown below. For the fuel input, oil is used, and 80% of the required oxygen for its combustion is supplied as technically pure oxygen; the rest is supplied by air infiltrating into the furnace. The latter also supplies the needs for oxidizing labile sulfur. In the Reverb off-gas, Stream 5, sulfur from fuel oil and from oxidation of labile sulfur are combined to estimate total gas volume based on an analysis of 9% SO₂ by volume, which explains the presence of some free oxygen in addition to the other gas species. This type of correction was not made in the Offgas Stream for the air-natural gas reverb. In spite of the omission of excess air in that tabulation the decrease in total gas is dramatic, and fully explains the decreased fuel requirements.

2.15.3 Comparison of Reverb Gas Streams with Oil Oxygen and Air Natural Gas

Item	Air Natural Gas		Oil Oxygen	
	(3) tons	(5) tons	(3) tons	(5) tons
H ₂ O	1,208	1,606	251	251
SO	—	1,239	13	1,252
O ₂		?		498
CO ₂	1,584	1,584	810	810
N ₂	7,379	7,379*	537	4,193
Total	10,171	11,807		7,004
Percent SO ₂	2-3			9

* A sulfur balance was not used in conjunction with sulfur analysis to estimate dilution air. So the reported nitrogen is surely low.

2.15.4 Energy Requirements

Table 2.15-1 presents the Level I energy requirements for Oxy-Fuel reverberatory smelting. The analysis does not include oxygen enrichment of converter air. However, as an oxygen plant is present one would expect oxygen enrichment of converter air as well.

Table 2.15-2 presents the Level II energy requirements for Oxy-Fuel reverberatory smelting.

2.15.5 Conclusion

The replacement of air-oil burners by oxy-fuel burners leads to a significant decrease in fuel usage in smelting. The effect of oxy-fuel operation on NO_x emissions is not known and needs to be studied.

2.15.6 References

Herman Schwarze: Oxy-fuel burners save energy at El Teniente's Caltones smelter, World Mining, May 1977, pp. 58-61.

H. D. Schwarze, G. B. Vera and O. F. Pino: Use of new technologies at Caltones smelter, TMS Paper No. A77-90, TMS-AIME New York, 1977.

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TABLE 2.15-1

ENERGY REQUIREMENTS

Level 1

OXY FUEL SMELTING

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
*	Materials Handling				
	A) Electrical Energy	KWH	69.1	0.0105	0.726
1	Dryer				
	A) Fuel	GAL	0.7	0.139	1.350
2	Reverb. Smelting				
	A) Fuel: Fuel Oil	GAL	66.7	0.139	9.270
	B) Electrical Energy	KWH	60.8	0.0105	0.638
	C) Waste Heat Recovery: Steam	LBS	2650	0.0014	-3.710
3	Converting				
	A) Electrical Energy	KWH	155	0.0105	1.628
	B) Fuel: Fuel Oil	GAL	3.6	0.139	0.500
4	Gas Cleaning				
	A) Hot Gas Cleaning				
	1- Reverb. (9% SO ₂)	Thous. SCF	166.8	0.00336	0.560
	2- Converters (7% SO ₂)	Thous. SCF	211.8	0.00336	0.717
	B) Cold Gas Cleaning				
	1- Reverb.	Thous. SCF	166.8	0.00126	0.210
	2- Converter	Thous. SCF	211.8	0.00126	0.267
	3- Fugitive Emissions Control	KWH	340.0	0.0105	3.570
5	Acid Plant				
	A) Reverb. & Converter Gas (7.9% SO ₂)	Thous. SCF	378.6	0.0119	4.505
*	Water Pollution Control				
	A) Electrical Energy	KWH	9.0	0.0105	0.095

TABLE 2.15-1 (cont.) ENERGY REQUIREMENTS Level 1					
OXY FUEL SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	26.145

*Not shown on flowsheet.

TABLE 2.15-2		ENERGY REQUIREMENTS			Level 2
OXY FUEL REVERBERATORY					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Reverb. Smelting				
	A) Silica Flux	TON	0.518	0.042	0.022
	B) Oxygen	TON	0.498	1.78	1.882
3	Converting				
	A) Silica Flux	TON	0.437	0.042	0.018
4	Water Pollution Control				
	A) Lime	EBS	30.0	0.0027	0.081
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	2.471

*Not shown on Flowsheet

2.16 OXYGEN SPRINKLE SMELTING

2.16.1 Introduction

The oxygen sprinkle smelting process concept proposed by P. E. Queneau and R. Schuhmann, Jr. consists of modifying existing reverberatory furnaces by the installation of oxygen sprinkler burners. The oxygen sprinkler burner was developed in collaboration with Professor H. Richter of Dartmouth College. We understand that the burner has been designed, manufactured and a full scale prototype has been tested for solids flow and mixing at ambient temperatures. Full scale hot testing of the sprinkler burner began in November 1980. The sprinkler burner has been installed in the roof of an operating reverberatory furnace at the Morenci branch of Phelps Dodge Corporation and is being tested at this time. Under conditions of limited head room the design offers excellent gas-liquid-solid contact of reactants and dispersion of particulates over a wide area. The modification transforms an existing reverberatory furnace into an oxygen flash smelting unit with improved performance with respect to productivity, operating costs, energy conservation, higher metal recovery and environmental control.

2.16.2 Process Description

The process flowsheet is presented in Figure 2.16-1 and an isometric view of the oxygen sprinkle smelting furnace is presented in Figure 2.16-2.

An existing reverberatory furnace can be modified for "oxygen sprinkle smelting" by closing all unnecessary openings and installing four sprinkler burners. The burners are designed to accomplish several important functions within the existing structure. These include (a) the intimate mixing of finely divided concentrates with the oxygen-rich gas for flash smelting, and (b) uniform sprinkling of particulates over most of the bath surface. Provision is made for the admixture of a small percentage of pulverized coal with the solids feed, normally only to the burner nearest to the slag-tapping end to produce a lower grade matte for slag cleaning purposes. The slag is cleaned prior to discharge by drenching it with a shower of low grade matte produced by flash melting of the copper concentrates. Thus, in addition to flash oxidation of the sulfide concentrate, the burner design aims at optimizing interphase heat and mass transfer and the control of heat and mass distribution throughout the furnace volume. The accomplishment of these aims converts the reverberatory furnace which is primarily an inefficient melting reactor into a relatively efficient and flexible chemical reactor.

In addition to modifications of the reverberatory furnace, a concentrate dryer and an oxygen plant have to be added. Converting is carried out in Peirce-Smith converters as in conventional reverberatory smelters. The blister copper from converting is cast into anodes and finally electro-refined to produce cathode copper.

2.16.3 Energy Requirements

Table 2.16-1 presents the Level I energy requirements for "oxygen sprinkle" reverberatory smelting. The analysis does not include oxygen enrichment of converter air. However, as an oxygen plant is present, one would expect enriched air to be used for converting as well.

Table 2.16-2 presents the Level II energy requirements for "oxygen sprinkle" reverberatory smelting.

FIGURE 2.16-2 ISOMETRIC VIEW OF OXYGEN SPRINKLE SMELTING FURNACE
(CONVERTED CONVENTIONAL COPPER REVERBERATORY FURNACE)

TABLE 2.16-1		ENERGY REQUIREMENTS			LEVEL 1
OXYGEN SPRINKLE SMELTING					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
*	Materials Handling				
	A. Electrical Energy	KWH	69.1	0.0105	0.726
1	Dryer				
	A. Fuel: Fuel Oil	GAL	12.4	0.139	1.724
2.	Reverb Smelting				
	A. Fuel: Coal	TON	0.055	25.0	1.375
	B. Electrical Energy	KWH	60.8	0.0105	0.638
	C. Waste Heat Recovery	LBS	780	0.0014	-1.092
3	Converting				
	A. Electrical Energy	KWH	120	0.0105	1.260
	B. Fuel: Fuel Oil	GAL	2.3	0.139	0.230
4	Gas Cleaning				
	A. Hot Gas Cleaning				
	1- Reverb	THOUS. SCF	24.0	0.00336	0.081
	2- Converters	THOUS. SCF	167.3	0.00336	0.562
	B. Cold Gas Cleaning				
	1- Reverb	THOUS. SCF	24.0	0.00126	0.030
	2- Converters	THOUS. SCF	167.3	0.00126	0.211
	3- Fugitive Emissions Control	KWH	340	0.0105	3.57
5	Acid Plant				
	A. Reverb and Converter Gas (dilute to 9%)	THOUS. SCF	310.3	0.0126	3.909

TABLE 2.16-1 (Cont.)

ENERGY REQUIREMENTS
OXYGEN SPRINKLE SMELTING

Level 1

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
*	Water Pollution Control				
	A. Electrical Energy	KWH	9.0	0.0105	0.095
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	5.824	5.824
				TOTAL	19.143

TABLE 2.16-2		ENERGY REQUIREMENTS OXYGEN SPRINKLE SMELTING			LEVEL 2
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Reverb Smelting				
	A. Silica Flux	TON	0.375	0.042	0.016
	B. Oxygen	TON	0.716	3.78	2.706
3	Converting				
	A. Silica Flux	TON	0.290	0.042	0.012
4	Water Pollution Control				
	A. Lime	LBS	30.0	0.0027	0.081
6,7	Anode Furnace and Electrorefining	TON OF CATHODE COPPER	1.0	0.468	0.468
				TOTAL	3.283

2.16.4 Discussion

The "oxygen sprinkle" reverberatory smelting concept results in decreased energy consumption due to flash oxidation of concentrates, with the use of oxygen and the energy savings due to decreased gas handling requirements. This analysis has been based on the available published information (Queneau and Schuhmann, 1979). Experimental data are needed to demonstrate adequate refractory life under actual operating conditions and to establish the quantity of air infiltration to the reverbs and the extent to which this will dilute the strong sulfur dioxide produced at the burner.

2.16.5 References

Queneau, P.E., and R. Schuhmann, Jr.. "Metamorphosis of the Copper Reverberatory Furnace: Oxygen Sprinkle Smelting," *Journal of Metals*, December 1979, pp. 12-15.

3.0 HYDROMETALLURGICAL PROCESSES FOR TREATING CHALCOPYRITE CONCENTRATES

3.1 INTRODUCTION

The copper industry of the United States has in recent years been impacted by regulatory requirements relative to emissions standards. Of special concern have been sulfur, trace metal and particulate emissions. As a consequence, hydrometallurgical processing of copper concentrates has continued to attract attention. The ability of hydrometallurgical processes to scale-down to relatively small size is an attractive feature but capital and operating costs generally exceed those of new pyrometallurgical processes. Hydrometallurgical processes employing electrowinning are energy intensive and in general fail to compete in large scale operation with pyrometallurgical processes. Nevertheless, advantages in the handling of waste residues and the ability to compete for small scale operations continues to spur interest in the potential application of hydrometallurgical processes.

This study concerns itself with the energy requirements of selected, proposed or commercialized hydrometallurgical processes. These processes are sub-divided into four process categories as follows:

- a) chloride leaching;
- b) ammoniacal leaching;
- c) acid leaching; and
- d) pre-treated concentrates.

Of the chloride processes the Cymet Ferric Chloride Process and the Duval Process are examples. The Duval (CLEAR) Process is in operation and reportedly treated twenty-five percent of all of Duval's concentrate production in 1973^a. Unfortunately we were not able to obtain sufficient information on the CLEAR process to include in this study. The extensively piloted Cymet Cupric-ferric chloride leach is included in this analysis. The Arbiter process is the only process developed using ammoniacal leaching chemistry. The commercial plant constructed in 1974 is not in operation currently. Two acid leach processes, the Nitric-Sulfuric Acid Leach Process developed by Kennecott Copper Company and the DuPont Company is considered as is also the Ferric Sulfate-Sulfuric Acid leach process proposed jointly by the University of Utah and Martin Marietta resulting from an NSF/RANN supported project.

Processes which include pre-treatment of concentrate prior to leaching are the Roast-Leach-Electrowin (RLE) Process, the Sulfite-Reduction Process and the Sherritt-Cominco Copper Process. The RLE, Lakeshore plant closed when the depressed price of copper rendered it uneconomic for continued operation. Most of the hydrometallurgical processes reviewed here use electrowinning. Exceptions are the Cymet process utilizing hydrogen reduction and the Sulfite-Reduction processes utilizing ammonium bisulfite as the reductant. Table 3.1-1 lists the above processes and includes the reviewing organization and such features as lixiviant, separation (purification), reduction and residues characteristic of each process. The reviewing sub-contractors are Arthur D. Little (ADL), Mountain States Research and Development (MS), and Ford Bacon and Davis (FBD).

a) Report given by R. W. Livingston at the Copper Hydrometallurgy Economics Panel Session, National A.I.M.E. Meeting, New Orleans, February, 1979.

TABLE 3.1-1 HYDROMETALLURGICAL PROCESSES INCLUDED IN THE ENERGY ANALYSIS

Process Name	Reviewing Sub-Contractor	Lixiviant(s)	Method of Separation-Purification	Reduction	Residue (other than undissolved residual solids)
Cymet Ferric Chloride Leach	ADL	cupric-ferric chlorides	centrifugal separation of crystallized cuprous chloride	fluidized bed hydrogen reduction	hydronium jarosite-ferric oxide
Arbiter Ammonia Leach	ADL	ammonia, oxygen	counter current deam-tation (CCD) - solvent extraction	Electrowinning	gypsum, ferric oxide
Roast-Leach-Electrowin	MS	spent electrolyte	CCD	Electrowinning	iron oxides
Nitric-Sulfuric Acid Leach	FBD	nitric acid, sulfuric acid, oxygen	filtration	Electrowinning	ammonium jarosite, elemental sulfur
Sherritt-Cominco	ADL	Sulfuric acid, oxygen	filtration	Electrowinning	ammonium jarosite, ferric oxide, elemental sulfur
Ferric Sulfate-Sulfuric Acid	ADL	Ferric sulfate, oxygen	filtration	Electrowinning	ammonium jarosite, gypsum, elemental sulfur
*Electroslurry	ADL	Ferric sulfate, oxygen	filtration	Electrowinning	ferrous sulfate (or calcium jarosite) gypsum, elemental sulfur
Sulfite-reduction	FBD	sulfuric acid	filtration	ammonium bisulfite	gypsum, ferric oxides

*Analysis provided by Envirotech Corporation

3.2 ARBITER AMMONIA LEACH PROCESS

3.2.1 Introduction

This section contains an estimate of the material and energy requirements for the Arbiter Process, which utilizes countercurrent leaching techniques to extract copper by ammonia solution under oxygen atmosphere at low pressure and low temperature. This estimate is based on published information on the process, and on similar processes. The basis of these calculations is 1 ton of cathode copper from chalcopyrite concentrate. The process is, however, much more successful in extracting a high percentage of copper from chalcocite concentrates than it is with chalcopyrite concentrates used as a standard of comparison in this study.

A full-sized commercial plant using the Arbiter Process was built in 1974 at Anaconda's Montana smelter to produce 100 tons per day of cathode copper. The plant is not currently in operation due to the unavailability of concentrates with a high proportion of chalcocite which the process dissolves more readily than the chalcopyrite (McNulty, 1979).

3.2.2 Process Description

The Arbiter Process is an ammonia leach process using oxygen as an oxidizing agent under a pressure of 5 psig and a temperature of 60-90°C to extract copper from low grade or highly pyritic concentrates.

The process basically consists of five major steps as shown in Figure 3.2-1, the Arbiter Process flow diagram: (1) concentrate preparation, (2) countercurrent leaching, (3) organic solvent extraction and stripping, (4) copper electrowinning and (5) ammonia recovery and sulfate disposal.

The slurried concentrate is leached with ammonia under oxygen in a series of rubber-lined tanks with decantation and washing performed countercurrently. An organic-liquid-ion-exchange reagent is used to extract copper from the pregnant solution. The copper is, in turn, stripped from the organic solvent by an acid electrolyte and recovered by electrowinning. A portion of the barren raffinate is purged out of the system for the removal of sulfate by the addition of limestone producing gypsum slurry as a byproduct of the process. Ammonia is recovered for re-use.

3.2.3 Material Balance

The material balances are derived from the chemistry and knowledge of process conditions. The leaching chemistry of chalcopyrite can be described by the following equation:

The liquid ion exchange steps are represented by the following general equation:

The gypsum production and ammonia recovery can be shown by the following equation:

FIGURE 3.2-1 ARBITER AMMONIA LEACH PROCESS

Although the process is capable of achieving high recovery of copper, to the range of 95 to 97 percent by increasing the residence time in the leach circuit, recoveries in actual operation may be deliberately kept low (about 80 percent in the Montana operation) to enhance the recovery of precious metals contained in the concentrates (Kuhn, 1974).

Major effluents are the leach residues and gypsum slurry. These streams are sent to settling ponds. Overflows from these ponds can be used for water makeup. A material balance for this process is shown in Table 3.2-1.

The process does not generate any air pollutants but produces gypsum as a byproduct. Operating experiences indicate that the gypsum produced from the Arbiter Process, however, has not been of sufficiently high quality in physical characteristics and color to be suitable for wallboard manufacturing (McNulty, 1979). This may present a solid disposal problem to the plant operator.

3.2.4 Energy Requirements

The direct or Level I energy requirements for the Arbiter Process are shown in Table 3.2-2. The electrical energy includes all grinding, pumping, agitation and electrodeposition of copper, but does not include the energy for producing gaseous oxygen. The total electrical and thermal energy is equivalent to 37.9 million Btu per ton of copper ingot. The Level II energy required to produce the reagents used in the process, is presented in Table 3.2-3. An additional 25.5 million Btu per ton of copper is required to produce the reagents used in the process, largely in the form of oxygen, ammonia and lime.

3.2.5 Discussion

The Arbiter Process, using lime boil as a means to recover ammonia and to remove sulfate, as used at the Montana plant, requires substantially more energy than do the conventional smelting and refining plants equipped with sulfur dioxide emission control devices. According to the plant operator, the leaching, solvent extracting and electrowinning and lime boiling steps of the Arbiter Process would require 63 million Btu/ton of copper (McNulty, 1979). The high energy requirement of 35 million Btu/ton copper involved in the lime boil step is the result of a fairly dilute raffinate. A stronger raffinate can be produced but only at the expense of other upstream problems. Most other operators of hydrometallurgical plants have also found that the treatment of dilute discard streams require major energy use particularly in areas where solar evaporation is not an effective way of eliminating water.

Alternative methods for the disposal of sulfur and metal production have been studied by Anaconda.

Replacing the electrowinning step with copper cementation with iron was projected to save about 20 million Btu per ton of copper (McNulty, 1979).

3.2.6 References

Arbiter, N., "New Advances in Hydrometallurgy," Symposium for Efficient Use of Fuels in the Metallurgical Industries, December 9-13, 1974. Sponsored by IGT.

TABLE 3.2-1		ARBITER PROCESS								
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CONCENTRATE		SLUCING WATER		FEED SLURRY		OXYGEN		AMMONIA	
COMPOSITION	wt.	wet wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	1.250	22.50			1.250	15.00				
Fe	1.33722	24.07			1.33722	16.05				
S	1.550	27.90			1.550	18.60				
SiO ₂	0.43167	7.77			0.43167	5.18				
Al ₂ O ₃	0.17222	3.10			0.17222	2.07				
FeO	0.03444	0.62			0.03444	0.41				
Fe ₂ O ₃	0.05222	0.94			0.05222	0.63				
CaO	0.10333	1.86			0.10333	1.24				
MgO	0.04278	0.77			0.04278	0.51				
Others	0.02611	0.47			0.02611	0.31				
H ₂ O	0.55556	10.00	2.77777	100.00	3.33323	40.00			1.60503	100.00
NH ₃							2.14004	100.00		
O ₂										
(NH ₄) ₂ SO ₄										
CaSO ₄ · 2H ₂ O										
H ₂ SO ₄										
Cu(NH ₃) ₄ SO ₄										
Ca(OH) ₂										
Cu SO ₄										
Fe ₂ (SO ₄) ₃										
TOTAL	5.55555	100.00	2.77777	100.00	8.33332	100.00	2.14004	100.00	1.60503	100.00

TABLE 3.2-1 (cont.)

ARBITER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)	(7)	(8)	(9)	(10)
STREAM NAME	LEACH RESIDUES *	PREGNANT SOLUTION **	WASH WATER ***	HARRIN RAFFINATE	SLAKE LIQUOR
COMPOSITION	wt. wt. %	wt. wt. %	wt. wt. %	wt. wt. %	wt. wt. %
Cu	0.250 2.97				
Fe	0.45838 5.44				
S	0.54104 6.42				
SiO ₂	0.43167 5.12				
Al ₂ O ₃	0.17222 2.04				
FeO	0.03444 0.41				
Fe ₂ O ₃	1.30871 15.54				
CaO	0.10333 1.23				
MgO	0.04278 0.51				
Others	0.02611 0.31				
H ₂ O	5.05302 60.00	33.35404 85.49	38.54575 100.00	33.35404 87.66	
NH ₃				0.53502 1.41	
O ₂					
(NH ₄) ₂ SO ₄		2.97951 5.33		4.15608 10.93	
CASO ₄ · 2H ₂ O					
H ₂ SO ₄					
Cu(NH ₃) ₄ SO ₄		3.58159 9.18			
Ca(OH) ₂					2.33148 100.00
CuSO ₄					
Fe ₂ (SO ₄) ₃					
TOTAL	8.4217 100.00	39.01513 100.00	38.54575 100.00	38.04514 100.00	2.33148 100.00

* Assume: Chalcopyrite 80% dissolved, Pyrite 0% dissolved
 ** Based on a copper concentration of 30 gpl in the strong solution (s)
 *** Amount calculated for water balance only

TABLE 3.2-1 (cont.)

ARBITER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)	(12)	(13)	(14)	(15)
STREAM NAME	STEAM	GYPSON	EXCESS H ₂ O TO RE-USE	LOADED ELECTROLYTE*	SPIRIT ELECTROLYTE**
COMPOSITION	wt.	wt.	wt.	wt.	wt.
Cu					
Fe					
S					
SiO ₂					
Al ₂ O ₃					
FeO					
Fe ₂ O ₃					
CaO					
MgO					
Others					
H ₂ O	0.050	8.12616	20.10359	220.7025	220.02508
NH ₃					
O ₂					
(NH ₄) ₂ SO ₄		5.41744			
CASO ₄ · 2H ₂ O		40.00			
H ₂ SO ₄				28.70463	30.14116
Cu(NH ₃) ₄ SO ₄					
Cu(OH) ₂				20.58478	18.85852
CuSO ₄				1.57509	1.54224
Fe ₂ (SO ₄) ₃					
TOTAL	0.050	11.54360	20.10359	271.5670	270.5670

*Based on Reference 2: Cu: 37ppm Fe: 2.0 ppm H₂SO₄: 132 gpl
 **Based on Reference 2: Cu: 34.0ppm Fe: 1.97ppm H₂SO₄: 137 gpl

TABLE 3.2-1 (cont.)			ARBITER PROCESS		
(TONS PER TON CATHODE COPPER)					
STREAM NO.	(16)				
STREAM NAME	CATHODE COPPER				
COMPOSITION	wt.	wt. %			
Cu	1.000	100.00			
Fe					
S					
SiO ₂					
Al ₂ O ₃					
FeO					
Fe ₂ O ₃					
CaO					
MgO					
Others					
H ₂ O					
NH ₃					
O ₂					
(NH ₄) ₂ SO ₄					
CASO ₄ · 2H ₂ O					
H ₂ SO ₄					
Cu(NH ₃) ₄ SO ₄					
Ca(OH) ₂					
CuSO ₄					
Fe ₂ (SO ₄) ₃					
TOTAL	1.000	100.00			

TABLE 3.2-2

ENERGY REQUIREMENTS

Level 1

ARBITER PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	<u>Electrical Energy</u>				
	A) Combined Amount for Electrowinning, Grinding, Pumping and Agitation	KWH	3000	0.0105	31.5
	<u>Fuel for Process</u>				
	A) Heating (Natural Gas)	SCF	1500	0.001	1.5
	B) Fuel for Lime Boil (Natural Gas)	SCF	4900	0.001	4.9
				TOTAL	37.90

TABLE 3.2-3		ENERGY REQUIREMENTS			Level 2
ARBITER PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Leaching				
	A) Oxygen	TON	2.14	3.78	8.089
6	B) Ammonia Manufacture (5% loss/cycle)	TON	0.0805	41.73	3.359
	Ammonia Recovery				
	A) Lime	TON	2.33	5.45	12.699
				TOTAL	24.147

Arthur D. Little, Inc., "Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Vol. VII. Ammonia Industry Report." Report to Environmental Protection Agency, EPA 600/7-76-034g, December 1976.

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E/MJ, February 1973, pp. 74-75.

Energy Use Patterns for Metal Recycling, Bureau of Mines Circular 8781, 1978.

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Kuhn, M.S., et al, "Anaconda's Arbiter Process for Copper," *CLM Bulletin*, February 1974, pp. 62-73.

McNulty, Anaconda Corporation, Private Communication, June 1979.

Monhemius, A.J., "Trends in Copper Hydrometallurgy," *Chem. & Process Engineering*, January 1970, Vol. 51(1), pp. 65-68.

3.3 THE ROAST-LEACH-ELECTROWIN (RLE) PROCESS

3.3.1 Introduction

All material and energy requirements described in this section are based on the pilot plant and commercial results of the roast-leach-electrowin (RLE) process. Included in the estimates are evaluation of material and energy flows developed by Hecla Mining Company and El Paso Natural Gas Company. (Griffith, Day, Jordan, and Nyman, 1973.) Included in the estimates are evaluation of material and energy flows for incoming process streams, outgoing process streams, and circulating streams.

The RLE process is not new. It has been extensively described in the metallurgical literature and the basic patent utilizing a fluid bed roaster was issued in 1957 (Foley, 1957). Prior to the Hecla Mining — El Paso Natural Gas development, the process had not been used commercially in North America. It was successfully piloted by Bagdad Copper Company and Dorr-Conner, Inc. in 1957 (Howell, Grothe, and McLeod, 1957). Subsequent process development work abroad led to successful commercial installations in Zambia and Zaire, with over 300,000 metric tons of copper now being produced annually by this type of process in Zaire alone.

The process described by Griffith, et al., (Griffith, Day, Jordan, and Nyman, 1973) was piloted using concentrates from both Cyprus, Pima and Hecla Lakeshore operations. A full scale plant using a modification of the RLE process was the Hecla Lakeshore plant, a joint venture of Hecla Mining Company and El Paso Natural Gas Company, near Casa Grande, Arizona. The feed for the sulfide mill (and oxide mill, as well) came from an underground mine containing a large, complex deposit of both ore types (*E/MJ*, 1977). As a result of the decrease in copper prices the Lakeshore plant was shut down in 1978.

3.3.2 Process Description

The process is comprised of a fluid-bed sulfating roast (process step 1), followed by a leach (process step 4) and electrowinning of the copper to cathodes (process step 6). In the treatment of a typical chalcopyrite concentrate the major reactions are:

Fluid-bed sulfating roast

(1) chalcopyrite

(2) pyrite

Acid leach

The copper sulfide concentrate is slurry fed into the roaster wherein copper sulfides are converted to copper sulfate by controlling air flow rate and temperature. The iron sulfides in the feed are oxidized to hematite. The calcine is hot quenched and leached with dilute sulfuric acid to dissolve the copper sulfate. The leach slurry is separated into a clear pregnant solution and a leach residue by countercurrent decantation.

The copper is recovered from the pregnant solution in electrowinning by deposition on copper starter sheets. Spent electrolyte is divided between the agitation leach circuit and cementation for contact with metallic iron in a proportion that satisfies solution needs and overall copper recovery. Effluent liquor from the cementation step is rejected for the purposes of this analysis. Pregnant electrolyte contains about 49 gpl copper entering the starter section. Depletion of copper during electrolysis in the starter section reduces the solution concentration to 40 gpl copper. Current density in the electrowinning plant is designed to be in the range of 15 to 20 amps per square foot (E/MJ, 1977). In the test work performed by Griffith, et al., the following were established as the important variables in the RLE process:

- (1) Roaster space rate
- (2) Roaster temperature
- (3) Roaster feed sulfur to air ratio
- (4) Current density
- (5) Spent electrolyte composition

The data used to construct the model of the RLE process were taken from the plant data of the Hecla Lakeshore operation. The Lakeshore process produced some cement copper which contains 40 percent copper. This was sent to a custom smelter where it was further processed into cathode copper. For this study the cementation process is followed by a redissolution step so that the final product from the RLE process is cathode copper.

The Lakeshore operation included a sponge iron plant. However, in this analysis, the preparation of sponge iron is not included in the heat requirement. It is assumed that the metallic iron for the copper cementation step would be provided from the most economical source.

The analysis of the concentrate from the Lakeshore operation was 25.92 percent copper, 25.55 percent iron, and 29.27 percent sulfur. Therefore, the data have been adjusted to the standard concentrate value of 25.00 percent copper, 29.00 percent iron, and 31.00 percent sulfur. The energy equivalents for some items were taken from Kellogg and Henderson (1967).

The flowsheet for the RLE process shown in Figure 3.3-1 is the original flow sheet and does not include a solvent extraction step which was to be added later. The material and energy requirements for the process are shown in Tables 3.3-1, 3.3-2, and 3.3-3. Table 3.3-2 includes all direct energy inputs and their contribution to the energy requirement for each process step. Table 3.3-3 includes the consumable materials and their energy contribution to the process.

It is evident from Table 3.3-2 that about 70 percent of the total energy for the process is in the form of electrical energy used in the electrowinning process. Large amounts of energy are also used in the production of acid. The cementation step requires a small amount of energy.

The process has basic limitations or disadvantages which are well known. Copper recovery (94.3 percent) is generally slightly lower than that achieved in reverberatory smelting, converting, and electrolytic refining. Precious metals in the sulfide concentrate are lost in the leach residue. Disposal of relatively large volumes of copper bearing acidic spent electrolyte is required, since more acid is generated in the electrolysis than is required in leaching. Although roaster gases are of a strength adequate for autothermal conversion to sulfuric acid, the gas strength is near the lower limit for autothermal operation. Because of the limitations, the process is applicable only where the limitations are not economically important or where low cost solutions to them can be developed.

3.3.3 Conclusions

The RLE process appears to be more efficient in energy utilization than the electric smelting process and as effective as conventional reverberatory calcine smelting. The overall energy consumption is 30.0 million Btu's per ton cathode copper as compared to 39.4 million Btu's per ton for electric smelting and 31.0 million Btu's per ton for the reverberatory calcine smelting. However, the process has basic limitations. Even with close control of the sulfate roaster, the exit

TABLE 3.3-1										
ROAST-LEACH ELECTROWINNING PROCESS										
(10NS PER TON CATHODE COPPER)										
STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CONCENTRATE		ROASTING AIR		FUEL		ROASTING OFF GAS		DILUTION AIR	
COMPOSITION	wt.	dry wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	1.061	25.001					.016	.101		
Fe	1.134	26.739					.013	.085		
S	1.315	30.997					.015	.098		
CuO							.732	4.644		
CuSO ₄							.490	3.106		
FeO	.029	.690								
Fe ₂ O ₃	.044	1.040					1.208	7.664		
FeSO ₄							.090	.568		
SiO ₂	.425	10.014					.319	2.022		
Al ₂ O ₃	.146	3.450					.110	.697		
CaO	.088	2.070					.066	.418		
H ₂ O	.579						.579	3.675		
Fuel					.001	100.000				
O ₂			2.750	23.000			.526	3.336	.383	23.000
N ₂			9.206	77.000			9.206	58.420	1.282	77.000
CO ₂							.002	.014		
SO ₂							1.819	11.545		
SO ₃							.568	3.607		
TOTAL	4.821	100.000	11.956	100.000	.001	100.000	15.759	100.000	1.665	100.000
TEMP. (F)	60		60		60		1274		60	
STATE	S		C		L		G		G	

TABLE 3.3-1 (cont.) ROAST-LEACH ELECTROWINNING PROCESS									
(TONS PER TON CATHODE COPPER)									
STREAM NO.	(6)		(7)		(8)		(9)		(10)
STREAM NAME	SO ₂ ACID GAS		DUST RECYCLE		CALCINE		LEACH TAILS		WATER
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. wt. %
Cu			.016	.520	.005	.520	.021	.446	
Fe			.013	.436	.004	.436	.018	.373	
S			.015	.506	.005	.506	.021	.434	
CuO			.732	23.937	.244	23.937	.049	1.026	
CuSO ₄			.490	16.010	.163	16.010	.257	5.407	
Fe ₂ O ₃			1.208	39.497	.403	39.497	1.610	33.861	
FeSO ₄			.090	2.928	.030	2.928	.042	.873	
SiO ₂			.319	10.421	.106	10.421	.425	8.934	
Al ₂ O ₃			.110	3.590	.037	3.590	.146	3.078	
CaO			.066	2.154	.022	2.154	.088	1.847	
H ₂ O	.579	4.031					2.073	43.589	8.322 100.000
H ₂ SO ₄							.006	.131	
O ₂	.909	6.325							
N ₂	10.488	73.007							
CO ₂	.002	.015							
SO ₂	1.819	12.664							
SO ₃	.568	3.957							
TOTAL	14.366	100.000	3.058	100.000	1.019	100.000	4.755	100.000	8.322 100.000
TEMP. (F)	600		1000		1112		123		60
STATE	G		S		S		S		L

TABLE 3.3-1 (cont.)				ROAST-LEACH ELECTROWINNING PROCESS						
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	RECYCLE WASH		CCD TAILS		PREGNANT ELECTROLYTE		ELECTROWINNING OFF GAS		CATHODE Cu	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu			.021	.446					1.000	100.000
Fe			.018	.373						
S			.021	.434						
CuO			.049	1.026						
CuSO ₄	.256	3.074	.001	.027	3.114	10.814				
Fe ₂ O ₃			1.610	33.861						
FeSO ₄	.041	.496	.000	.004	.503	1.746				
SiO ₂			.425	8.934						
Al ₂ O ₃			.146	3.078						
CaO			.088	1.847						
H ₂ O	8.019	96.355	2.376	49.968	25.101	87.177				
H ₂ SO ₄	.006	.075	.000	.001	.076	.262				
O ₂							.252	100.000		
TOTAL	8.322	100.000	4.755	100.000	28.793	100.000	.252	100.000	1.000	100.000
TEMP. (F)	74		74		123		104		104	
STATE	L		S		L		G		S	

TABLE 3.3-1 (cont.) ROAST-LEACH ELECTROWINNING PROCESS									
(TONS PER TON CATHODE COPPER)									
STREAM NO.	(16)		(17)		(18)		(19)		(20)
STREAM NAME	SPENT ELECTROLYTE		ELECTROLYTE RECYCLE		REDISSOLUTION LIQUOR		CEMENTATION FEED		CEMENTATION IRON
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. wt. %
Fe									.086 100.000
CuSO ₄	.837	2.846	.602	2.847	.048	2.847	.187	2.847	
FeSO ₄	.533	1.812	.383	1.813	.030	1.813	.119	1.813	
H ₂ O	26.350	89.582	10.946	89.578	1.504	89.578	5.899	89.578	
H ₂ SO ₄	1.694	5.759	1.219	5.762	.097	5.762	.379	5.762	
TOTAL	29.415	100.000	21.150	100.000	1.680	100.000	6.585	100.000	.086 100.000
TEMP. (F)	104		104		104		104		60
STATE	L		L		L		L		S

TABLE 3.3-1 (cont.)		ROAST-LEACH ELECTROWINNING PROCESS								
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	CEMENTATION AIR		BARREN LIQUOR		CEMENT CU		ACID		REDISSOLUTION AIR	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu					.075	100.000				
FeSO ₄			.353	3.151						
H ₂ O			5.905	52.727			.007	7.000		
H ₂ SO ₄			.344	3.071			.093	93.000		
O ₂	1.059	23.000	1.053	9.402					.019	100.000
H ₂	3.545	77.000	3.545	31.650						
TOTAL	4.603	100.000	11.199	100.000	.075	100.000	.100	100.000	.019	100.000
TEMP. (F)	60		104		104		60		60	
STATE	G		L		S		L		G	

TABLE 3.3-1 (cont.)		ROAST-LEACH ELECTROWINNING PROCESS						
		(TONS PER TON CATHODE COPPER)						
STREAM NO.	(26)		(27)		(28)			
STREAM NAME	RECYCLE SOLUTION		ACID TAIL GAS		SULPHURIC ACID			
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %		
FeO	.235	12.559						
FeSO ₄	.030	1.626						
H ₂ O	1.533	81.815			.262	7.000		
H ₂ SO ₄	.075	4.000			3.482	93.000		
O ₂			.454	4.151				
N ₂			10.488	95.829				
CO ₂			.002	.020				
TOTAL	1.873	100.000	10.945	100.000	3.744	100.000		
TEMP. (F)	157		100		100			
STATE	L		G		L			

TABLE 3.3-2

ENERGY REQUIREMENTS

Level 1

ROAST - LEACH - ELECTROWINNING PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	<u>Fluid Bed Roasting</u>				
	A) Electrical Power	KWH	110.61	0.0105	1.161
	B) Fuel (Start-Up)	GAL	0.212	0.1474	0.031
2	<u>Roaster Gas Cleaning</u>				
	A) Hot Gas Handling	MILLION SCF	296.11	0.00252	0.746
4	<u>Leaching</u>				
	A) Electrical Power	KWH	59.756	0.0105	0.627
5	<u>CCD</u>				
	A) Electrical Power	KWH	37.294	0.0105	0.392
6	<u>Electrowinning</u>				
	A) Electrical Power	KWH	2134.0	0.0105	22.407
7	<u>Cementation</u>				
	A) Electrical Power	KWH	30.675	0.0105	0.322
8	<u>Redissolution</u>				
	A) Electrical Power	KWH	16.275	0.0105	0.171
9	<u>Acid Plant</u>				
	A) Electrical Power	MILLION SCF	234.36	0.0113	2.648
	B) Cold Gas Cleaning	MILLION SCF	234.36	0.00132	0.309
				TOTAL	28.814

TABLE 3.3-3 ENERGY REQUIREMENTS Level 2					
ROAST - LEACH - ELECTROWINNING PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
7	<u>Cementation</u> A) Iron	TON	0.08625	18.00	1.553
8	<u>Redissolution</u> A) Sulfuric Acid	TON	0.10125	.83	.084
				TOTAL	1.637

gas will contain excessive quantities of sulfur trioxide. Also, the recovery of copper as well as precious metals is lower, and disposal of large volumes of spent electrolyte is required. Moreover, the quality of cathode copper may not meet the electrolytic copper grade. Inclusion of the solvent extraction system appears to overcome some of these problems.

3.3.4 Recommendations

The RLE process is very well suited for mixed sulfide-oxide copper deposits. Because of some inherent disadvantages, the process needs additional research and development efforts. Of primary importance are the following:

- (1) Recovery of precious metals
- (2) Alternative methods for making the process suitable for all sulfide ores
- (3) Alternate methods for sulfur removal other than excess acid production.

There appears to be little opportunity for major energy savings since electrowinning requires the major proportion of the total energy. However, if a method could be used for copper precipitation other than electrowinning considerable energy savings could result. For example, about 3×10^6 Btu per ton of cathode copper would be saved by utilizing the electroslurry electrowinning process.

3.3.5 References

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Foley, R.M.. Method for Treating Copper Ore Concentrates, U.S. Patent No. 2,783,141, February 25, 1957.

Griffith, W.A., H.E. Day, T.S. Jordan, and V.C. Nyman, "Development of the Roast-Leach-Electrowin Process for Lakeshore," Hecla Mining Company Report; Wallace, Idaho, 1973.

Howell, E.S., J.D. Grothe, and B.H. McLeod, "Bagdad Reports Metallurgical Test Results on Copper Recovery Method," Engineering and Mining Journal, Vol. 258, No. 7, pp. 86-89, July, 1957.

Kellogg, H.H. and J.M. Henderson, Extractive Metallurgy of Copper, Vol. 1, Ch. 19, American Institute of Mining, Metallurgical and Petroleum Engineers, Baltimore, MD, 1967.

3.4 CYMET PROCESS

3.4.1 Introduction

This process is analyzed for its material and energy requirements for extracting copper from chalcopyrite concentrate. The summary of material flows includes the raw materials and other process influents, internal process streams, and process effluents. The basis for all material and energy requirement is the production of one ton of cathode grade copper. The process in its present form has undergone extensive pilot plant testing since 1977 and the process at the pilot level is well understood.

3.4.2 Process Description

The process employs a cupric-ferric chloride to leach concentrates at 90° to 95°C to produce a solution rich in cuprous chloride as shown in Figure 3.4-1. The cuprous chloride is crystallized from solution by cooling to 38°C and separated from the solution in a centrifuge. The dried cuprous chloride crystals are fed to a fluidized bed reduction process that employs heated hydrogen as a reducing agent. After the copper nodules formed in the fluidized bed grow to a large enough size, they are removed by screening. The hydrogen chloride formed in the fluidized bed is removed by scrubbers and returned to the leach solution. The unreacted hydrogen is recycled back to the fluidized bed with the addition of make-up hydrogen. It is necessary to remelt the copper nodules in a refining furnace with an appropriate flux to remove any entrained sand and to fire refine the copper before casting into ingots.

The depleted liquor shown as stream 4 in Figure 3.4-1 is now rich in both cuprous and ferrous chloride. The liquor is regenerated back to ferric and cupric chloride with oxygen and by the addition of the hydrogen chloride recovered from the fluidized bed scrubbers. The reactions are exothermic and the solution leaves the step at 93°C. The excess iron in the regenerated leach liquor is precipitated as hydronium jarosite or ferric hydroxide. The major effluent streams from the process are the gangue minerals from the concentrate and the jarosite precipitates. These solid materials are sent to a tailings pond after recovery of the elemental sulfur and molybdenite they contain. The yield of copper metal in finished form from concentrate is 95 percent.

3.4.3 Material Balances

The material balances depend directly on the chemistry of the process. McNamara gave the following net reactions in his 1978 paper.

Cupric Leach

Ferric Leach

Metal Reduction

Hydrolysis/Reagent Regeneration

FIGURE 3.4-1 CYMET FERRIC CHLORIDE LEACH PROCESS

Summation

Material balance for the Cymet process is presented in Table 3.4-1. Since the process is still proprietary, many of the details on reaction times, temperatures, and concentrations are not known. The balances should present, however, a general idea of the material flows to produce one ton of copper.

The material balances and energy flows for the process are found in a number of references (McNamara, 1978), (McNamara, 1979), and (Bailey, 1978). Additional references to an earlier version of this process are found in earlier papers (Allen, 1974; Kruesi, 1973; and Kruesi, 1974).

3.4.4 Energy Requirements

The Level I energy requirements for Cymet Process for direct thermal and electrical energy are presented in Table 3.4-2. The electrical energy is reported to include all grinding, pumping, and agitation but not the energy used to produce oxygen by air separation. The total direct energy is 23.8 million Btu per ton of copper ingot. Looking at the energy needed to produce the chemicals consumed in the process, we find an additional 7.1 million Btu is consumed per ton of copper ingot. The energy content of the chemicals is presented in Table 3.4-3 with the production of gaseous oxygen and hydrogen requiring most of the energy input.

3.4.5 Discussion

The total energy for fuel, electricity and chemicals is equivalent to 30.9 million Btu per ton of copper ingot. The energy consumption is the lowest of all hydrometallurgical processes because of the use of the hydrogen fluidized bed for copper reduction. The energy consumption of 3.7 million Btu per ton of copper for hydrogen is considerably lower than energy consumption for electrowinning.

Extensive pilot plant testing has been completed by the Cyprus Metallurgical Process Corporation in Tucson, Arizona and the process has been evaluated both technically and economically. Cyprus plans to build a commercial plant using this process.

3.4.6 Conclusions and Recommendations

This process appears to be an attractive hydrometallurgical process with a relatively-low-energy consumption. The process is being actively developed and it may find several commercial applications. Like all hydrometallurgical processes, it may be most attractive at a smaller scale with a capacity of below 75,000 tons of copper per year where pyrometallurgical techniques are less attractive. It offers the potential of being a low-pollution method of extracting copper from chalcopyrite concentrates.

TABLE 3.4-1 CYMET HYDROMETALLURGICAL PROCESS									
(TONS PER TON OF FIRE REFINED COPPER)									
STREAM NO.	(1)		(2)		(3)		(4)		(5)
STREAM NAME	COPPER CONCENTRATE		LIQUOR FROM CUPRIC LEACH		FILTERED LIQUOR		DEPLETED LIQUOR		CRYSTALLIZED CUPROUS CHLORIDE
COMPOSITION	wt.	wt. %	wt.	dry wt. %	wt.	dry wt. %	wt.	dry wt. %	wt. wt. %
Cu	1.050	25.0							
Fe	1.126	26.7							
S	1.305	31.0							
SiO ₂	0.365	8.6							
Al ₂ O ₃	0.145	3.5							
FeO	0.029	0.7							
Fe ₂ O ₃	0.044	1.0							
CaO	0.087	2.1							
MgO	0.036	0.9							
Others	0.022	0.5							
O ₂									
H ₂									
HCl									
Fe(OH) ₃									
NH ₄ Fe ₂ (SO ₄) ₂ ·(OH) ₆									
Cu ₁			1.400	18.90	1.400	18.90	0.400	6.3	1.000 100.00
Cu ₂			5.997	80.10	5.997	80.10	5.997	93.7	
Fe ₁									
Fe ₂			14.000		14.000		14.000		
H ₂ O									
TOTAL	4.209	100.00	21.397	100.00	21.397	100.00	20.397	100.00	1.000 100.00

TABLE 3.4-1 (cont.) CYMET HYDROMETALLURGICAL PROCESS									
(TONS PER TON OF FIRE REFINED COPPER)									
STREAM NO.	(6)		(7)		(8)		(9)		(10)
STREAM NAME	REGENERATED LEACH LIQUOR		SOLID WASTE		SULFUR		OXYGEN OXYGEN GAS		HYDROGEN CHLORIDE
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %			
Cu			0.050	1.40					
Fe			0.044	1.20					
S			0.050	1.40	1.004	100.00			
S ₁ O ₂			0.363	10.30					
Al ₂ O ₃			0.145	4.00					
FeO			0.029	0.80					
Fe ₂ O ₃			0.044	1.20					
CaO			0.087	2.40					
MgO			0.036	1.00					
Others			0.022	0.60					
O ₂							0.909	100.00	
H ₂									0.575 100.00
HCl									
Fe(OH) ₃	0.813	10.1	0.813	22.90					
NH ₄ Fe ₂ (SO ₄) ₂ ·(OH) ₆	1.884	23.5	1.884	52.80					
Cu ⁺¹									
Cu ⁺²	0.400	5.0							
Fe ⁺³	4.915	61.4							
H ₂ O	14.000								
TOTAL	22.012	100.00	3.567	100.00	1.004	100.00	0.909	100.00	0.575 100.00

TABLE 3.4-1 (cont.)										
CYMET HYDROMETALLURGICAL PROCESS										
(TONS PER TON FIRE REFINED COPPER)										
STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	SAND IN FLUID BED		HYDROGEN GAS		COPPER NODULES		SAND SLAG		COPPER INGOT	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu					1.000	90.00			1.000	100.00
Fe										
S										
SiO ₂	0.110	100.00			0.110	10.00	0.110	100.00		
Al ₂ O ₃										
FeO										
Fe ₂ O ₃										
CaO										
HgO										
Others										
O ₂										
H ₂			0.0157	100.00						
HCl										
Fe(OH) ₃										
NH ₄ Fe ₂ (SO ₄) ₂ (OH) ₆										
Cu ⁺¹										
Cu ⁺²										
Fe ⁺²										
Fe ⁺³										
H ₂ O										
TOTAL	0.110	100.00	0.0157	100.00	1.110	100.00	0.110	100.00	1.000	100.00

TABLE 3.4-2		ENERGY REQUIREMENTS			Level 1
CYMET HYDROMETALLURGICAL PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	<u>Refining Furnace</u>				
	A) Fuel	SCF	6000	0.001	6.0
	<u>Electrical Energy</u>				
	A) For Overall Operations	KWH	1690	0.0105	17.8
				TOTAL	23.8

<div> <div>TABLE 3.4-3</div> <div>ENERGY REQUIREMENTS</div> <div>Level 2</div> </div>					
CYMET HYDROMETALLURGICAL PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Hydrolysis				
	A) Oxygen	TON	0.909	3.78	3.436
	Fluidized Bed				
	A) Hydrogen	TON	0.0157	234.00	3.674
	B) Sand	TON	0.11	0.042	0.005
				TOTAL	7.115

3.4.7 References

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3.5 SHERRITT-COMINCO PROCESS

3.5.1 Introduction

The unusual features of the Sherritt-Cominco process are an activating roast and an initial leach to reduce the iron content of the chalcopyrite concentrates. The estimates in this section include calculations of material flow for raw materials, internal process streams, and process effluents. A basis of one ton of cathode copper from a specified chalcopyrite concentrate is used in all calculations. The process has been extensively tested in a 9 ton per day pilot plant on a complex concentrate containing chalcopyrite, iron pyrite and recoverable zinc, gold and silver. A simpler process without zinc recovery is proposed for the purer chalcopyrite concentrate used in this comparison.

3.5.2 Process Description

The process for treating Arizona type chalcopyrite concentrates is a simplification of the process to treat the more complicated pyritic copper concentrates. As is outlined in Figure 3.5-1, the process employs a two-stage activating roast and a two-stage leach to produce a solution rich in cupric sulfate.

An oxidizing roast of the chalcopyrite concentrate followed by a reducing roast with hydrogen produce a calcine of bornite and troilite. All leaching steps are carried out in lead-clad-brick autoclaves at elevated pressures. The milder-first-stage sulfuric acid leach, conducted at 70°C and atmospheric pressure, dissolves the ferrous ion in troilite without dissolving the copper in the bornite. The dissolved iron is removed from the liquor as ammonium jarosite by first treating it with oxygen and ammonia and then by separating the precipitated jarosite from the liquid. In the stronger-oxidative leach, sulfuric acid and oxygen at 100°C and 13.5 atmospheres pressure dissolve 98 percent of the copper content. The leach liquor is purified of much of the iron and trace impurities in a pressurized oxygen reactor. The purified leach solution is sent to copper electrowinning cells for copper recovery.

In the electrolytic cells most of the electrolyte is recycled to the oxidative leach step. A small bleed stream of electrolyte controls the concentration of trace impurities not removed elsewhere in the process. The process employs a two-stage sulfuric acid plant to produce the acid required for leaching and a Claus plant to control the hydrogen sulfide produced in the reduction roast and first-stage leach. The major solid effluents from the process are the undissolved portion of the concentrate, the ammonium jarosite precipitate and a small amount of ferric oxide precipitate. Precious metals can be recovered from the oxidation leach residue, while elemental sulfur is recovered in the Claus plant and the precious metals circuit.

3.5.3 Material Balance

The material balances are derived from the chemical reactions involved. The chemistry is summarized below.

Destabilization Roast

Reduction Roast

Acid Leach

Jarosite Precipitation

Oxidation Leach

Electrowinning

The material balances that result from this chemistry are shown in Table 3.5-1. Hydrogen reduction could replace the electrowinning but it has not yet been demonstrated on a large-pilot-plant basis (Maschmeyer, 1978). The background for material flow requirements was taken from a number of recent papers (Kawulka, 1978; Maschmeyer, 1978; and Swinkels, 1978).

3.5.4 Energy Requirements

The Level 1 energy requirements for the Sherritt-Cominco process are shown in Table 3.5-2. The electrical energy includes all grinding, pumping, agitating, and electrodeposition of copper, but does not include the energy for producing gaseous oxygen. The total electrical and thermal energy is 38.7 million Btu per ton of copper ingot. The Level 2 energy, which is required to produce the reagents used in the process, is presented in Table 3.5-3. An additional 9.4 million Btu per ton of copper is required to produce the reagents used in the process, largely in the form of oxygen, hydrogen and ammonia.

3.5.5 Discussion

The total energy for fuel, electricity and chemicals is 48.1 million Btu per ton of copper ingot. The energy consumption is in the mid-range of other hydrometallurgical processes analyzed in this study. The use of the hydrogen reduction version of this process could lower the total energy consumption when it is commercially proven.

The process has undergone extensive pilot plant evaluation with all materials of construction, process control, and operating procedures well defined. The companies believe they understand all parameters necessary to design a commercially viable copper refinery capable of treating a wide variety of concentrates. Other versions of this process can successfully treat mixed sulfide concentrates and recover zinc, molybdenum, precious metals as well as copper.

3.5.6 Conclusions and Recommendations

One of the major attractions of this process is its stage of development and its ability to process very complex concentrates. Its energy consumption is in the mid-range for hydrometallurgical processes analyzed in this study, and the hydrogen reduction version could result in lower energy consumption. Like all hydrometallurgical processes, it may be most attractive in smaller plants with a capacity of less than 75,000 tons per year.

3.5.7 References

Arthur D. Little, Inc., *Environmental Considerations of Selected Energy Conserving Manufacturing Process Options: Vol. VII Ammonia Industry Report*, Interagency Energy-Environment Research and Development Program Report, EPA 600/7-76-034g, December 1978.

Energy Conservation Program Guide for Industry and Commerce, National Bureau of Standards Handbook 115, September, 1974.

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Kawulka, P., C.R. Kirby and G.L. Bolton, "The Sherritt-Cominco Copper Process — Part II: Pilot-Plant Operations," *CIM Bulletin*, February 1978, pp. 122-130.

TABLE 3.5-1		SHERRITT-COMINCO COPPER PROCESS							
		(TONS PER TON CATHODE COPPER)							
STREAM NO.	(1)		(2)		(3)		(4)		(5)
STREAM NAME	COPPER CONCENTRATE		AIR		HYDROGEN		SULFUR DIOXIDE		SULFURIC ACID
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.
Cu	1.02	25.00							
Fe	1.089	26.70							
S (Combined)	1.265	31.00							
S (Free)									
S ₁₀₂	0.351	8.60							
Al ₂ O ₃	0.143	3.50							
FeO	0.028	0.70							
Fe ₂ O ₃	0.041	1.00							
CaO	0.086	2.10							
MgO	0.037	0.90							
Others	0.020	0.50							
NH ₃									
O ₂									
O ₂ (In Air)			0.300	21.00					
H ₂					0.014	100.00			
SO ₂							0.600*		
N ₂			1.130	79.00					
NH ₄ Fe ₂ (SO ₄) ₂									
(OH) ₆									
H ₂ O									
Cu ₁₂									
Fe									0.910
H ₂ SO ₄									100.00
H ₂ S									
TOTAL	4.080	100.00	1.430	100.00	0.014	100.00			0.910
									100.00

*Dry basis and SO₂ content only

TABLE 3.5-1 (cont.)		SHERRITT-COMINCO COPPER PROCESS					
		(TONS PER TON CATHODE COPPER)					
STREAM NO.	(6)	(7)	(8)	(9)	(10)		
STREAM NAME	ACTIVATED CALCINE	HYDROGEN SULFIDE	SULFUR	SULFURIC ACID MAKE-UP	OXIDATIVE LEACH LIQUOR		
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. %
Cu	1.020	27.00					
Fe	1.089	28.80					
S (Combined)	0.960	25.40					
S (Free)			0.595	100.00			
S ₁ O ₂	0.351	9.30					
Al ₂ O ₃	0.143	3.80					
FeO	0.028	0.80					
Fe ₂ O ₃	0.041	1.10					
CaO	0.086	2.30					
HgO	0.037	1.00					
Others	0.020	0.50					
NH ₃							
O ₂							
O ₂ (In Air)							
H ₂							
SO ₂							
N ₂							
NH ₄ Fe ₂ (SO ₄) ₂ · (OH) ₆							
H ₂ O							11.800*
Cu ₂							1.246 82.08
Fe ₂							0.119 7.84
H ₂ SO ₄					4.170 100.00		0.153 10.08
H ₂ S			0.632 100.00				
TOTAL	3.775 100.00	0.632 100.00	0.595 100.00	4.170 100.00	1.518*	100.00	

*Water not included in totals

TABLE 3.5-1 (cont.)		SHERRITT-COMINCO COPPER PROCESS								
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	ACID LEACH LIQUOR		AMMONIA JAROSITE		OXYGEN		AMMONIA		OXYGEN	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu										
Fe										
S (Combined)										
S (Free)										
SiO ₂										
Al ₂ O ₃										
FeO										
Fe ₂ O ₃										
CaO										
MgO										
Others										
NH ₃					0.305	100.00	0.08	100.00	0.429	100.00
O ₂										
O ₂ (In air)										
H ₂										
SO ₂										
N ₂										
NH ₄ Fe ₂ (SO ₄) ₂ · (OH) ₆			2.851	94.7						
H ₂ O	14.300*		2.500*							
Cu ⁺ ₂			0.010	0.30						
Fe ⁺ ₂	0.998	70.6								
H ₂ SO ₄	0.415	29.4	0.150	5.0						
H ₂ S										
TOTAL	1.413*	100.00	3.011*	100.00	0.305	100.00	0.08	100.00	0.429	100.00

*Water not included in totals

TABLE 3.5-1 (cont.)

SHERRITT-COMINCO COPPER PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(16)		(17)		(18)		(19)		(20)	
STREAM NAME	OXIDATION RESIDUE		FREE SULFUR		TAILINGS		OXYGEN FOR PURIFICATION		FERRIC OXIDE PRECIPITATE	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	0.010	0.90			0.010	1.30				
Fe	0.091	8.10			0.091	11.80				
S (Combined)	0.017	1.50			0.017	2.20				
S (Free)	0.353	31.60	0.353	100.00						
S ₂ O ₂	0.351	31.40			0.351	45.80				
Al ₂ O ₃	0.143	12.80			0.143	18.70				
FeO	0.028	2.50			0.028	3.70			0.039	100.00
Fe ₂ O ₃	0.041	3.60			0.041	5.40				
CaO	0.028	2.50			0.028	3.70				
MgO	0.037	3.30			0.037	4.80				
Others	0.020	1.80			0.020	2.60				
NH ₃										
O ₂							0.012	100.00		
O ₂ (In Air)										
H ₂										
SO ₂										
H ₂										
NH ₄ Fe ₂ (SO ₄) ₂ ·(OH) ₆										
H ₂ O										
Cu ₂										
Fe ₂										
H ₂ SO ₄										
H ₂ O										
TOTAL	1.119	100.00	0.353*	100.00	0.766	100.00	0.012	100.00	0.039	100.00

*Material quantities on a dry basis and major components only

TABLE 3.5-1 (cont.) SHERRITT - COMINCO COPPER PROCESS (TONS PER TON CATHODE COPPER)									
STREAM NO.	(21)		(22)		(23)		(24)		(25)
STREAM NAME	PURIFIED SOLUTION		COPPER METAL		SPENT ELECTROLYTE RECYCLED		SPENT ELECTROLYTE TO BLEED		BLEED LIQUOR
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. %
Cu			1.000	100.00					
Fe									0.002
S (Combined)									1.5
S (Free)									
S ₂ O ₂									
Al ₂ O ₃									
FeO									
Fe ₂ O ₃									
CaO									
MgO									
Others									
NH ₃									
O ₂									
O ₂ (In Air)									
H ₂									
SO ₂									
N ₂									
NH ₄ Fe ₂ (SO ₄) ₂ (OH) ₆									
H ₂ O	11.80*				11.082		0.718		0.718
Cu ₂	1.246	84.6			0.231	12.20	0.015	12.20	
Fe	0.027	1.8			0.025	1.60	0.002	1.60	
H ₂ SO ₄	0.200	13.6			1.637	86.20	0.106	86.20	0.129
H ₂ S									98.5
TOTAL	14.73*	100.00*	1.000	100.00	1.893	100.00	0.123	100.00	0.131

*Water not included in totals

TABLE 3.5-1 (cont.) SHERRITT - COMINCO COPPER PROCESS					
(TONS PER TON CATHODE COPPER)					
STREAM NO.	(26)		(27)		
STREAM NAME	Copper Sulfide		Hydrogen Sulfide		
COMPOSITION	wt.	wt. %	wt.	wt. %	
Cu	0.015	66.4			
Fe					
S (Combined)	0.0076	33.6			
S (Free)					
S ₁₀					
Al ₂ O ₃					
FeO					
Fe ₂ O ₃					
CaO					
MgO					
Others					
NH ₃					
O ₂					
O ₂ (In Air)					
H ₂					
SO ₂					
N ₂					
NH ₄ Fe ₂ (SO ₄) ₂ ·(OH) ₆					
H ₂ O					
Cu ₂					
Fe					
H ₂ SO ₄			0.008	100.00	
H ₂ S					
TOTAL	0.0226	100.00	0.008	100.00	

TABLE 3.5-2

ENERGY REQUIREMENTS
SHERRETT - COMINCO COPPER PROCESS

Level 1

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
5	<u>Electrowinning and Process Use</u>				
	A) Electrical Energy	KWH	3000	0.0105	31.5
	<u>Total Fuel Requirement</u>				
	A) Process Steam 1.25 Ton/Ton Copper	LBS	5143	0.0014	1.2
				TOTAL	38.7

TABLE 3.5-3 ENERGY REQUIREMENTS Level 2					
SHERITT - COMINCO COPPER PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
	Total Oxygen Use In System	TON	0.746	3.78	2.820
2	Roaster Bottom A) Hydrogen	TON	0.014	234.0	3.276
9	Jarosite Precipitation A) Ammonia	TON	0.08	41.73	3.338
				TOTAL	9.434

Maschmeyer, D.E.G., P. Kawulka, E.F.G. Milner and G.M. Swinkels, "Application of the Sherritt-Cominco Copper Process to Arizona Copper Concentrates," *Journal of Metals*, July 1978, pp. 27-31.

Maschmeyer, D.E.G., E.F.G. Milner and B.M. Parakh, "The Sherritt-Cominco Copper Process — Part III: Commercial Implications," *CIM Bulletin*, February 1978, pp 131-138.

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3.6 NITRIC-SULFURIC ACID LEACH PROCESS

3.6.1 Introduction

This evaluation of material and energy requirements is for a copper extraction process referred to as the nitric-sulfuric acid leach process ("NSL process" or "nitric acid process"). The evaluation includes calculations for raw materials, process steam, electrical power consumption, fuels, consumables, internal process streams, effluents, and heat losses. Energy requirements are assessed in two respects, (1) an operational requirement that does not include special processing features for economizing or recycling heat generated by the processing reactions and (2) a theoretical requirement that includes heats of the processing reactions, indicative of potential energy savings.

The nitric-sulfuric acid leach process is basically hydrometallurgical; the process design considered for this study is for the treatment of chalcopyrite concentrates recovered by froth flotation. The flow scheme is characterized by the hot vat leaching of the concentrates with an oxidizing lixiviant mixture of nitric and sulfuric acid. Following lixiviant purification, electrowinning is employed for copper recovery. A detailed description of the processing operations is presented by Brennecke, et al (1978). Improvements in the flowsheet are described by Davies, et al (1978). The experiments conducted to develop the process, and results of economic and energy evaluations by the staff of the Ledgemont Laboratory, Kennecott Copper Corporation, are discussed in these two papers. Some general conclusions drawn by the Kennecott investigators are:

1. The nitric-sulfuric acid leach process can produce electrowon copper capable of meeting typical chemical specifications for electrorefined-copper quality.
2. Energy requirements for the nitric-sulfuric acid leach process are higher than for equivalent pyrometallurgical extractions (as much as 2.5 times).
3. Operating costs of the nitric-sulfuric acid leach process are higher than for an equivalent pyrometallurgical extraction in medium- or large-size plants. Very small plants could have a slight cost advantage.

3.6.2 Process Description

The process design incorporates the improvement discussed by Davies, et al (1978). The major processing sections are an oxidizing nitric-sulfuric acid leach of the chalcopyrite concentrates, a series of purification steps (nitrate, iron and selenium removal) for the copper-rich lixiviant, and electrowinning to recover the copper as wire-grade cathodes. The oxidant for the leach, nitrogen peroxide (NO_2), is regenerated with oxygen via a gas-phase reactor (see flowsheet, Figure 3.6-1).

Leaching is conducted in nonpressurized vats at 90°C. The nitrate-removal and iron-removal purification steps (Process Steps 3 & 4 in Figure 3.6-1) are conducted at 1350 kPa and 180°C. Oxidant regeneration (Process Step 14, NO Oxidizer) requires moderate pressures and some cooling. Other process steps are conducted at or near ambient conditions. Brief, but informative, descriptions of electrowinning and the other conventional hydrometallurgical process steps employed in the process design are given in Biswas and Davenport (1976). A short text on the nitrogen oxide chemistry is that by Jolly (1964).

The major stoichiometric relationships for the processing reactions are as follows:

Vat Leaching of Chalcopyrite Concentrates, Process Step 2

- a. Copper dissolution

- b. Iron dissolution

- c. Sulfur oxidation

- d. Nitrate formation

NO Oxidizer, Process Step 9

Nitrate Removal, Process Step 3

- a. Iron oxidation

- b. Hydrogen jarosite formation (incomplete)

Iron Removal, Process Step 4

Ammonium jarosite formation

Selenium Removal. Process Step 6

a. Selenium precipitation

b. Iron reduction

As indicated above, the process has been laboratory tested and technically and economically evaluated by the staff of Kennecott Copper Corporation at their Ledge-mont Laboratory. Further processing improvements could consist of the optimization of some of the processing steps; however, such improvements would probably have minor impact on the costs or energy requirements. Presently, development has not been attempted beyond the laboratory stage.

3.6.3 Material Balance

The evaluation of the material requirements is based on the process as described by Brennecke, et al (1978) and Davies, et al (1978). A water-removal step is added to maintain the water balance of the leaching-purification-electrowinning loop. A backwashing circuit is added to clean the tailings slurry and reduce copper loss. A wet grinding step is added for particle size control of the feed to the leach vats. The flowsheet employed is presented in Figure 3.6-1 with identifiers for each processing step and stream. The evaluation of material requirements is summarized in Table 3.6-1. For the evaluation, the production rate of cathodes is set at about 100,000 ton/yr and the copper recovery is 98%. The feed is considered to be a chalcopryite concentrate recovered by froth flotation, to be non-refractory to the leaching process, and having a composition of 25% copper, 29% iron and 31% sulfur.

3.6.4 Energy Requirements

A summary for the energy requirements for the process is listed in Tables 3.6-2 and 3.6-3. The energy evaluation is based on the material evaluation presented above. Table 3.6-2 is a listing of Level 1 requirements. The listing is on a modular basis in sequential processing order. At Level 1, the chemicals and other consumables in the process are not included except for the fuel used. Table 3.6-3 is a listing of Level 2 energy requirements — chemicals, fluxes, refractories and other consumables used on a continuous basis in association with the process. Energy equivalent estimates are included in the tables and the equivalent fuel requirements are calculated and summed. This information supports the values given in the tables, but is too extensive for inclusion as footnotes.

The energy requirements presented in Tables 3.6-2 and 3.6-3 are evaluated for a process considered to be operated in a conventional manner. The totals are termed "operational" in the above summary table. The operational estimate does not consider special processing features for economizing or recycling heat generated by the processing reactions. The following is a discussion of a "theoretical" energy requirement for the process, that includes consideration of the heats of the processing reactions. The difference between the operational estimate and the theoretical estimate is indicative of the potential of the process for energy savings.

The following energy calculations were provided by Goel (1979). Thermochemical data for the calculations can be found in Barner and Schenerman (1978) unless noted otherwise.

TABLE 3.6-1 NITRIC-SULFURIC ACID LEACH PROCESS									
(TONS PER TON CATHODE COPPER)									
STREAM NO.	(1)		(3)		(8)		(9)		(16)
STREAM NAME	CHALCOPYRITE CONCENTRATE		PREMANT LEACH LIQUOR		ELECTROWINNING FEED		CATHODES		CLEAN TAILINGS SOLIDS
COMPOSITION	wt.	dry wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. wt. %
Cu	1.020	25.00	1.540	5.97	1.440	6.53	1.000	100.00	0.020 0.37
Fe	1.140	27.94	1.100	4.27					1.140 20.88
S	1.270	31.13							1.270 23.26
H ₂ O			16.910	65.57	15.500	70.33			
SO ₄ ⁻²			4.860	18.84	3.210	14.56			
NO ₃ ⁻¹			0.410	1.59					
H ₂ SO ₄			0.970	3.76	1.890	8.58			
Other	0.650	15.93							3.030 55.49
O ₂									
HNO ₃									
NH ₃									
CaCO ₃									
Scrap Iron									
Steam									
TOTAL	4.080	100.00	25.790	100.00	22.040	100.00	1.000	100.00	5.460 100.00

TABLE 3.6-1 (cont.)

NITRIC-SULFURIC ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(20)		(35)		(36)		(37)		(38)	
STREAM NAME	CEMENT COPPER		STEAM, PROCESS HEATING		STEAM, PROCESS HEATING		STEAM, PROCESS HEATING		STEAM, PROCESS HEATING	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	0.05	100.00								
Fe										
S										
H ₂ O										
SO ₄ -2										
NO ₃ -1										
H ₂ SO ₄										
Other										
O ₂										
HNO ₃										
NH ₃										
CaCO ₃										
Scrap Iron										
Steam			13.36	100.00	13.36	100.00	13.36	100.00	13.36	100.00
TOTAL	0.05	100.00	13.36	100.00	13.36	100.00	13.36	100.00	13.36	100.00

TABLE 3.6-1 (cont.) NITRIC-SULFURIC ACID LEACH PROCESS									
(TONS PER TON CATHODE COPPER)									
STREAM NO.	(40)		(41)		(42)		(43)		(44)
STREAM NAME	OXYGEN		AMMONIA		NITRIC ACID		SCRAP IRON		LIMESTONE
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt. %
Cu									
Fe									
S									
H ₂ O									
SO ₄ ⁻²									
NO ₃ ⁻¹									
H ₂ SO ₄									
Other									
O ₂	1.770	100.00							
HNO ₃			0.070	100.00	0.068	100.00			
NH ₃									
CaCO ₃									0.640 100.00
Scrap Iron							0.080 100.00		
Steam									
TOTAL	1.770	100.00	0.070	100.00	0.068	100.00	0.080	100.00	0.640 100.00

TABLE 3.6-2		ENERGY REQUIREMENTS			Level 1
NITRIC - SULFURIC ACID LEACH PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	<u>Wet Grinding</u>				
	A) Electrical Energy	KWH	21.42	0.0105	0.225
2	<u>Countercurrent Leaching</u>				
	A) Steam, Process Heating	TON	2.90	2.8	8.120
3	<u>Nitrate Removal</u>				
	A) Steam, Process Heating	TON	4.64	2.8	12.992
	B) Pumping (electrical energy)	KWH	7.15	0.0105	0.075
4	<u>Iron Removal</u>				
	A) Steam, Process Heating	TON	0.19	2.8	0.532
8	<u>Electrowinning</u>				
	A) Electrical Energy	KWH	2300	0.0105	24.15
12	<u>Water Removal</u>				
	A) Steam, Distillation	TON	5.63	2.8	15.764
*	<u>Ancillary loads</u>				
	A) Electrical Energy	KWH	50	0.0105	0.525
				TOTAL	62.383

*Not shown on flowsheet

TABLE 3.6-3		ENERGY REQUIREMENTS			Level 2
NITRIC - SULFURIC ACID LEACH PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	<u>Countercurrent Leaching</u>				
	A) Nitric Acid	TON	0.068	14.2	0.966
4	<u>Iron Removal</u>				
	A) Ammonia	TON	0.0695	39.0	2.711
9	<u>Nitric Oxide Oxidizer</u>				
	A) Oxygen	TON	1.77	3.78	6.691
10	<u>Sulfate Removal</u>				
	A) Limestone	TON	0.64	3.6	2.304
11	<u>Copper Purge</u>				
	A) Scrap Iron	TON	0.08	2.0	0.160
				TOTAL	12.064

Energy generated by leaching reactions

$$\begin{aligned} \Delta H_{298}^0 &= - [2,800 + 7,900] + [15,500 - 15,300 - 57,800 + 21,600] \\ &= -15,900 \text{ cal/mole} \end{aligned}$$

Copper dissolved - 1.02 kg = 16.05 moles

$$\begin{aligned} \text{Energy Generated} &= (16.05)(15,900)(3.60 \times 10^{-6}) \\ &= .92 \text{ million Btu/ton product} \end{aligned}$$

$$\begin{aligned} \Delta H_{298}^0 &= - [-39,200 + 7,900] + [-21,300 - 15,300 - 57,800 + 21,600] \\ &= -41,500 \text{ cal/mole} \end{aligned}$$

Iron dissolved - 1.14 kg = 20.41 moles

$$\begin{aligned} \text{Energy Generated} &= (20.41)(41,500)(3.60 \times 10^{-6}) \\ &= 3.05 \text{ million Btu/ton product} \end{aligned}$$

$$\begin{aligned} \Delta H_{298}^0 &= - [15,300 + 3(7,900) - 57,800] + [-232,700 + 3(21,600)] \\ &= -118,500 \text{ cal/mole} \end{aligned}$$

Sulfur oxidized - all sulfur from FeS_2 + 35% from CuFeS_2 oxidized to sulfate
= .602 kg = 18.78 moles

$$\begin{aligned} \text{Energy Generated} &= (18.78)(118,500)(3.60 \times 10^{-6}) \\ &= 8.01 \text{ million Btu/ton product} \end{aligned}$$

$$\begin{aligned} \Delta H_{298}^0 &= - [3(7,900) - 57,800] + [2(-49,600) + 21,600] \\ &= -43,500 \text{ cal/mole} \end{aligned}$$

Nitrate formation - .42 kg = 6.8 moles

Nitrate production is kept to a minimum as required for complete oxidation of Fe^{++} to Fe^{+3} . Excess nitrate must be removed.

$$\begin{aligned} \text{Energy Generation} &= (6.8)(43,500)(3.60 \times 10^{-6}) \\ &= 1.06 \text{ million Btu/ton product} \end{aligned}$$

Total Energy Generation

$$\text{by Leach Reactions} = .92 + 3.05 + 8.01 + 1.06$$

$$= 13.04 \text{ million Btu/ton product}$$

Heat evolution by NO oxidation

$$\Delta H_{298}^\circ = -13,700 \text{ cal/mole}$$

$$\text{NO produced in the leach vessels} - 3.01 \text{ kg} = 100.3 \text{ moles}$$

$$\text{Heat Evolved} = (100.3) (13,700) (3.60 \times 10^{-6})$$

$$= 4.95 \text{ million Btu/ton product}$$

$$50\% \text{ credit from Heat Exchanger} = 2.47 \text{ million Btu/ton product}$$

Heat required in nitrate-removal reactions (Retention Time: 10 minutes at 180°C and 1350 kPa)

$$\Delta H_{298}^\circ = - [49,600 + 3 (-21,300)] + [21,600 + 2 (-57,800) + 3 (-11,600)]$$

$$= -15,300 \text{ cal/mole}$$

No heat credit given.

$$\Delta H_{298}^\circ = - [3 (-11,600) + 6 (-57,800) + 2 (-232,700)] + [-796,570^*]$$

$$= 50,250 \text{ cal/mole}$$

Hydrogen jarosite formation - 40% of dissolved iron removed as hydrogen jarosite = 8.16 moles

$$\text{Heat Required} = (8.16) (50,250) (3.60 \times 10^{-6})$$

$$= 1.48 \text{ million Btu/ton product}$$

(* ΔH_f° of hydrogen jarosite is from M.R. Spedden, Kennecott Copper, Nov. 1971; available from M.E. Wadsworth's personal file)

Heat required in iron-removal reactions (Retention Time: 85 min. at 180°C and 1350 kPa)

$$\Delta H_{f,98}^{\circ} = 61,250 \text{ cal/mole}$$

Iron precipitated

$$\text{Heat Required} = (12.25)(61,250)(3.60 \times 10^{-6})$$

$$= 2.70 \text{ million Btu/ton product}$$

(ΔH_f of ammonium jarosite assumed the same as for hydrogen jarosite)

Total Heat Generated by Processing Reactions

$$= 13.04 + 4.95 - 1.482 - 2.50$$

$$= 13.18 \text{ million Btu/ton product}$$

The heat generated by the process reactions can, in theory, be employed to offset steam requirements necessary for process heating. Some special design considerations may be necessary to accomplish the savings in steam, however. Such is the case with vat leaching where the process streams must be heated prior to leaching. An equipment design that transfers heat from the leaching vats to the influent streams would be needed. The theoretical energy requirement for this special design is as follows:

Total Level 1 Energy Requirement — 62.38 million Btu/ton product (See Table 3.6-3)

Offset from Heat Generated by Processing Reactions — 13.18 million Btu/ton product

Steam Conserved by Improved Water Balance — 13.18 million Btu/ton product

Total Theoretical Level 1 — Requirement — 36.02 million Btu/ton product

Total Level 2 Energy Requirement — (unchanged, see Table 3.6-3) — 12.06 million Btu/ton product

Total Theoretical Energy — Requirement — 46.42 million Btu/ton product

3.6.5 Discussion

Highly significant aspects in the evaluation of material and energy requirements for the nitric-sulfuric acid leach process are ascertaining the compositions of the streams of the leaching-purification-electrowinning loop (streams with 20-25 times the mass flow of the product) and evaluating the control of the water balance (a control that is highly sensitive to the tailings backwash operation and the direct injection of steam for process heating).

The Level 1 energy requirements are dominated by the process heating for the countercurrent-leaching and nitrate-removal steps and by the energy required to remove water from the leaching-purification-electrowinning loop to maintain the water balance. Electrowinning is also a heavy energy consuming step. The energy required for electrowinning is determined by the production rate of cathodes and is fairly independent of process design considerations. Thus,

electrowinning offers little potential for energy reduction via design improvements. The process heating energy requirements have potential for reduction via refinements in design that economize or recycle heat (with an increase in equipment complexity, of course).

The energy requirements for Level 2 are dominated by ammonia and oxygen consumptions. These requirements are dependent on the composition of the chalcopyrite concentrate feed, and thus, offer little opportunity for improvement via design refinement. Make up of nitric acid in the counter-current leaching step is a critical design consideration. The makeup of nitric acid is dependent on the gas-tight integrity of the leach vats, gas handling, and gas processing equipment (all design considerations). Nitric acid is also a strong energy consuming item (14.2 million Btu/ton, see Table 3.6-2); thus, potential energy requirement increases from design variances relevant to the gas-tight integrity of the equipment is discernible. Additional significance is placed on nitric acid make up if the energy required for air pollution control of NO losses were considered.

With the exception of electrowinning electrical energy and the ammonia and oxygen consumption, the energy requirement for the process is mainly in the form of low-pressure process-heating steam. Many opportunities are thus afforded for the economizing or recycling of heat and for utilizing waste heat from other processing activities. The extent to which these energy conservation measures might be carried would depend on the optimization of an operational design.

3.6.6 Conclusions and Recommendations

The processing energy requirements are significantly sensitive to process design factors that influence the utilization of heat generated by the processing reactions or the economizing and recycle of heat from the leaching and purification steps. Second to the process design factors, chalcopyrite concentrate composition differences causing variances in ammonia and oxygen consumption are most significant.

The six largest energy consuming items are electrowinning, water removal for control of the water balance of the leaching-purification-electrowinning loop, process heating steam for the nitrate-removal step, process heating steam for counter-current leaching, oxygen for NO oxidation, and ammonia consumption for iron precipitation, respectively. The total energy requirement for an operational process is 74.44 million Btu/ton product of which 62.38 million Btu/ton product (84%) is in the form of direct fuel, steam and electrical power consumption. The theoretical energy evaluation indicates that the effective use of heat generated by the processing reactions would significantly reduce the total energy required (38% reduction, from 74.44 million Btu/ton product to 46.42 million Btu/ton product). Both the operational and the theoretical assessments are significantly above the energy required for more conventional pyrometallurgical processing.

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3.7 UNIVERSITY OF UTAH-MARTIN-MARIETTA PROCESS

3.7.1 Introduction

This process, with attrition grinding of concentrate and ferric sulfate leach, is analyzed for its material and energy requirements for extracting copper from chalcopyrite concentrates. The estimates include calculations of material flow for raw materials, internal process streams, and process effluents. The basis for the calculations is the production of one ton of copper from chalcopyrite concentrates. The process was evaluated at a pre-pilot plant stage by the University of Utah, Salt Lake City, Utah and Martin Marietta of Baltimore, Maryland. This evaluation was supported by the National Science Foundation under NSF/RANN Grant Award No. GI 40538.

3.7.2 Process Description

The process requires attrition milling of concentrates to produce small particles necessary for efficient leaching. In an acid ferric sulfate leach, a layer of elemental sulfur builds up on the surface of the concentrate particles that inhibits the leaching process. The specified mean particle size of 1 micrometer is a trade-off between the desire to have particles as small as possible without expending an excessive amount of energy for the attrition milling. As shown in Figure 3.7-1, a two-step leach is employed with an intermediate step to remove the coating of sulfur from the concentrate particles so that the second leach step can proceed at a faster rate. The leaching processes are carried out at 90°C under atmospheric pressure: three stages at four hours per stage in step 1 and 3 stages at one hour per stage in step 2. The resulting solution rich in cupric sulfate is treated for iron removal by addition of ammonia and oxygen to form ammonium jarosite precipitate which must be separated from the solution. Selenium is subsequently removed by precipitation with metallic copper before the purified solution flows into electrolytic cells for the electrowinning of cathode copper. The spent electrolyte is recycled to the leaching stages after removing the excess liquid and precipitating excess sulfate as gypsum. The active ferric ion is regenerated in the electrolyte from the ferrous ion in the leaching vessels by the action of oxygen and sulfur dioxide.

3.7.3 Material Balance

The material balances were derived from the chemical reactions occurring during the extraction of copper. The chemistry may be summarized as:

Leach Stages

Iron Removal

Selenium Removal

FIGURE 3.7-1 FERRIC SULFATE ACID LEACH PROCESS

Electrowinning

Sulfate Removal

Recovery of Copper Sulfate from Waste Solution

The material balances resulting from this chemistry are presented in Table 3.7-1. The quantities involved are sufficient to produce one ton of cathode copper. Stream numbers are the same as appeared in Figure 3.7-1.

The material flow requirements were taken from a flowsheet prepared by J. L. Sepulveda of the University of Utah and modified for a chalcopyrite concentrate composition consistently used in this report. The process reactions and kinetics are detailed in a recent paper (Beckstead, 1976). Other references, (Baily, 1978; Goel, 1979; and Rosswog, 1979), present energy estimates for electrowinning copper from a cupric sulfate solution and general process energy for the hydrometallurgical leaching.

3.7.4 Energy Requirements

The Level 1 energy requirements that include all direct thermal and electrical inputs are shown in Table 3.7-2. The electrical energy includes milling, pumping, agitation and electro-deposition of copper, but does not include the energy for producing gaseous oxygen or ammonia. The total energy which is all electrical, is equivalent to 55.3 million Btu per ton of cathode copper. The reasons for this relatively large energy requirement center around the energy intensive nature of the electrowinning step and the attrition milling step. The Level 2 requirements for chemicals consumed in the process are shown in Table 3.7-3 for a total of 10.0 million Btu per ton of copper. The major chemical contributors to the total energy load are gaseous oxygen used in several process steps, and the ammonia used for iron precipitation.

3.7.5 Discussion

The total energy for both fuel, electricity and chemicals is equivalent to 65.3 million Btu per ton of cathode copper. The energy consumption is in the upper range for hydrometallurgical processes because of the energy intensive attrition milling of concentrates and the electrowinning of copper. The energy consumption figures could change for this process as it is developed further since it is still in a laboratory testing stage. The process is currently being technically and economically evaluated at the University of Utah.

3.7.6 Conclusion and Recommendations

This process appears to have the attraction of being a low-pollution route for the extraction of copper from chalcopyrite concentrates. Its energy requirements are quite high at its present state of development. These energy figures might be improved as more is learned about the process. Like all hydrometallurgical processes, it may be more attractive in smaller plants with a capacity of around 75,000 tons per year.

TABLE 3.7-1										FERRIC SULFATE ACID LEACH PROCESS											
(TONS PER TON CATHODE COPPER)																					
STREAM NO.		(1)				(2)				(3)				(4)				(5)			
STREAM NAME		WATER				COPPER CONCENTRATE				CONCENTRATE SLURRY				LEACH 1 SOLIDS				SOLIDS FROM SULFUR REMOVAL			
COMPOSITION		wt.	wt. %	wt.	dry wt. %	wt.	dry wt. %	wt.	dry wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %				
Cu				1.013	25.00	1.013	25.00	0.081	3.70	0.081	6.30										
Fe				1.083	26.70	1.083	26.70	0.231	10.40	0.231	18.10										
S (Combined)				1.256	31.00	1.256	31.00	0.264	11.90	0.264	20.70										
S (Free)								0.943	42.5												
SiO ₂				0.350	8.60	0.350	8.60	0.350	15.80	0.350	27.40										
Al ₂ O ₃				0.140	3.50	0.140	3.50	0.140	6.30	0.140	11.00										
FeO				0.028	0.70	0.028	0.70	0.028	1.20	0.028	2.20										
Fe ₂ O ₃				0.042	1.00	0.042	1.00	0.042	1.90	0.042	3.30										
NH ₄ Fe ₂ (SO ₄) ₂ ·(OH) ₆																					
Others				0.140	3.50	0.140	3.50	0.140	6.30	0.140	11.0										
NH ₃																					
O ₂																					
H ₂																					
SO ₂																					
H ₂ O		3.647	100.00	0.405		4.052															
CaSO ₄ · 2H ₂ O																					
CaCO ₃																					
Cu ⁺²																					
Fe ⁺²																					
CuS																					
TOTAL		3.647	100.00	4.457	100.00	8.104	100.00	2.219	100.00	1.276	100.00										

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS									
(TONS PER TON CATHODE COPPER)									
STREAM NO.	(6)		(7)		(8)		(9)		(10)
STREAM NAME	SOLID WASTES		LIQUOR FROM LEACH I		LIQUOR FROM LEACH II		SULFUR		AMMONTUM JAROSITE
COMPOSITION	wt.	wt. %	wt.	dry wt. %	wt.	dry wt. %	wt.	wt. %	wt. wt. %
Cu	0.008	0.70	1.226	57.91	0.171	59.40			
Fe	0.140	12.70	0.890	42.10	0.117	40.60			
S (Combined)	0.160	14.50							
S (Free)	0.092	8.40					0.296	100.00	
S ₂ O ₂	0.350	31.80							
Al ₂ O ₃	0.140	12.70							
FeO	0.028	2.50							
Fe ₂ O ₃	0.042	4.00							
NH ₄ Fe ₂ (SO ₄) ₂ (OH) ₆									2.654 100.00
Others	0.140	12.70							
NH ₃									
O ₂									
N ₂									
SO ₂									
H ₂ O			21.133		5.321				
CaSO ₄ · 2H ₂ O									
Ca CO ₃									
Cu ⁺²									
Fe ⁺²									
CuS									
TOTALS	1.100	100.00	23.249	100.00	5.609	100.00	0.296	100.00	2.654 100.00

TABLE 3.7-1 (cont.)

FERRIC SULFATE ACID LEACH PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	AMMONIA		AIR		IRON PRECIPITATION LIQUOR		SELENIUM REMOVAL LIQUOR		CATHODE COPPER	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	dry wt. %	wt.	dry wt. %	wt.	wt. %
Cu									1.000	100.00
Fe										
S (Combined)										
S (Free)										
SiO ₂										
Al ₂ O ₃										
FeO										
Fe ₂ O ₃										
NH ₄ Fe ₂ (SO ₄) ₂ (OH) ₆										
Others										
NH ₃	0.094	100.00								
O ₂			0.133	21.00						
N ₂			0.632	79.00						
SO ₂										
H ₂ O					26.455		26.455			
CaSO ₄ · 2H ₂ O										
CaCO ₃										
Cu ⁺²					1.395	94.60	1.397	94.6		
Fe ⁺²					0.079	5.40	0.079	5.4		
CuS										
TOTAL	0.094	100.00	0.765	100.00	27.929	100.00	27.931	100.00	1.000	100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS									
(TONS PER TON CATHODE COPPER)									
STREAM NO.	(16)		(17)		(18)		(19)		(20)
STREAM NAME	SPENT ELECTROLYTE TO LEACH I		SPENT ELECTROLYTE TO SULFATE REMOVAL		DESULFATED LIQUOR TO LEACH I		DESULFATED LIQUOR TO CuS PRECIP.		CALCIUM CARBONATE
COMPOSITION	wt.	dry wt. %	wt.	dry wt. %	wt.	dry wt. %	wt.	dry wt. %	wt. wt. %
Cu									
Fe									
S (Combined)									
S (Free)									
SiO ₂									
Al ₂ O ₃									
FeO									
Fe ₂ O ₃									
NH ₄ Fe ₂ (SO ₄) ₂ ·(OH) ₆									
Others									
NH ₃									
O ₂									
N ₂									
SO ₂									
H ₂ O	14.799		11.656		3.534		3.647		
CaSO ₄ · 2H ₂ O									
Ca CO ₃									
Cu ⁺²	0.222	83.50	0.175	83.5	0.053	83.5	0.055	83.5	.938 100.00
Fe ⁺²	0.044	16.50	0.035	16.5	0.011	16.5	0.011	16.5	
CuS									
TOTAL	15.065	100.00	11.866	100.00	3.598	100.00	3.713	100.00	.938 100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS										
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	COPPER SULFIDE		EXCESS FLUID		SULFUR DIOXIDE TO LEACH II		SULFUR DIOXIDE TO LEACH II		SULFUR DIOXIDE TO CuS PRECIP.	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu										
Fe										
S (Combined)										
S (Free)										
SiO ₂										
Al ₂ O ₃										
FeO										
Fe ₂ O ₃										
NH ₄ Fe ₂ (SO ₄) ₂ ·(OH) ₆										
Others										
NH ₃										
O ₂										
N ₂										
SO ₂										
H ₂ O			3.647	100.00						
CaSO ₄ · 2H ₂ O										
Ca CO ₃										
Cu ⁺²										
Fe ⁺²										
CuS	0.082	100.00								
TOTAL	0.082	100.00	3.647	100.00	0.115	100.00	1.125	100.00	0.055	100.00

TABLE 3.7-1 (cont.)		FERRIC SULFATE ACID LEACH PROCESS								
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(26)		(27)		(28)		(29)		(30)	
STREAM NAME	SPENT ELECTROLYTE TO LEACH II		DESULFATED LIQUOR TO LEACH II		SULFUR		OXYGEN FOR LEACH I		OXYGEN FOR LEACH II	
COMPOSITION	wt.	dry wt. %	wt.	dry wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu										
Fe										
S (Combined)					0.0277	100.00				
S (Free)										
S ₁ O ₂										
Al ₂ O ₃										
FeO										
Fe ₂ O ₃										
NH ₄ Fe ₂ (SO ₄) ₂ (OH) ₆										
Others										
NH ₃							0.829	100.00	0.117	100.00
O ₂										
N ₂										
SO ₂										
H ₂ O	0.852		4.474							
CaSO ₄ · 2H ₂ O										
Ca CO ₃										
Cu ⁺²	0.0128	83.5	0.067	83.5						
Fe ⁺²	0.0025	16.5	0.013	16.5						
CuS										
TOTAL	0.8673	100.00	4.554	100.00	0.0277	100.00	0.829	100.00	0.117	100.00

TABLE 3.7-1 (cont.) FERRIC SULFATE ACID LEACH PROCESS					
(TONS PER TON CATHODE COPPER)					
STREAM NO.	(31)		(32)		
STREAM NAME	OXYGEN FOR SULFUR OXIDATION		CALCIUM SULFATE PRECIPITATE		
COMPOSITION	wt.	wt. %	wt.	wt. %	
Cu Fe S (Combined) S (Free) SiO ₂ Al ₂ O ₃ FeO Fe ₂ O ₃ NH ₄ Fe ₂ (SO ₄) ₂ (OH) ₆ Others NH ₃ O ₂ N ₂ SO ₂ H ₂ O CaSO ₄ · 2H ₂ O CaCO ₃ Cu ⁺² Fe ⁺² CuS	0.648	100.00	1.613	100.00	
TOTAL	0.648	100.00	1.613	100.00	

TABLE 3.7-2		ENERGY REQUIREMENTS			Level 1
FERRIC SULFATE ACID LEACH PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Attrition Milling				
	A) Electrical Energy (2 to 3 micron mean particle size 4.05 ton concen- trate/ton copper)	KWH	408.2	0.0105	4.286
1	Copper Electrowinning				
	A) Electric Energy	KWH	2445	0.0105	25.673
	Process Pumping and Agitation				
	A) Electrical Energy	KWH	900	0.0105	9.45
				TOTAL	19.409

TABLE 3.7-3 ENERGY REQUIREMENTS					
FERRIC SULFATE ACID LEACH PROCESS					
Level 2					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Leach I A) Oxygen	TON	0.829	3.78	3.134
3	Sulfur Oxidation A) Oxygen	TON	0.648	3.78	2.449
4	Leach II A) Oxygen	TON	0.117	3.78	0.442
5	Iron Precipitation A) Ammonia	TON	0.094	41.73	3.923
9	Sulfate Removal A) Limestone	TON	0.938	0.104	0.098
				TOTAL	10.046

3.7.7 References

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3.7A THE ELECTROSLURRY™ — ENVIROTECH CORPORATION PROCESS

3.7A.1 Introduction

This process uses ferric sulfate leaching to extract the copper from chalcopyrite concentrates. An analysis will be made of the material balance for raw materials, internal process streams, and process effluents on the basis of 1 ton of copper product. The energy requirements are estimated on the basis of a commercial plant with a production rate of 50,000 tons per year of copper cathodes. In collaboration with Dr. Milton Wadsworth, Professor of Metallurgy and Metallurgical Engineering at the University of Utah, the process has been developed at the bench level at the Envirotech Research Center in Salt Lake City, Utah.

3.7A.2 Process Description

Overall, chalcopyrite concentrate is converted to covellite (CuS) and digenite ($\text{Cu}_{1.8}\text{S}$) and the converted solids are then processed through a slurry electrowinning cell to recover copper as electrowon cathodes. The slurry electrowinning cell offers a new concept in copper electrowinning in that it generates ferric iron at the anode instead of oxygen when compared to conventional copper electrowinning. This eliminates the oxygen over potential which is the major contributor to the high energy requirement in conventional electrowinning. The ferric iron, generated at the anode, is used to leach copper from the copper bearing solids which have been fed to the cell. Thus, leaching and electrowinning take place simultaneously.

The flowsheet is shown in Figure 3.7A-1. Copper concentrate is mixed with water to produce a slurry of 50 wt.% solids and is fed to an attritor milling circuit to produce a mean particle size of approximately 2 micron. This improves reaction rates in subsequent leaching and conversion circuits. 39% of the ground concentrate is leached in an acidic ferric sulfate solution to produce a copper sulfate, iron sulfate, sulfuric acid solution for feed to the conversion circuit. Ferric iron is generated "in-situ" by sparging the agitated slurry with oxygen gas. A 97% copper leach is obtained in 5 hours. The reaction is carried out at 90°C. 61% of the ground concentrate is mixed with the leach liquor and the resulting slurry is reacted with sulfur dioxide gas in an agitated vessel to convert the chalcopyrite to covellite and digenite. Retention times are approximately 2.5 hours and the reaction is carried out at 90°C. The converted solids are mixed with electrolyte from the slurry electrowinning circuit and processed in the electrowinning cells to produce copper cathodes. The conversion liquor contains ferrous sulfate and sulfuric acid and is sent to an iron removal step to remove iron as hydrated ferrous sulfate; after iron is removed, the acid liquor is returned to the leach circuit. A bleed stream is removed from the conversion liquor before iron removal to maintain a water and impurity balance. Iron removal is accomplished by adding the sulfuric acid required for leaching to the conversion liquor which is saturated with ferrous sulfate.

Sulfuric acid addition lowers the solubility of ferrous sulfate and hydrated ferrous sulfate precipitates out of solution and forms crystals which are easily filtered and washed. Approximately 85% of the copper contained in the conversion solids can be leached in the slurry electrowinning cells before an appreciable amount of iron begins to accumulate in the electrolyte. The cell circuit is controlled so that the electrolyte slurry exits the circuit at this point and goes to liquid solid separation where the electrolyte is recovered and returned to the electrowinning cells and the residual cells solids are directed to the leach step to recover residual copper. Sulfur contained in the feed concentrate is converted to elemental sulfur and reports to the tailings from the leach circuit. The elemental sulfur is recovered by pressure filtration, on plate and frame filter, with steam at 35 PSIG. Bleed streams and the hydrated ferrous sulfate (if it cannot be sold as by-product) are directed to a waste treatment and circuit where the acid is neutralized and iron is oxidized and precipitated as ferric hydroxide before being disposed to a tailings pond. Laboratory testing has shown a 98% copper recovery for the process.

3.7A.3 Material Balance

The process chemistry is shown by the following reactions:

Leaching

Overall:

Conversion

Slurry Electrowinning

Waste Treatment

Overall Process Chemical Reaction

The material balances resulting from the above chemistry are presented in Table 3.7A-1. The quantities involved are sufficient to produce 1 ton of copper product. Stream numbers are the same as appear in Figure 3.7A-1.

3.7A.4 Energy Requirements

The Level 1 energy requirements that include all direct thermal and electrical inputs are shown in Table 3.7A-2. The electrical energy includes milling, pumping, agitation, and electro-deposition of copper, but does not include the energy for producing gaseous oxygen. The total energy which is in the form of electricity, is equivalent to 31.2 million Btu per ton of copper cathode. The electrowinning step requires approximately 19.1 million Btu per ton of copper cathode (61.2% of the total). This is approximately 21% lower than that required by conventional electrowinning which is estimated to be 24 million Btu per ton of cathode copper. The Level 2 requirements for chemicals consumed in the process are shown in Table 3.7A-3 for a total of 8.4 million Btu per ton of copper. The major contributor to the Level 2 energy requirements is burnt lime which is used for iron precipitation.

3.7A.5 Discussion

The total energy for both fuel, electricity, and chemicals is equivalent to 39.6 million Btu per ton of copper cathode. The energy consumption is in the lower range for hydrometallurgical processes. This can be attributed mainly to the lower power requirements of the slurry electrowinning cells. Further reductions in energy requirements are possible since this process is still at the preliminary stages of development. The process has been checked at the bench scale level and the electrosolurry cell has been studied extensively in continuous operation.

3.7A.6 Conclusions and Recommendations

As with all hydrometallurgical processes, this process offers a less polluting route for the extraction of copper from chalcopyrite concentrates. The estimated energy requirements show the

TABLE 3.7A-1 THE ELECTROSLURRY TM PROCESS (TONS PER TON CATHODE COPPER)									
STREAM NO.	(1)		(2)		(3)		(4)		(5)
STREAM NAME	Copper Concentrate		Water		Concentrate Slurry		Concentrate Slurry		Oxygen
COMPOSITION	wt.	dry wt. %	wt.	wt. %	wt.	dry wt. %	wt.	dry wt. %	wt. wt. %
Cu	1.0204	25.0			0.39795	25.0	0.62245	25.0	
Fe	1.1430	28.0			0.4457	28.0	0.6973	28.0	
S (Combined)	1.2653	31.0			0.4935	31.0	0.7718	31.0	
S (Free)						16.0			
Others	0.653	16.0			0.2547	16.0	0.3983	16.0	
H ₂ O	0.5045		3.5772	100.00	1.5918		2.4898		
H ₂ SO ₄									
CuSO ₄									
FeSO ₄									
CaCO ₃									
Ca(OH) ₂									
Fe(OH) ₃									
CaSO ₄ ·2H ₂ O									
O ₂									0.28 100.00
N ₂									
SO ₂									
CO ₂									
TOTAL	4.5862	100.00	3.5772	100.00	3.18365	100.00	4.97965	100.00	0.28 100.00

TABLE 3.7A-1 (cont.)		THE ELECTROSLURRY TM PROCESS					
		(TONS PER TON CATHODE COPPER)					
STREAM NO.	(6)	(7)	(8)	(9)	(10)		
STREAM NAME	Leach Liquor	Leach Solids	Sulfur Dioxide	Conversion Solids	Conversion Liquor		
COMPOSITION	wt.	wt. %	wt.	wt.	wt.	wt. %	wt. %
Cu	(0.5559)		0.0204	0.9	1.1784	44.4	
Fe	(0.7147)		0.264	12.0	0.3064	11.5	(1.106)
S (Combined)			0.258	11.7	0.7718	29.1	
S (Free)			1.01	45.8			
Others			0.654	29.6	0.3983	15.0	
H ₂ O	8.3194	61.0	0.4667				10.7267 66.9
H ₂ SO ₄	1.9718	14.5					2.3148 14.4
CuSO ₄	1.3959	10.2					
FeSO ₄	1.9441	14.3					3.006 18.7
CaCO ₃							
Ca(OH) ₂							
Fe(OH) ₃							
CaSO ₄ · 2H ₂ O							
O ₂							
N ₂							
SO ₂				0.112 100.00			
CO ₂							
TOTAL	13.6302	100.00	2.6721	100.00	2.6549	100.00	16.0475 100.00

TABLE 3.7A-1 (cont.) THE ELECTROSLURRY TM PROCESS (TONS PER TON CATHODE COPPER)										
STREAM NO.	(11)		(12)		(13)		(14)		(15)	
STREAM NAME	Conversion Liquor To Iron Removal		Conversion Liquor To Waste Treatment		Conc. Sulfuric Acid		Ferrous Sulfate (Crystalline)		Acid Liquor	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu										
Fe										
S (Combined)	(0.6192)		(0.4865)				(0.3931)		(0.226)	
S (Free)										
Others										
H ₂ O	6.0069	66.9	4.7198	66.9	0.1258	5.0	0.1929	15.3	5.9399	58.0
H ₂ SO ₄	1.2963	14.4	1.0185	14.4	2.3905	95.0			3.6868	36.0
CuSO ₄										
FeSO ₄	1.6834	18.7	1.3226	18.7			1.0689	84.7	0.6145	6.0
CaCO ₃										
Ca(OH) ₂										
Fe(OH) ₃										
CaSO ₄ · 2H ₂ O										
O ₂										
N ₂										
SO ₂										
CO ₂										
TOTAL	8.9866	100.00	7.0609	100.00	2.5163	100.00	1.2618	100.00	10.2412	100.00

TABLE 3.7A-1 (cont.)

THE ELECTROSLURRY™ PROCESS
(TONS PER TON CATHODE COPPER)

STREAM NO.	(16)		(17)		(18)		(19)		(20)	
STREAM NAME	Copper Cathode		Recycle Electrolyte		Residual Cell Solids		Steam		Sulfur	
COMPOSITION	wt.	dry wt. %	wt.	wt. %	wt.	dry wt. %	wt.	wt. %	wt.	wt. %
Cu	1.0	100.00	1.2274	3.2	0.1784	10.8				
Fe			0.9196	2.4	0.3064	18.5				
S (Combined)					0.3234	19.5				
S (Free)					0.4484	27.1			.9086	100.00
Others			3.4351	9.0	0.3983	24.1				
H ₂ O			28.7395	75.7			0.315	100.00		
H ₂ SO ₄			3.6784	9.7						
CuSO ₄										
FeSO ₄										
CaCO ₃										
Ca(OH) ₂										
Fe(OH) ₃										
CaSO ₄ · 2H ₂ O										
O ₂										
N ₂										
SO ₂										
CO ₂										
TOTAL	1.0	100.00	38.0	100.00	1.6549	100.00	0.315	100.00	.9086	100.00

TABLE 3.7A-1 (cont.)			THE ELECTROSLURRY™ PROCESS (TONS PER TON CATHODE COPPER)							
STREAM NO.	(21)		(22)		(23)		(24)		(25)	
STREAM NAME	Process Tailings		Water From Sulfur Removal		Air		Calcium Carbonate		Calcium Hydroxide	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	dry wt. %	wt.	dry wt. %
Cu	0.0204	1.6								
Fe	0.264	20.4								
S (Combined)	0.2581	19.9								
S (Free)	0.101	7.8								
Others	0.653	50.3								
H ₂ O			0.7817	100.00						
H ₂ SO ₄										
CuSO ₄										
FeSO ₄										
CaCO ₃							1.0393	100.00		
Ca(OH) ₂									1.1654	100.00
Fe(OH) ₃										
CaSO ₄ · 2H ₂ O										
O ₂					0.126	21.0				
N ₂					0.474	79.0				
SO ₂										
CO ₂										
TOTAL	1.2965	100.00	0.7817	100.00	0.6	100.00	1.0393	100.00	1.1654	100.00

TABLE 3.7A-1 (cont.)

THE ELECTROSLURRYTM PROCESS
(TONS PER TON CATHODE COPPER)

STREAM NO.	(26)	(27)	(28)	(29)	
STREAM NAME	Waste Solids	Wash Water	Wash Water	Carbon Dioxide	
COMPOSITION	wt. dry wt. %	wt. wt. %	wt. wt. %	wt. wt. %	
Cu					
Fe	(.8796)				
S (Combined)					
S (Free)					
Others					
H ₂ O	4.7986	0.9334 100.00	0.937 100.00		
H ₂ SO ₄					
CuSO ₄					
FeSO ₄					
CaCO ₃					
Ca(OH) ₂					
Fe(OH) ₃	1.6828 27.2				
CaSO ₄ · 2H ₂ O	4.4964 72.8				
O ₂					
N ₂					
SO ₂					
CO ₂				.4573 100.00	
TOTAL	10.9778 100.00	0.9334 100.00	0.937 100.00	4.573 100.00	

TABLE 3.7A-2 ENERGY REQUIREMENTS THE ELECTROSLURRY TM PROCESS					
Level 1					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Attritor Milling				
	A) Electrical energy for grinding equip. (2-3 micron mean particle size, 4.0d17 ton concen- trate/ton copper product).	KWH	403.17	0.0105	4.2858
	B) Electrical energy for circuit pumping and agitation.	KWH	13.65	0.0105	0.1433
2	Leach				
	A) Steam for circuit heating.	BTU			2.4460
	B) Electrical energy for circuit pumping and agitation.	KWH	42.89	0.0105	0.4503
3	Conversion				
	A) Steam for circuit heating.	BTU			2.3630
	B) Electrical energy for circuit pumping and agitation.	KWH	93.88	0.0105	0.9857

TABLE 3.7A-2 (cont.)			ENERGY REQUIREMENTS		Level 1
THE ELECTROSLURRY TM PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
4	Slurry Electrowinning				
	A) Electrical energy for electrowinning cells (to recti- fiers and cell recirculation pumps)	KWH	1820	0.0105	19.1100
	B) Electrical energy for circuit pumping, agitation and cathode handling.	KWH	39.91	0.0105	0.4191
5	Iron Removal				
	A) Electrical energy for circuit pumping and agitation.	KWH	14.16	0.0105	0.1487
6	Sulfur Removal				
	A) Steam for circuit heating.	BTU			0.59
	B) Electrical energy for circuit pumping and agitation.	KWH	3.22	0.0105	0.0338
7	Waste Treatment				
	A) Electrical energy for circuit pumping and agitation.	KWH	23.82	0.0105	0.2501
				TOTAL	31.2258

TABLE 3.7A-3

ENERGY REQUIREMENTS

Level 2

THE ELECTROSLURRYTM PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
2	Leach A) Oxygen	TON	0.28	3.78	1.058
3	Conversion A) Oxygen (for sulfur burner)	TON	0.056	3.78	0.212
5	Iron Removal A) Sulfuric Acid	TON	2.3905	0.83	1.984
7	Waste Treatment A) Limestone B) Lime	TON TON	1.15 0.928	0.104 5.4	0.120 5.011
				TOTAL	8.385

process to be potentially competitive with conventional smelting. Removal of hydrated ferrous sulfate from the process as a by-product could lower the energy requirements by approximately 2.5 million Btu per ton of cathode copper. Research is currently underway at the bench level to further reduce the energy requirements of the slurry electrowinning circuit. Two approaches being studied are lower current density operation in the range of 60 amps per square feet and the use of more conductive lead alloys for anodes.

The slurry electrowinning concept may have application to the recovery of other metals. Tests conducted by Envirotech Corporation have shown recovery of chrome, zinc, nickel, and cobalt may be feasible with this technique.

3.8 ROAST/SULFITE-REDUCTION PROCESS

3.8.1 Introduction

This section contains estimates of the material and energy requirements for a copper extraction process referred to as the sulfite-reduction process. The estimate includes the evaluation of material flows of raw materials, other influents, internal process streams, and effluents. Energy values are evaluated for raw materials, fuels, steam, electrical power and other consumables. Energy requirements are assessed in two respects, (1) an operational requirement that does not include special processing features for economizing or recycling of heat between or within processing steps and (2) a theoretical requirement that includes improved heat transfer and utilization. The theoretical energy evaluation is indicative of potential energy savings.

The sulfite-reduction process is hydrometallurgical with the exception of the initial roasting step and the anode furnaces prior to conventional electrorefining of the copper product. The process design evaluated is for the treatment of chalcopyrite concentrates recovered by froth flotation.

A fairly detailed description of the novel processing steps is given by Bartlett (Feb.-Mar. 1978) in the report "A Process that Uses Sulfur From a Copper Concentrate to Reduce Leached Copper." The more conventional processing steps are described in standard texts on copper extraction such as that by Biswas and Davenport (1976). Some advantages claimed for the process are reduced energy and labor requirements by the elimination of electrowinning typical of hydrometallurgical copper extraction, low requirements for raw materials and utilities, and few corrosion problems. The process is fairly complex as is evident by the many process streams shown on the flow sheet (see Figure 3.8-1). The flow scheme consists of three recycle loops, interconnected: (1) The lixiviant recycle loop for the leaching and precipitation of copper, (2) the scrubber-liquor recycle loop for the adsorption of sulfur dioxide from the roaster gas and the removal of sulfate, and (3) the ammonia recycle loop for the adsorption of ammonia into the sulfite liquor (indicated as the Gas Scrubber Circuit, Process Step 7, in Figure 3.8-1).

3.8.2 Process Description

The main features of the sulfite-reduction process are a roasting of the chalcopyrite to oxidize the copper and iron sulfide minerals (Process Step 1, Fluid-Bed Roasting in Figure 3.8-1), a sulfuric acid leach of the calcine from the roaster (Process Step 2, Leach Circuit in Figure 3.8-1), and a copper reduction step (Process Step 3, Reduction Autoclaves in Figure 3.8-1), that utilizes a sulfite-rich liquor generated by the adsorption of sulfur dioxide from the roaster gas. The roasting

is controlled at 650°C to prevent the formation of ferrites — acid-insoluble, copper-containing compounds. Leaching is conducted in open vats at 85°C, and the reduction step is conducted under pressure at 160°C and 854 kPa. A roaster-gas sulfur dioxide concentration of 5% is sufficient for adsorption and sulfite-rich liquor generation. The fluid-bed roaster is capable of producing gases with sulfur dioxide levels well in excess of 5%.

The main stoichiometric relationships for the processing reactions are as follows:

Fluid-Bed Roasting, Process Step 1

- a. Chalcopyrite oxidation

- b. Pyrite oxidation

Sulfuric Acid Leaching, Process Step 2

Reduction Chemistry, Process Step 3

- a. Reduction of copper by ammonium bisulfite

- b. Reduction of copper by ammonium sulfite

Gas-Scrubbing and Sulfite Regeneration Chemistry, Process Step 7

- a. Ammonium sulfite formation

- b. Ammonia adsorption

Sulfur Disposal and Ammonia Regeneration Chemistry, Process Step 10

- a. Acid neutralization with limestone

- b. Ammonia recovery with lime

3.8.3 Material Requirements Evaluations

The evaluation of material requirements is based on the description of the process by Bartlett (Feb.-Mar. 1978). Melting of the copper precipitate from the reduction autoclaves; fire refining to remove iron, oxygen and sulfur; anode casting; and electrorefining have been added to provide a processing scheme comparable with conventional pyrometallurgical technology. The flow sheet is that of Figure 3.8-1 which shows the identifiers for the process steps and streams used in the material and energy requirements evaluations. A summary of the material flows is listed in Table 3.8-1. A complete accounting of pertinent supportive calculations, data and references for the material flows is given in Appendix 3.8-A. Considered for this evaluation is a cathode production rate of about 100,000 ton/year and a copper recovery of 98%. The feed is considered to be a chalcopyrite concentrate recovered by froth flotation having a composition of 25% copper, 29% iron and 31% sulfur that is amenable to the process.

3.8.4 Energy Requirements Evaluation

Tables 3.8-2 and 3.8-3 list a summary of the energy requirements for the process. The energy requirement evaluation is based on the above material requirements evaluation. Level 1 requirements for fuels, steam and electrical power (excluding chemicals and consumables) are listed in Table 3.8-2. Level 2 requirements for chemicals, fluxes, refractories and other consumables, are listed in Table 3.8-3. Equivalent fuel requirements are calculated and summed using appropriate energy equivalent estimates. Relevant calculations and descriptive information for the energy requirements tables can be found in Appendix 3.8-B if such information is too extensive for inclusion as footnotes.

The evaluation for Tables 3.8-2 and 3.8-3 is an "operational" estimate in that it reflects a process designed and operated in a conventional, operational mode. The bottom-line totals are termed "operational" in the above summary table. This operational estimate does not consider any special features for the economizing or recycling of heat within the process. The "theoretical" estimate discussed below includes such considerations. The main aspect of the theoretical estimate is the utilization of the heat generated by the processing reactions to offset process heating requirements. The difference between the operational and theoretical estimates is indicative of the potential of the process for energy savings.

The following energy calculations were provided by Goel (1979). Thermochemical data for the calculations can be found in Barnier and Schenerman (1978).

Energy generated by the leaching reaction

$$\text{H}_2^{\circ}_{98} = (-37,600 - 232,700) + (15,500 - 232,700 - 57,800)$$

$$= -4,700 \text{ cal/mole}$$

$$\text{Copper dissolved— } 1.00 \text{ kg} = 15.73 \text{ moles}$$

$$\text{Energy Generated} = (15.73)(4,700)(3.60 \times 10^{-6})$$

$$= .27 \text{ million Btu/ton product}$$

TABLE 3.8-1 SULFITE REDUCTION PROCESS										
(TONS PER TON CATHODE COPPER)										
STREAM NO.	(1)		(2)		(3)		(4)		(5)	
STREAM NAME	CHALCOPYRITE CONCENTRATE		CALCINE		PREGRADE LIQUOR*		COPPER SLURRY SOLIDS		ANODES	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	1.02	25.06	1.02	29.74	1.00	7.23	0.99	100.00	0.99	100.00
Fe	1.14	28.01	1.14	33.24						
S	1.26	30.96	0.01	0.29						
Other	0.65	15.92	1.26	36.73	3.173	9.09				
NH ₄ HSO ₃					0.097	0.28				
(NH ₄) ₂ SO ₃					0.0156	0.04				
(NH ₄) ₂ SO ₄					2.062	5.91				
H ₂ SO ₄										
H ₂ O					26.48	75.65				
NH ₃										
Scrap Fe										
Ca(OH) ₂										
CaCO ₃										
SO ₂										
CaSO ₄										
pH					1.0					
TOTAL	4.07	100.00	3.43	100.00	34.91	100.00	0.99	100.00	0.99	100.00

*Copper is figured as CuSO₄. 10% of the total weight is allowed for minor impurity buildup which is included as "Other".

TABLE J.B-1 (cont.)

SOLTECH REDUCTION PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	(6)		(7)		(8)		(9)		(10)	
STREAM NAME	ANODES		CATHODES		ROASTER GAS		OFF GAS		BARREN LIQUOR*	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu	1.00	100.00	1.00	100.00					1.01	
Fe										
S										
Other									1.801	9.09
NH ₄ HSO ₃									1.140	0.33
(NH ₄) ₂ SO ₄									1.019	0.05
(NH ₄) ₂ SO ₄									1.763	9.00
H ₂ SO ₄									2.235	5.34
H ₂ O									1.870	16.19
NH ₃										
Scrap Fe										
Ca (OH) ₂										
Ca CO ₃										
SO ₂						5.0		5.0		
Ca SO ₄										
pH									0.95	
TOTAL	1.00	100.00	1.00	100.00					1.83	100.00
*Copper is figured as CuSO ₄ , which is included as "Other".										

*Copper is figured as CuSO₄, which is included as "Other".

4 of the total weight is allowed for minor impurity buildup

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(TONS PER TON CATHODE COPPER)

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TABLE 3.8-1 (cont.)

SULFITE REDUCTION PROCESS

(TONS PER TON CATHODE COPPER)

STREAM NO.	IRON		LIME		LIMESTONE	
STREAM NAME	IRON		LIME		LIMESTONE	
COMPOSITION	wt.	wt. %	wt.	wt. %	wt.	wt. %
Cu Fe S Other NH_4HSO_3 $(\text{NH}_4)_2\text{SO}_3$ $(\text{NH}_4)_2\text{SO}_4$ H_2SO_4 H_2O NH_3 Scrap Fe $\text{Ca}(\text{OH})_2$ CaCO ₃ SO ₂ CaSO ₄ pH	0.02	100.00	0.71	100.00	0.76	100.00
TOTAL	0.02	100.00	0.71	100.00	0.76	100.00
*Copper is figures as CuSO ₄ . 10% of the total weight is allowed for minor impurity buildup which is included as "Other".						

TABLE 3.8-2

ENERGY REQUIREMENTS

Level 1

SULFATE REDUCTION PROCESS

STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
1	Roaster				
	A) Waste Heat Recovery	BTU	-4.25	1.00	-4.25
	B) Fuel (Start Up only)	BTU	0.2	1.00	0.20
2	Leach Circuit				
	A) Electrical Power	KWH	59.756	0.0105	0.627
	B) Process Heating, Steam				
3	Reduction Autoclaves				
	A) Pumping, Electrical	KWH	8.04	0.0105	0.084
	B) Process Heating, Steam	LBS	2164	0.0014	11.43
4	Filter				
	A) Electrical	KWH	2	0.0105	0.021
5	Melting, Refining, and Anode Casting				
	A) Heating and Melting (Fuel Oil)	GAL	19.5	0.15	2.925
	B) Poling Gas	SCF	225	0.0010	0.225
6	Electrorefining				
	A) Electrical	KWH	222	0.0105	2.336
	B) Process Heating (Fuel Oil)	LBS	1300	0.0014	1.82
7	Gas Scrubber Circuit				
	A) Electrical	KWH	132.43	0.0105	1.39
	Ancillary Loads				
	A) Electrical	KWH	50.0	0.0105	0.525
				TOTAL	17.769

TABLE 3.B-3		ENERGY REQUIREMENTS			Level 2
SULFITE - REDUCTION PROCESS					
STEP NUMBER	PROCESS	UNIT	UNITS PER NET TON CATHODE COPPER	MILLION BTU REQUIRED PER UNIT	MILLION BTU PER NET TON CATHODIC COPPER
5	Melting, Refining, and Anode Casting				
	A) Flux	TON	0.1	0.71	0.076
6	Electrorefining				
	A) Acid and Reagents	TON	0.0165	0.83	0.014
7	Gas Scrubber Circuit				
	A) Make-up Ammonia	TON	0.035	39.0	1.365
9	Cementation				
	A) Scrap Iron	TON	0.02	18.0	0.36
10	Regeneration Circuit				
	A) Lime	TON	0.71	5.45	3.870
	B) Limestone	TON	0.75	0.24	0.182
				TOTAL	5.867

Energy generated by the reduction-autoclave reactions

(90% of copper is assumed to be reduced by bisulfite $[\text{NH}_4\text{HSO}_4]$, and the remaining copper is assumed to be reduced by sulfite $[(\text{NH}_4)_2\text{SO}_3]$ at a reduction efficiency at 99%)

In an aqueous solution, this equation can be expressed as

$$\Delta H_{298}^0 = (15,500 - 165,000 - 57,800) + (-232,700)$$

$$= -25,400 \text{ cal/mole}$$

$$\text{Energy Generated} = (15.73) (.90) (.99) (25,400) (3.6 \times 10^{-6})$$

$$= 1.28 \text{ million Btu/ton product}$$

In an aqueous solution, this equation can be expressed as

$$\Delta H_{298}^0 = (15,500 - 167,200 - 57,800) + (-232,700)$$

$$= -23,200 \text{ cal/mole}$$

$$\text{Energy Generated} = (15.73) (.19) (.99) (23,200) (3.6 \times 10^{-6})$$

$$= .13 \text{ million Btu/ton product}$$

$$\begin{aligned} \text{Total Heat Generated} &= .27 + 1.28 + .13 \\ \text{by Processing Reactions} &= 1.68 \text{ million Btu/ton product} \end{aligned}$$

With some special design features, the heat generated by the processing reactions can be utilized to heat the influents of the reaction vessels and, thus, offset a process heating requirement. Generally, the processing equipment is increased in either size or complexity to accomplish this heat transfer — e.g., employing bulkier continuous-stirred tanks as compared to more efficient tube or staged reaction vessels. The theoretical energy requirement is evaluated as follows:

Total Level 1 Energy Requirement — (see Table 3.8-3) — 35.40 million Btu/ton product

Offset from Heat Generated by Processing Reactions — 1.68 million Btu/ton product

Total Theoretical Level 1 Requirement — 33.72 million Btu/ton product

Total Level 2 Energy Requirement (unchanged, see Table 3.8-3) — 5.87 million Btu/ton product

Total Theoretical Energy Requirement — 39.59 million Btu/ton Product

3.8.5 Discussion

The sulfite-reduction process does not involve novel technology in that it integrates processing steps developed for other metallurgical or environmental pollution control purposes. The roasting of chalcopyrite concentrates is similar to the technology for autogeneous oxy-sulfate roasting developed by Hecla Mining Co. at their Lakeshore, Arizona property (Bartlett, Feb.-Mar. 1978) or equipment employed by Cities Service Co., Minerals Group at their Copperhill, Tennessee operation for roasting pyrite in the production of sulfuric acid. Roaster gas scrubbing is similar to the ammonia-based processes for sulfur dioxide removal from power-plant stack gases that have been developed by Nippon Kokan KK, a steel company in Japan; Ugine Kuhlmann in France; Smelter Control Research Association, U. S., and others (Slack and Hollinder, 1975; Radian Corp., 1976). The leaching circuit is typical of hydrometallurgical acid-leaching operations employed for metal extractions such as for copper and uranium (Biswas and Davenport, 1976, Ch. 13; Merritt, 1971). The copper reduction step is the Jamau 1907 patent (Jamau, 1907) and has been recently investigated and reported on by Parker and Muir (1976). Regeneration of ammonia (Process Step 10, Regeneration Circuit in Figure 3.8-1) has been shown to be effective in the Nippon Kokan KK process (Slack and Hollinder, 1975). The other process steps (cementation, melting, fire refining, anode casting, and electrorefining) are common to conventional copper production.

Each step of the sulfite-reduction process was extensively laboratory tested, and technically and economically evaluated by the staff of Kennecott Copper Corp. Research Center at Salt Lake City, Utah (Bartlett, Feb.-Mar. 1978 and Oct. 1978). Further development has been recommended by Bartlett (SRI International, 1977). Present development has not gone beyond attempting laboratory experiments.

The evaluations provided by this study clearly demonstrates the validity of combining the various processing technologies. Of particular interest is the interplay of reductant (sulfites) and acid levels in the lixiviant recycle loop (see calculations in Appendix 3.8-A). A significant element in the operation and control of this loop and the other two interacting recycle loops (see discussion in Introduction above) is the splitter (Process Step 8, Figure 3.8-1). Control of the flow of solution returned to the leach vats and the flow of the bleed stream to the ammonia regeneration circuit is intimately related to the chemistry of the leach circuit and reduction autoclaves. The material flow calculations show that operation and control are feasible.

3.8.6 Conclusions and Recommendations

The processing energy requirements are not significantly sensitive to processing design factors that influence the utilization of heat generated by the processing reactions (such theoretical considerations would produce an energy requirement reduction of 1.68 million Btu/ton product or 4% of the operational energy requirement estimate). The processing scheme is also fairly insensitive to the composition of the chalcopyrite concentrate feed. This insensitivity is the

result of the energy requirements being dominated by process heating steam and other loads that are fairly independent of the feed composition. The roaster waste heat recovery is the energy value most dependent on feed copper, iron and sulfur levels. A reduction of 10% in roaster waste heat recovery would increase the total energy requirement by about 1% (see values on Tables 3.8-2 and 3.8-3).

The two largest energy consuming items are process heating steam for the reduction autoclaves, and process heating steam for the leach circuit. These two major energy items constitute 71% of the total. The operational energy requirement is estimated as being 41.32 million Btu/ton of copper produced with 35.45 million Btu/ton product (86%) in the form of direct fuel, steam and electrical power consumption. The theoretical energy requirement that considers the utilization of the heat generated by the processing reactions is estimated as 39.64 million Btu/ton product, only slightly less (4%) than the operational estimate.

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