

# **RADIAN**

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THE BEHAVIOR OF MINOR AND TRACE  
ELEMENTS IN A SMELTER TREATING  
COPPER/NICKEL CONCENTRATES  
FROM THE MINNESOTA DULUTH GABBRO COMPLEX

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## SECTION 1

### INTRODUCTION

This report is an overview intended to focus on potential operational and/or environmental problems presented by minor and trace elements present in the copper/nickel ore of the Minnesota Duluth Gabbro Complex. Metals such as arsenic, cadmium, lead, and selenium occur naturally as sulfides in most copper or copper/nickel ores. Normally, these metals are present in concentrations less than 0.5 weight percent in the raw ore. However, copper ore, typically 0.7 to 1.0 weight percent copper, is subjected to a concentration process in order to prepare a concentrate (15 to 30 percent(w) Cu) which is suitable for smelting. The minor elements present as sulfides in the ore are also concentrated during this process.

Impurities in the copper concentrations are eliminated in the smelting processes either by volatilization or by slagging. The path of the major impurities through the smelting circuit is well defined. Sulfur exits as SO<sub>2</sub> in the process off gases and iron, silicon, and aluminum exit as either slag or tailings from a slag flotation process. The paths of minor or trace elements through the smelter are less well defined and depend greatly on the type of smelting furnaces used and the ways in which they are operated.

At this time, it is not possible to predict exactly the distribution of minor elements for any smelting scheme used to treat the Duluth Gabbro ore. The variations in concentrate composition make predictions impractical. However, it is certainly possible to make reasonable estimates based on available concentrate analyses and existing thermodynamic and smelter operating data in order to pinpoint the major potential environmental problems.

The approach taken in the remainder of this report is designed to make and justify these type of estimates. In Section 2, the elements presenting the greatest potential hazard are prioritized based on both chemical and process considerations. This is accomplished by:

- Presenting a theoretical framework which outlines the complexity of the problem of predicting minor element flow through smelting processes,
- Relating the theoretical concepts to measurable parameters which can be determined from actual smelter operating data, and

- Applying the existing smelter operating data to the problem of smelting the ore present in the Duluth Gabbro Complex.

Section 3 justifies the selection of Priority 1 elements, emphasizing both the process and control technology important for each element and the environmental impact they will create. Section 4 presents preliminary material balances for several key elements based on two possible smelter flow schemes. Section 5 is a review of the pertinent literature containing the smelter operating data used to draw each conclusion in this report.

## SECTION 2

### ELEMENT PRIORITIZATION

This prioritization identifies the key elements in the Duluth Gabbro ore body which may pose operational and environmental pollution problems if they are processed in a primary copper/nickel smelter. It is based on the analysis of a copper/nickel concentrate produced in a bench-scale flotation unit from mine ore samples (500 pounds each). One sample was taken from each of four mine sites. Five samples were taken from another site. Tables 1 and 2 present the analysis of the two bench-scale concentrates produced by different grinding/flotation techniques. As such, it is a preliminary effort and is intended to provide some direction for additional research. As data becomes available from pilot-scale flotation studies, the element prioritization will be changed, if necessary.

#### DEFINITION OF TERMS

Priority 1 includes elements which may be present in sufficient amounts in a concentrate to pose either operating problems with potential engineering and/or economic consequences to the company, or environmental problems with potential human health, air pollution, water pollution, or solid waste pollution implications.

Priority 2 includes elements which do not appear to be present in sufficient concentrations to pose the hazards of concern under the Priority 1 list.

#### PRIORITIZATION CRITERIA

The criteria used for placing an element in Priority 1 are:

- Quantity of element present in the concentrate,
- Toxicity to either human health or the environment, and
- Likelihood of release into the environment.

Existing smelter data will be used in each case to apply these criteria to the elements present in the Duluth Gabbro Complex. For the first criterion, comparisons will be made between the analyses of the bench scale concentrate produced from the Duluth Gabbro Complex and other ores, mainly copper ore. Expected problems based on the similarities or differences between the ore compositions will be noted.

TABLE 1. CONCENTRATE ANALYSIS FOR ONE-STAGE GRIND BENCH-SCALE FLOTATION TESTS (PPM BY WEIGHT)

Metal	Average	Stan.Dev.	Minimum	Maximum	Number of Samples
Al	20,088.5714	9,796.6107	7,420.0000	35,500.0000	7
B	372.2012	399.1216	-.0060	994.0000	5
Ba	86.1429	53.9766	40.0000	174.0000	7
Be	.0750	.1476	-.0050	.4000	7
Ca	12,864.2857	6,664.8927	3,360.0000	24,000.0000	7
Cu	110,942.8571	32,229.0685	74,700.0000	147,000.0000	7
Fe	270,148.0143	160,366.9511	36.1000	464,000.0000	7
K	743.7143	500.4031	300.0000	1,700.0000	7
Mg	17,940.0000	14,444.7003	3,450.0000	47,000.0000	7
Mn	363.7143	164.8795	143.0000	660.0000	7
Na	4,398.5714	1,875.9036	2,180.0000	7,370.0000	7
P*	10,360.2000	12,891.6756	-.7000	34,000.0000	7
Pb	45.2114	56.7297	-.1600	143.0000	7
Si**	1,951.3200	2,835.4723	98.6000	6,710.0000	5
Sr	56.5000	28.7092	18.6000	104.0000	7
Ti	1,111.0000	432.5579	539.0000	1,840.0000	7
V	75.2857	48.5628	18.4000	140.0000	7
Zn	904.5714	643.9614	28.0000	1,610.0000	7
Th	1.7657	4.5129	-.0600	12.0000	7
Ag	30.9143	8.9417	14.0000	41.0000	7
As	8.6914	22.6250	-.1400	60.0000	7
Cd	4.0500	7.6290	-.0700	20.0000	7
Co	1,283.5714	411.1414	898.0000	2,040.0000	7
Cr	361.1429	689.1442	30.8000	1,920.0000	7
Mo	38.7229	36.6897	-.0300	85.0000	7
Ni	24,457.1429	3,741.5938	19,100.0000	29,300.0000	7
Zr	25.8000	11.6435	15.0000	50.0000	7
Hg	.1633	.0252	.1400	.1900	3

\*80 to 200 ppm should be a more typical value

\*\*50000 to 120000 should be a more typical value

TABLE 2. CONCENTRATE ANALYSIS FOR TWO-STAGE GRIND BENCH-SCALE FLOTATION TESTS (PPM BY WEIGHT)

Metal	Average	Stan.Dev.	Minimum	Maximum	Number of Samples
Al	7,535.0000	4,165.7592	2,230.0000	12,700.0000	6
B	248.9197	393.7693	-.0068	874.0000	6
Ba	50.3333	49.3099	21.0000	147.0000	6
Be	.0050	0	-.0050	-.0050	6
Ca	4,645.0000	2,691.6965	1,440.0000	7,690.0000	6
Cu	173,166.6667	48,930.2224	82,000.0000	223,000.0000	6
Fe	369,833.3333	68,180.3980	302,000.0000	476,000.0000	6
K	580.1667	603.4966	-1.0000	1,300.0000	6
Mg	10,966.6667	8,839.7526	1,280.0000	25,000.0000	6
Mn	170.2833	91.8836	68.0000	315.0000	6
Na	1,683.3333	752.0018	400.0000	2,440.0000	6
P*	15,340.2333	22,690.9588	-.7000	56,900.0000	6
Pb	48.3867	51.8699	-.1600	130.0000	6
Si**	635.0000	963.6838	112.0000	2,590.0000	6
Sr	20.6567	11.2857	6.7400	32.4000	6
Ti	426.5000	138.0243	251.0000	642.0000	6
V	53.0500	56.4172	8.1000	130.0000	6
Zn	1,368.3333	1,065.8500	3.0000	2,280.0000	6
Th	3.2067	4.8850	-.0600	10.0000	6
Ag	39.7500	13.0033	17.0000	56.8000	6
As	11.7367	13.2179	-.1400	30.0000	6
Cd	8.3800	13.2565	-.0700	30.0000	6
Co	1,590.0000	542.8812	1,020.0000	2,320.0000	6
Cr	41.5857	47.3023	-.0070	108.0000	6
Mo	26.5150	39.0147	-.0300	89.0000	6
Ni	30,483.3333	2,948.5024	25,000.0000	32,900.0000	6
Zr	13.3167	4.0529	10.0000	19.7000	6

\*80 to 100 ppm should be a more typical value  
 \*\*50000 to 120000 should be a more typical value

The two accepted standards used to measure the relative toxicity of the elements present in the Duluth Gabbro Complex are the ACGIH TLV's and the NIH LD 50's. The toxicity of the pure elements or compounds likely to be present in the smelter exit streams were compared directly. Neither the synergistic nor antagonistic effects of each element on the others were considered in this report.

The third criterion is far more complex and requires some explanation. The likelihood that any particular element entering a smelter will be released into the environment as a pollutant depends on a number of chemical and process considerations. These are described below.

### Chemical Considerations

The important factors to consider to determine whether an element will be released into the environment as a pollutant are:

- Chemical form,
- Volatility, and
- Solubility.

Each of these factors is a function of the chemical equilibria and reaction kinetics inherent to the smelting processes. However, it is very difficult to rigorously describe the smelting processes in terms of equilibrium and kinetic expressions. It is much easier and no less accurate to consider the potential pollution problems in terms of observable, measurable parameters such as chemical form, volatility, and solubility. The copper/sulfur/oxygen system will illustrate the complexity of the theoretical approach.

Figure 1 is an equilibrium phase diagram showing volumes of stability occupied by various Cu/S/O compounds as a function of temperature and the partial pressures of SO<sub>2</sub> and O<sub>2</sub>. This diagram indicates the equilibrium conditions under which different Cu/S/O compounds can coexist. This information is useful for estimating what driving forces exist for the formation of one phase over another within an actual smelting furnace.

For example, at 800°K ( $10^4/T = 12.5$ ),  $\log p_{O_2} = -15$ , and  $\log p_{SO_2} = -2$ , Cu<sub>2</sub>S, Cu, and Cu<sub>2</sub>O are in equilibrium. If CuSO<sub>4</sub> is found in one of the smelting furnace exit streams, either there may be a driving force within the furnace for CuSO<sub>4</sub> to form one of the other phases, or other components present in the furnace have changed the Cu/S/O equilibria such that CuSO<sub>4</sub> is a stable compound at those conditions.

The effects of other compounds on the simple Cu/S/O equilibria cause the theoretical description of the smelting processes to be so complex. A phase diagram similar to that for the Cu/S/O systems can be constructed for each of the three or four dozen elements present in any smelting furnace. Each of the compounds present affects all of the other phase equilibria.

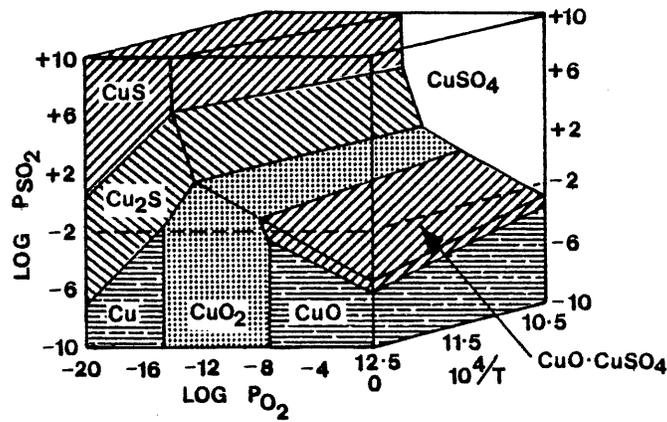
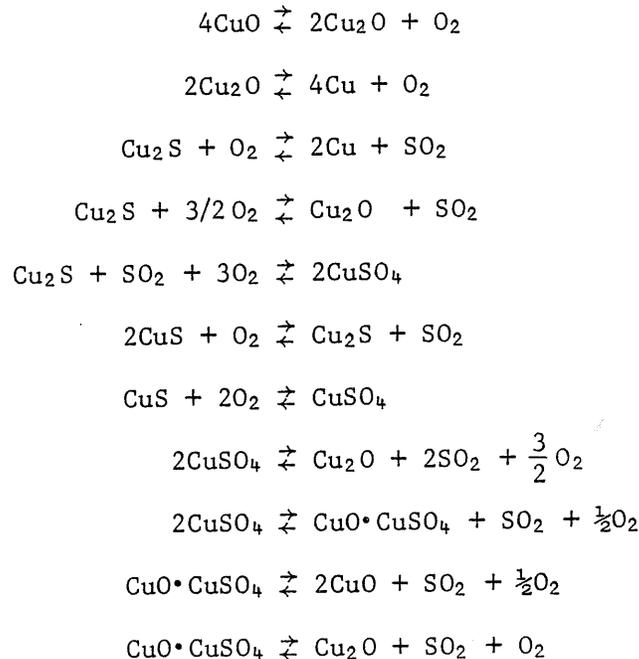


Figure 1. Predominance-volume diagram showing volumes of stability occupied by various Cu/S/O compounds in the range of  $\log p_{SO_2}$  from  $10^{-10}$  to  $10^{+10}$  atm,  $\log p_{O_2}$  from 1 to  $10^{-20}$  atm,  $p_{SO_2}$  and temperature from  $750^\circ$  to  $950^\circ$ K.

It is not possible to describe these interactions rigorously, especially for a system as nonideal and nonequilibrium as a smelting furnace.

The reaction kinetics or reaction rates add to the complexity of the problem. The following are some of the smelting reactions just for the Cu/S/O system:



It is more reasonable to use the parameters which can be easily measured using actual smelter operating data and simply keep in mind the theoretical framework which describes the system.

Fractional distribution,  $D_1$ , is a parameter which has been used in several sources (GI-134, GI-135, MA-740, MO-307) to present smelter operating data on minor elements. It is used in this report for the purpose of converting the available smelter operating data into usable form for material balances. The following definitions are used:

$$D_1 = \frac{\text{tons of X in off gas}}{\text{tons of X in furnace feed}}$$

$$D_2 = \frac{\text{tons of X in slag}}{\text{tons of X in furnace feed}}$$

$$D_3 = \frac{\text{tons of X in matte (or copper)}}{\text{tons of X in furnace feed}}$$

It should be emphasized that fractional distribution (D) as used here is a means of applying existing data to other similar smelter situations. It is not the same as either the empirically determined distribution ratios (MA-740) or the thermodynamic distribution coefficients (YA-078) used elsewhere in the literature. This approach is intended to give the best estimate of the importance of each element based on existing smelter operating data. The following discussion describes the three measurable parameters which affect the distribution of elements in smelter process streams.

#### Chemical Form--

The elements which occur naturally as sulfides are of major concern in this prioritization. Flotation is the step where the copper-containing particles are actually separated from the gangue or country rock. In this process, the finely ground ore is introduced into a series of flotation cells which are sparged with air after flotation agents are introduced. Flotation agents such as pine oil or long chain alcohols are used to generate froth. Chemicals known as "collectors" are also added which preferentially adsorb on the sulfide ore particle surfaces. This changes the properties of the sulfide particles so that they attract bubbles (or vice versa) preferentially over the gangue particles. The sulfides then concentrate in the interstitial liquid in the froth bubbles while the gangue sinks and passes out of the cell as tailings. As a result, the minor elements present in the ore as sulfides are concentrated along with the copper and nickel.

When metal sulfides are introduced into a smelting furnace with either air or oxygen-enriched air, they react quickly and adjust toward a new equilibrium state at furnace temperature. The oxidation potential in the furnace determines the quantity of each compound which forms as the sulfides react with oxygen. Of course, the driving force is different at the same temperature for each sulfide. As a result, bismuth and cadmium oxidize readily whereas copper and nickel remain as sulfides. This phenomenon allows the metals to be separated and accounts for the different paths

taken by each element through the smelting process.

The behavior of trace compounds present in smelter feed material is not well documented. Techniques for computing the thermodynamic equilibrium species distribution for a large number of trace elements are available (WI-R-304). But these have shown only semiquantitative agreement between predicted and actual element distributions. As a result, the conclusions drawn in this report are based on actual smelter operating data and reasonable judgement regarding the actual chemical form of the elements exiting the smelter processes.

#### Volatility--

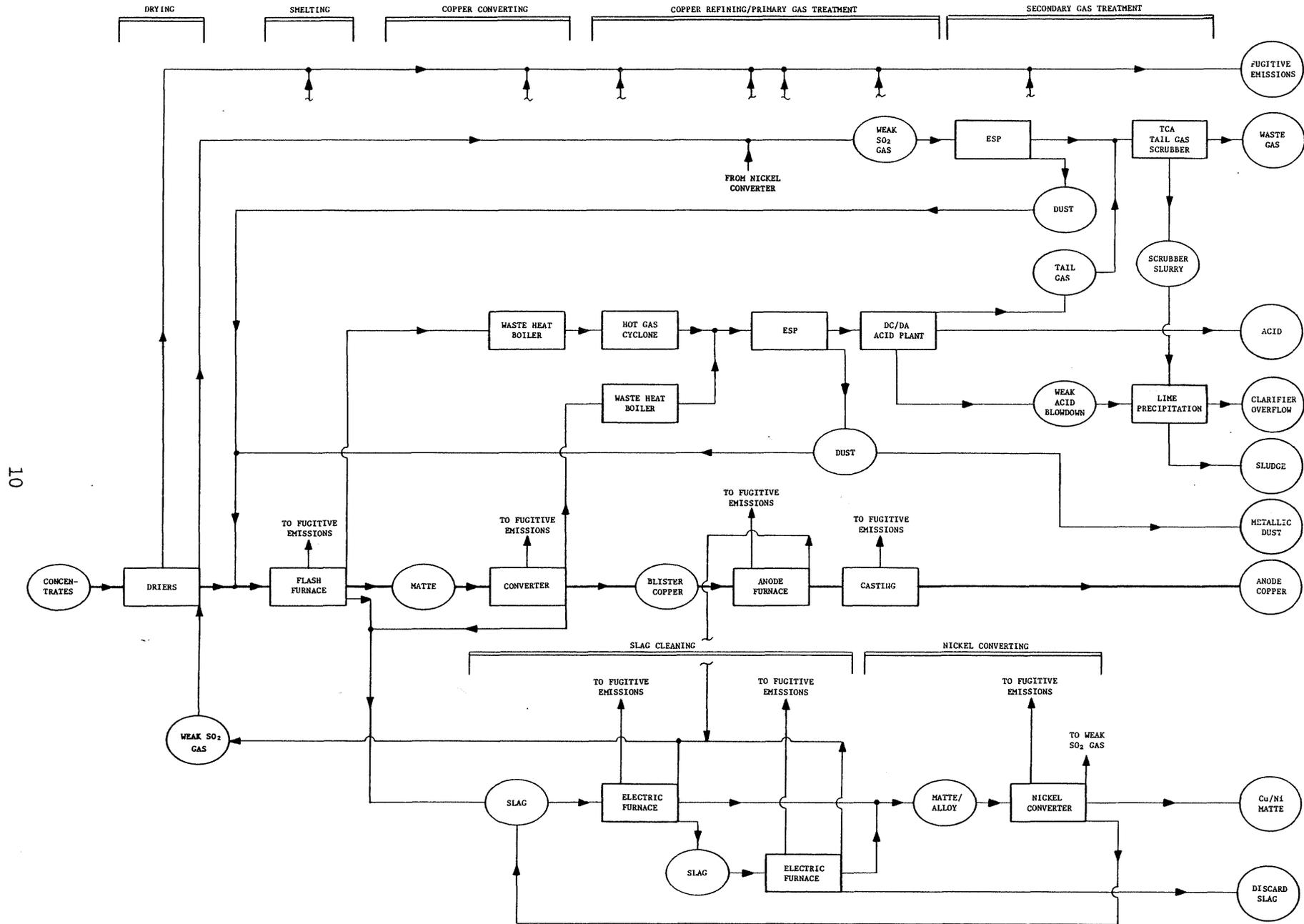
At furnace temperature, several metals and metal oxides are highly volatile. Mercury, both the oxides and sulfides, bismuth, cadmium, lead, antimony, and arsenic are volatile at 1200°C. Zinc oxide is also volatile at 1200°C as are many metal chlorides and fluorides. These volatile metals and compounds are likely to be emitted with process gases during upset conditions. They are also likely to be present as fugitive emissions from uncontrolled processes such as metal or slag transportation or from operations such as tapping or pouring where effective control technology does not exist.

#### Solubility--

The solubility of each compound formed in the smelting furnaces is important in two respects. First, within the furnace the differences in solubility between oxides and sulfides in the slag and matte phases determine the path taken by various metals through the smelting circuit. Second, after exiting the furnace the solubility of the compound in acidic aqueous solutions is important. The acidic wastewater emanating from smelters is one path for toxic metals to enter the environment. Leaching of metals from seemingly inert piles of tailings or slag is another path. The solubility of each compound exiting the smelter will determine to a large extent the environmental impact each element will create.

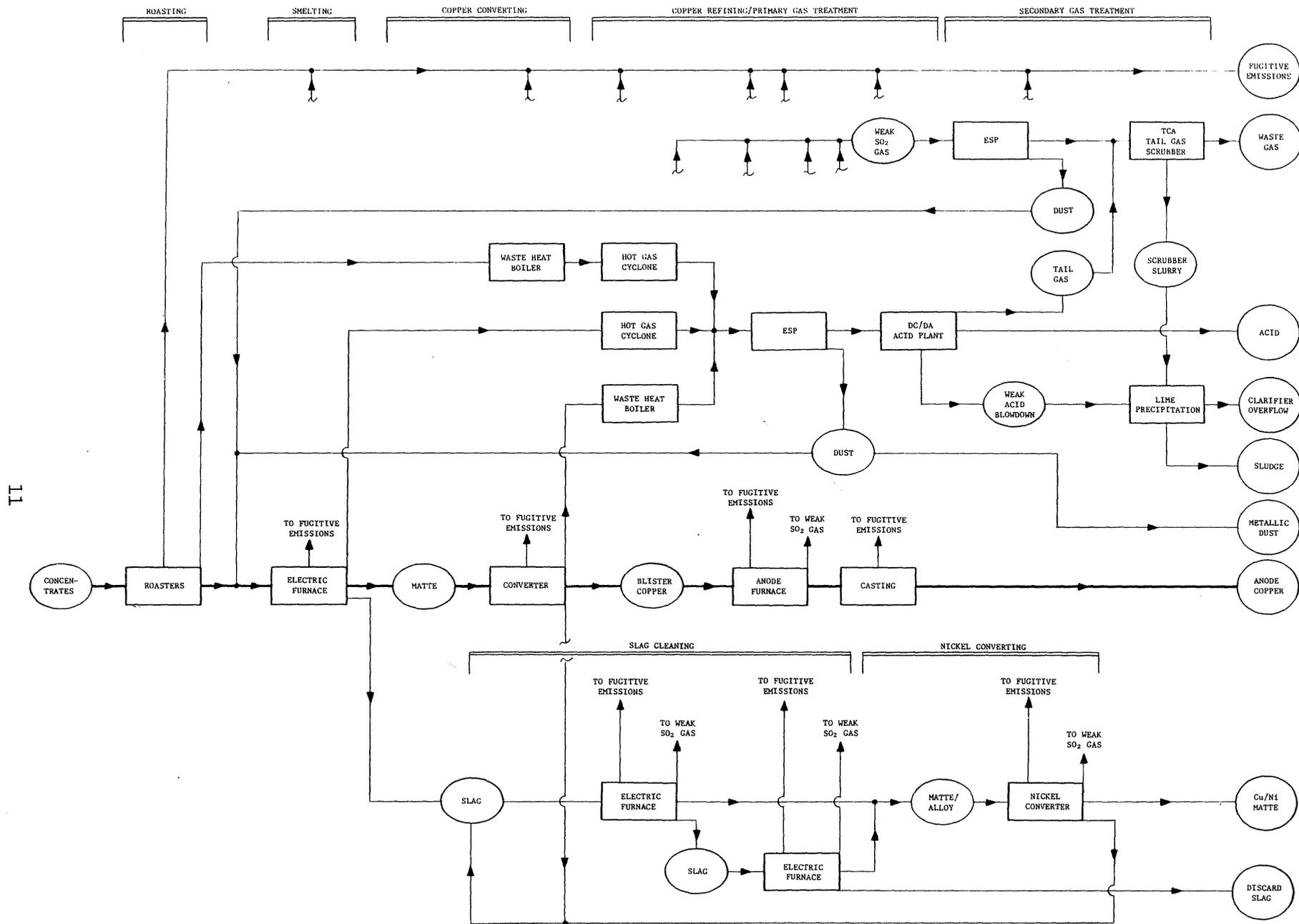
#### Process Considerations

Presumably, either a fluosolids roaster/electric furnace combination or a Outokumpu flash furnace equipped with electric induction heating capabilities will be used to process the Duluth Gabbro copper/nickel concentrates. Both schemes would be used along with Peirce-Smith or Hoboken type converters to produce blister copper. Nickel production will probably consist of one or two electric slag cleaning furnaces followed by an electrolytic nickel refinery. Figures 2, 3, and 4 present flow schemes for the copper/nickel smelter showing the different smelting furnaces and associated process, product, and emission streams. The problem of controlling the emissions from a copper/nickel smelter become clear upon examining both the large number and large variety of processes shown in these figures.



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Figure 2. Flowscheme for a copper/nickel smelter using a flash smelting furnace.



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Figure 3. Flowscheme for a copper/nickel smelter using a fluosolids roaster/electric furnace combination.

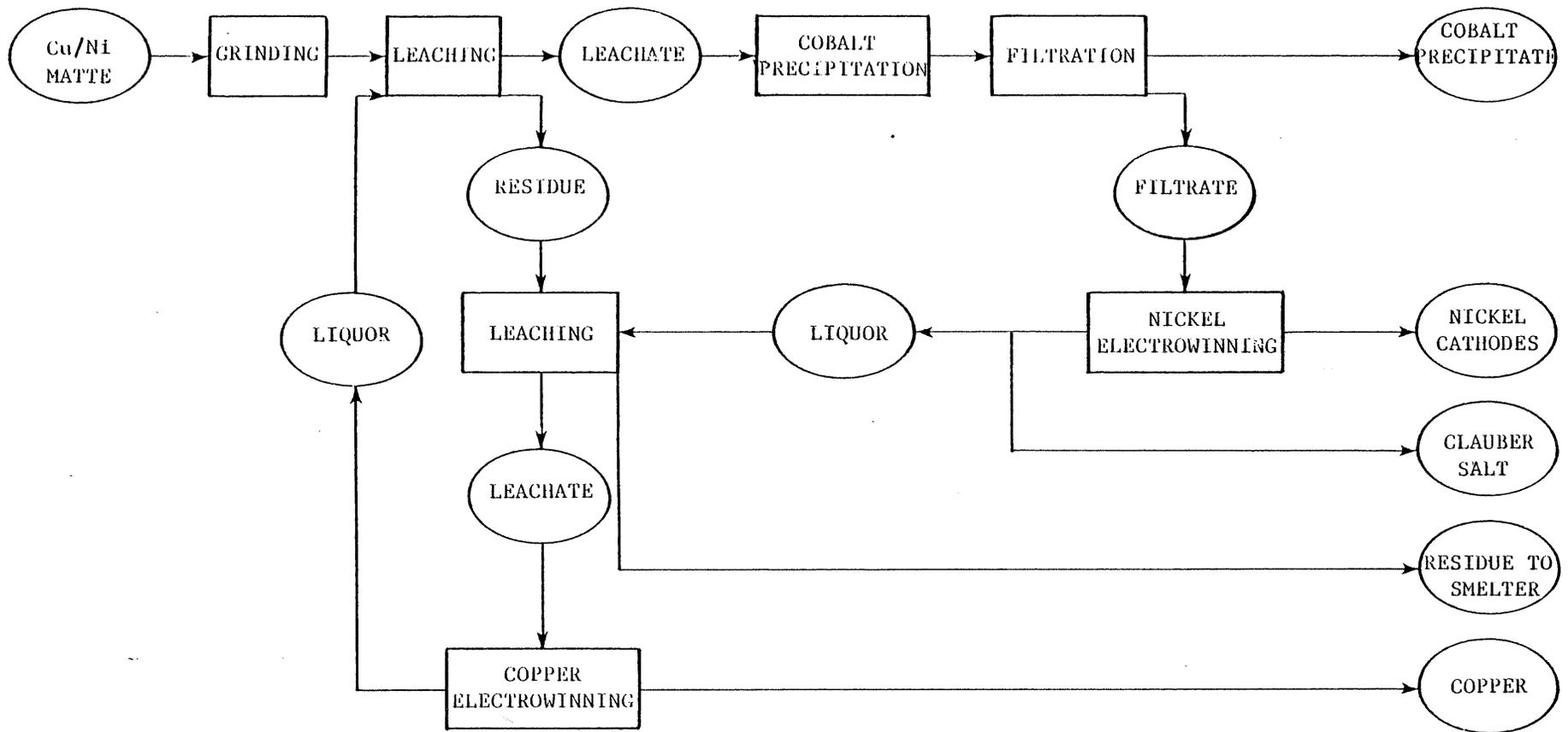


Figure 4. Flowscheme for a nickel refinery.

Most of the smelter products and by-products shown in Figures 1, 2, and 3 are produced on a daily basis. The metallic dust is one exception. Batches are removed from the smelting circuit when the impurities accumulate and are sold, discarded, or processed for their metals value. The small amount of air emissions, aqueous effluents, and solid wastes shown in Figures 1, 2, and 3 are generated by the smelter on a continuous basis. As the smelter ages, however, it is likely that the pollutants generated during upset periods will constitute the major smelter pollution problem. This situation is much different than that for conventional reverberatory smelting where the major pollution problem is the reverberatory furnace off gas.

Probability theory can be used to predict the potential environmental impact of pollution caused by process upsets. The probability that a piece of equipment will be functioning at the end of a time period  $t$ , or that can be repaired or maintained in time  $\tau$  and returned to functional status is given by the following equation (DI-R-174):

$$P = \exp \left[ -\lambda t e^{-\phi\tau} \right]$$

where:

$\lambda$  = The reciprocal of the mean time between full forced outages

$t$  = Time period to be considered

$\phi$  = The reciprocal of the mean time to repair a forced outage

$e$  = 2.718, the base of natural logarithms

This implies that there is a finite probability that upsets will occur due to process equipment failures and that they will become more frequent as time progresses.

Unfortunately, smelter operating data is not available, as it is for the electric power utility industry, to calculate the values of  $\lambda$  and  $\phi$ . As a result, neither the likelihood of occurrence nor the environmental impact of smelter process upsets can be calculated.

A qualitative evaluation can be made, however, which will identify the pollutants most likely to be generated during either upset conditions or during operations likely to produce fugitive emissions. This type of qualitative evaluation is included as part of the element prioritization. Specific process and control problems associated with each of the Priority 1 elements are discussed in Section 3.

#### PRIORITIZATION

Table 3 lists the elements placed in Priority 1. Table 4 divides Priority 2 elements into three categories: A, those which, if found to be

TABLE 3. PRIORITY 1 POLLUTANTS ASSOCIATED WITH COPPER/NICKEL CONCENTRATE SMELTING<sup>a</sup>

Element	Air Emission	Water Effluent	Solid Waste
Arsenic	V, T	S, T	L, T
Cadmium	V, T	S, T	L, T
Cobalt	v <sup>b</sup> , T	S, T	L, T
Copper	v <sup>b</sup> , T	S, T	L, T
Nickel		S, T	L, T
Sulfur	G, T		

T = toxic, V = volatile at furnace temperature, G = gas  
 S = soluble in acidic solution, L = leachable by acidic solution

<sup>a</sup>Based on analyses of bench-scale concentrate.

<sup>b</sup>Metal oxide is volatile at furnace temperatures. Volatile metal chlorides and metal fluorides have not been considered at this time.

TABLE 4. PRIORITY 2 ELEMENTS IN THE DULUTH GABBRO ORE

Group A.	Beryllium, Lead, Mercury, Zinc
Group B.	Aluminum, Barium, Boron, Calcium, Carbon, Chromium, Iron, Magnesium, Manganese, Molybdenum, Phosphorus, Potassium, Silicon, Silver, Sodium, Strontium, Titanium, Thorium, Vanadium, Zirconium
Group C.	Chlorine, Fluorine, Antimony, Bismuth

present in larger quantities, would be moved to Priority 1, B, those elements posing no major environmental threat, and C, those elements for which no data is available but which may pose environmental problems. Figure 5 is a chart showing the prioritization criteria for Priority 1, 2A, and 2C elements.

### Priority 1

The inclusion of the eight elements listed in Table 3 in Priority 1 is based on 1) a significant concentration in the bench-scale concentrate, 2) high toxicity relative to other elements present in the ore, and 3) the likelihood of release into the environment. Several accepted standards including the ACGIH TLV's, the NIH LD 50's, and OSHA regulation 29 CFR 1910 (AM-RF-232, CL-128) were used to compare the toxicity of the various elements. Smelter operating data presented in the literature as well as the theoretical framework described previously was used to determine whether first, the amount of any element present in the ore was significant and second, whether it was likely that the element would be released into the environment.

#### Arsenic--

Arsenic is a known carcinogen and has been identified both as being a serious health hazard and presenting a difficult control problem at most U.S. primary copper smelters (YO-054). A recent report (SC-R-467) identified arsenolite as the predominant crystalline form of arsenic emitted by copper smelters.  $As_2O_3$  is volatile, toxic, and soluble in water. The bench-scale concentrate contained only minor quantities of arsenic (8 to 12 ppm). However, large fluctuations in the arsenic concentration of smelting furnace feeds are known to occur (SC-R-467). This is due to changes in both ore composition and flue dust recycle rate.

#### Cadmium--

Cadmium is recognized as being a toxic material and presenting a significant environmental threat (AM-RF-232, FR-223). There is evidence that cadmium stored in the body may accumulate over a period of years (EN-521). It is more volatile than arsenic at furnace temperatures (YA-078) and is likely to escape as cadmium metal fume or CdO dust during either upset conditions or operations such as tapping, pouring, dust handling and furnace repair.

#### Cobalt--

Cobalt is a major component in the Duluth Grabbo complex and will likely be a by-product from the copper/nickel smelter. The toxicity of cobalt dust and fume is nearly the same as that of cadmium (AM-RF-232) but it is far less volatile. However, it is likely to be a major contaminant in the acidic wastewater generated by either the copper/nickel smelter or the cobalt refinery.

#### Copper--

Copper dust and fume is slightly less toxic than either cobalt or cadmium but more toxic than arsenic (AM-RF-232). It is likely to be

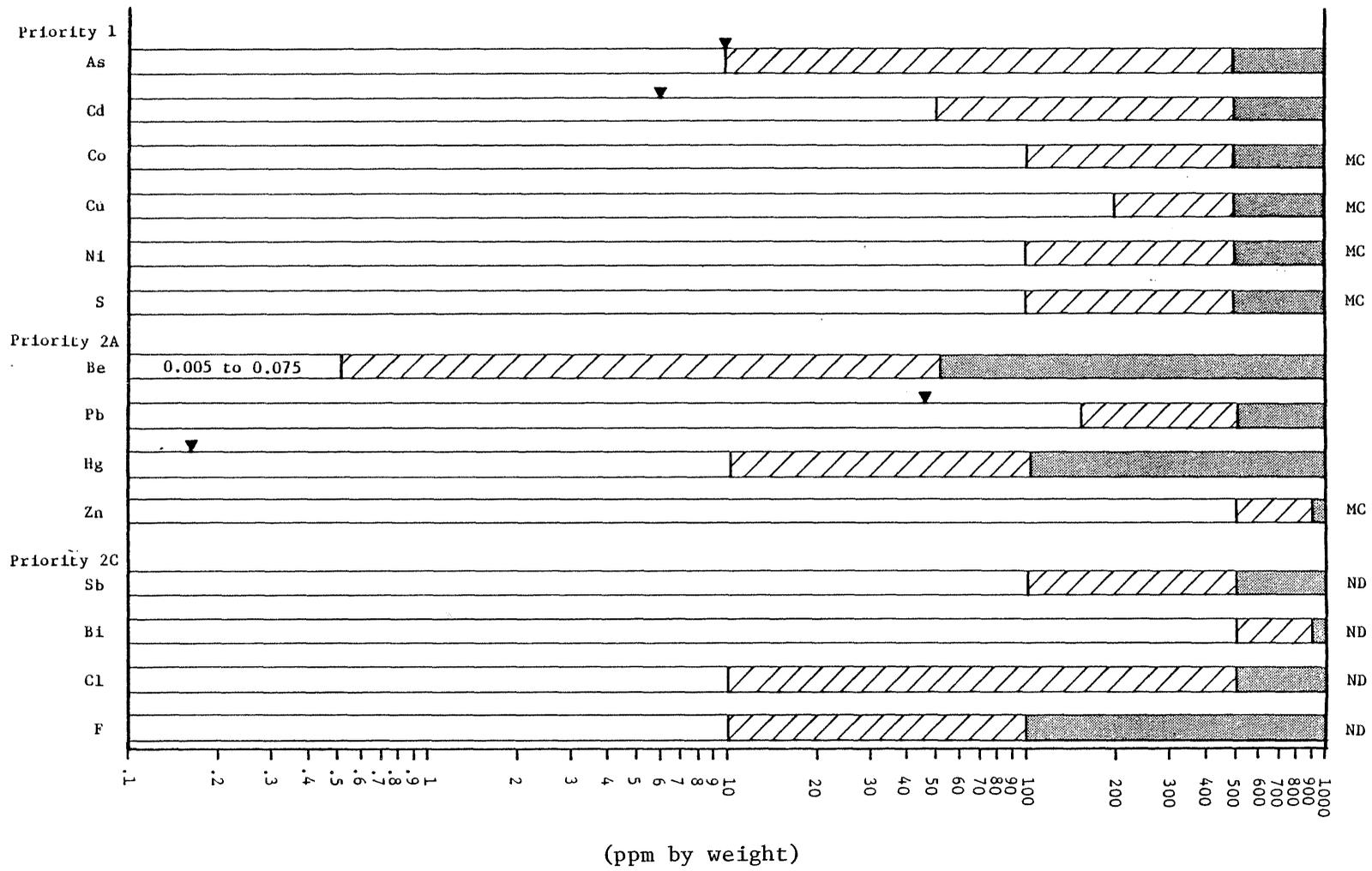


Figure 5. Concentrate composition ranges used as part of prioritization criteria.

## KEY TO FIGURE 5

▼ indicates average concentration  
in bench-scale concentrate

□ compositional range which is  
clearly no problem

▨ compositional range of  
uncertainty

■ compositional range which is  
a problem

ND - no data

MC - Major Component

emitted as fume and dust from tapping, pouring, dust handling, and furnace repair operations. Copper also should be a major contaminant in the acidic smelter wastewaters.

### Nickel--

Nickel dusts and fume have a toxicity similar to that for copper. Nickel carbonyl,  $\text{Ni}(\text{CO})_4$ , is extremely toxic and could pose a serious occupational hazard if present. Nickel can also be expected to be a major contaminant in smelter and refinery wastewaters.

### Sulfur--

Copper smelters are the second largest source of  $\text{SO}_2$  emissions in the U.S. As mentioned earlier, emissions during upset conditions and during tapping or pouring operations will occur. The difficulties of controlling  $\text{SO}_2$  emissions are well documented in the recent Economic Impact Statement prepared for the OSHA public hearings on  $\text{SO}_2$  (JR-001).

### Priority 2

The metals listed under Priority 2A present potential environmental hazards but are either present in very small quantities (Be, Pb, Hg, Zn), are expected to be relatively inert (Be), or are not extremely toxic (Zn) relative to the Priority 1 elements. In addition, it is expected that any technology designed to control Priority 1 elements will also control Priority 2 elements. Should any of these elements be found in significantly larger concentrations in the pilot-scale concentrate they may be included in Priority 1.

Table 5 lists the criteria used to select Priority 2B elements. Little emphasis should be placed on these elements for the reasons listed in Table 5.

No data is presently available for either fluorine or chlorine in the bench-scale concentrate. Metal fluorides and chlorides are potential volatile, toxic substances. Both present potential environmental problems. Their prioritization will be changed as data becomes available.

TABLE 5. FACTORS CONSIDERED IN PRIORITY 2B ELEMENT SELECTION

	Small Incoming Flow ( $\leq 100$ kg/day, based on 300 mtons Cu/day)	Low Toxicity (AM-RF-232, CL-128)	Unlikely to be Released into Environment in Hazardous Form
Al		x	x
B		x	x
Ba			x
Ca		x	x
Fe		x	x
K		x	
Mg		x	
Mn			x
Na		x	
P			x
Si			x
Sr	x		
Ti			x
V	x		x
Th	x		x
Ag	x		x
Cr			x
Mo	x		x
Zr	x		x
C		x	x

### SECTION 3

#### DISCUSSION OF PRIORITY 1 ELEMENTS

The two process flowschemes considered here generate nearly the same quantity of emissions, effluents, and solid waste under normal operating conditions. The actual pollution problems associated with both flowschemes depend more on the design and operation of the pollution control technology than on the process operation. Electrostatic precipitators, waste heat boilers, cyclones, hooding and ventilation systems, acid plants, tail gas scrubbers, and water treatment plants all experience outages due to equipment, power, and human failures. In addition, the control technology cannot be expected to perform effectively during either start-up or shutdown periods. The consequences of these different outages are the most important environmental consideration with respect to the Priority 1 pollutants identified in Section 2.

An analysis of all the potential failures in a smelter which would create an environmental impact is a large job in itself and is not attempted here. Rather, the framework for performing a detailed environmental impact analysis is described in terms of the following classes of failures:

- catastrophic failure, *e.g.*, loss of electric power or steam supply,
- loss of a particular pollution control device due to equipment failure,
- failure of a control device to perform due to overloads, and
- failures due to inadequate maintenance.

Ideally, the control technology used at the smelter should be designed to minimize the possibility of each of these type failures. However, it is unlikely that any control technology will be designed to prevent emissions in the event of a catastrophic failure. This is the least likely but potentially most serious failure. The high SO<sub>2</sub> concentration furnace gases may have to be vented to the atmosphere when this type of failure occurs in order to prevent any potential poisoning of the V<sub>2</sub>O<sub>5</sub> catalyst in the sulfuric acid plant. Without power, the electrostatic precipitators and process gas fans would not function. As a result, air emissions during this type of failure would consist of very high SO<sub>2</sub> concentration gases heavily laden with metal particulates and vapor. The emissions would likely occur at ground level since the gases could not be routed through the acid plant catalyst beds and out

the stack. A duct bypassing the acid plant would allow the stack to be used and could eliminate the immediate danger to the workers in the smelter.

The likelihood of losing a particular pollution control device due to equipment failure can be minimized by providing equipment spares and by using the proper materials of construction. Equipment redundancy will increase the cost of the control technology but is essential, especially for the key pollution controls. The sulfuric acid plant will be the key pollution control device because all of the Priority 1 elements are contained in the process gases it treats in a hazardous form. Loss of the acid plant would, for example, have a much larger impact than the loss of the weak SO<sub>2</sub> gas scrubber. As a result, the acid plant should be designed, operated, and maintained in a fashion which will insure that outages due to equipment failure, process fluctuations, or inadequate maintenance are minimized.

This type of qualitative discussion could be continued for each of the control devices and each failure mode. However, the problem of assigning some quantitative value to the environmental impact of upsets or failures in smelter operation is not so easily addressed. Of the Priority 1 elements listed in Table 1, sulfur is likely to be emitted in the largest quantities in the form of SO<sub>2</sub>. The best estimate of what SO<sub>2</sub> levels are likely to be associated with either an electric or flash smelter could be made by examining the ambient-air-quality data collected by EPA for the Anaconda, Montana, Inspiration, Arizona, and Hidalgo, New Mexico copper smelters. This data could also provide some feel for what levels of the other Priority 1 elements are likely to be generated by either an electric or flash smelter. Of course, the ores processed at these smelters will contain each element in different proportions than that found in the Duluth Gabbro Complex. However, that data may provide the best estimate of what the impact of a copper/nickel smelter might be in Minnesota.

No attempt was made to either collect or review the EPA data on the three smelters mentioned for this report. Without that data, it is not possible to accurately estimate the quantity of Priority 1 pollutants which will be generated by a copper/nickel smelter. This is especially true in this case because a major portion of the pollution will be caused during upset conditions.

It is expected that the volatile metals which do escape into the environment in the vapor state will condense as either oxides or sulfates. SO<sub>2</sub> will be the major form of sulfur exiting the smelter although SO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> mist may be present in the tail gas scrubber waste gas. The effluent from the lime precipitation process is expected to contain at least trace quantities of each Priority 1 metal. It is not clear how well the lime precipitation process kinetics will be affected by extremely cold weather. It is known that a smelter in Kellogg, Idaho experienced problems with lime precipitation due to cold weather. It is not clear whether a solution to the problem was found.

The potential problems associated with disposing of smelter solid wastes have not been adequately characterized. Little information is available which would allow an estimate to be made of the quantity of Priority 1 elements

which might be leached from either slag heaps or lime sludge. This is an area where further research is needed.

The distribution of the Priority 1 elements in the various smelter exit streams is more easily estimated for normal operating conditions. The material balances presented in the next section give the best estimate of what that distribution will be.

## SECTION 4

### MATERIAL BALANCES

The material balances presented in this section indicate the most probable distribution of the Priority 1 elements in the two smelting schemes shown in Figures 2 and 3. The material balances are based on the best available smelter operating data. Where data was not available for a particular element/furnace combination, the best estimate was made of the element's distribution in the furnace exit streams based on either similar smelting situations or on thermodynamic data available in the open literature. Section 5 reviews the pertinent literature used to develop the material balances.

#### STEADY-STATE MATERIAL BALANCES

The basic assumptions made in order to complete the material balances are as follows:

- The behavior of minor elements in the Duluth Gabbro Complex ore will not differ significantly from the behavior observed for other ores processed in the smelting furnaces shown in Figures 2 and 3.
- Data collected from copper reverberatory furnaces is applicable, at least for an order-of-magnitude approximation, to the electric and flash smelting cases considered.
- All furnace electrostatic precipitators (ESP) operate at 316°C (600°F).
- Fugitive emissions are not accounted for as part of the steady-state material balances.
- Emissions due to process upsets are not considered.
- No distinction has been made between gaseous and particulate emissions in gas streams. The data required to make that type of estimate is not available at this time.

The first two assumptions are valid with respect to this report. Obviously, each ore and smelter combination will result in a slightly different distribution of minor and trace elements. Tables 6 and 7 clearly

TABLE 6. COPPER CONCENTRATE COMPOSITIONS - MAJOR AND MINOR ELEMENTS

Reference	Element Composition (ppm)																
	Cu	Major Components				As	Bi	Ca	Mg	Minor Components			O <sub>2</sub>	Pb	Sb	Se	Zn
		Fe	S	Si	Al					Mn	Mo	Ni					
EN-217					<10,000								<5000	<5000		<40,000	
HA-358	248,000	230,000	330,000	60,000	13,000								81,000				
HA-358	313,000	227,000	298,000	68,000	500								77,500				
HA-358	233,000	242,000	310,000	44,000	13,000		17,000						68,000				
HA-358	154,000	310,000	369,000	51,000	23,000								79,000				
HA-397	270,000	270,000	535,000	42,000			41,000						49,000				
KA-160	200,000 to 500,000					2,500	200					500	110,000	1500	200	90,000	
KA-160	250,000					2,500	200						110,000	1500	200	10,000	
KA-160	150,000 to 500,000					1,300	200						50,000	900	200	7,500	
LA-315	150,000	330,000	234,000	67,000	21,000		10,000	25,000			31,800	130,000					
PE-274						>1000				>1000	>100		1,000 to 9,999	>1000		10,000 to 300,000	
PE-274						>1000				100 to 999	20 to 99		1,000 to 9,999	100 to 999	5 to 99	10,000 to 300,000	
PE-274						<200				100 to 999	>100		<1000	100 to 999	5 to 99	<10,000	
PE-274						200 to 999				100 to 999	>100		1,000 to 9,999	100 to 999	>100	<10,000	
PE-274						<200				100 to 999	>100		>10,000	<100		<10,000	
PE-274						<200				100 to 999	>100		<1,000	100 to 999	5 to 99	<10,000	
PE-274						<200				100 to 999	>100		1,000 to 9,999	<100		10,000 to 300,000	
PE-274						<200				100 to 999	20 to 99		<1,000	<100	5 to 99	<10,000	
PE-274						<200				100 to 999	20 to 99		1,000 to 9,999	100 to 999	5 to 99	10,000 to 300,000	
SC-R-467	320,000	210,000		210,000	8,000	3,900	15,000				1,600	14	980	120	200	830	
WE-189	229,000		296,000			33,000						1,100	10,000	3,000	240		
WE-189	237,000		300,000			38,000						400	10,000	4,000	180		
WE-189	219,000		288,000			28,000						400	11,000	3,000	150		

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TABLE 7. COPPER CONCENTRATE COMPOSITIONS - TRACE ELEMENTS

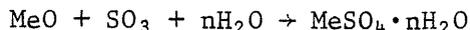
Reference	Element Composition (ppm)										
	Ag	Au	Ba	Be	Cd	Cl	Co	F	Hg	Te	V
EN-217				<10	<1000						<100
KA-160	12.5	.3			100	500	200	500		100	
KA-160					100					100	
KA-160					100					100	
LA-315							1,600				
PE-274					100 to 999				>10		
PE-274					100 to 999				<1		
PE-274					<100				1 to 9		
PE-274					<100				<1		
PE-274					<100				<1		
PE-274					100 to 999				1 to 9		
PE-274					<100				1 to 9		
PE-274					100 to 999				1 to 9		
SC-R-467			620	1.4	1,200			67	.37		18
WE-189					200				51		
WE-189					200				41		
WE-189					200				38		

show the variations in major, minor, and trace components in a number of copper concentrates. However, the general behavior trends of minor and trace elements in smelting processes are the same for most concentrated ores. The purpose of these material balances is to identify the important potential environmental problems using the existing knowledge of minor element behavior.

The second assumption affects the fate of the more volatile elements present in the Duluth Gabbro ore and concentrates. High temperature ESP's are typically designed to operate most efficiently between 288 to 343°C (550 to 650°F) (CO-R-555). This report assumes that the ESP's designed for a smelter processing Duluth Gabbro concentrates will also operate near 600°F. It is unlikely that either cold ESP's or fabric filters will be used. However, both the gas conditioning section of the sulfuric acid plant and the weak SO<sub>2</sub> gas scrubber will act as cold particulate removal devices. It is also unlikely that a sufficient quantity of volatile metals will escape the hot ESP's to make low temperature particulate collection economically attractive.

The final two assumptions are necessary in order to complete the material balances. No data is available which would allow a quantitative estimate of either fugitive or upset condition emissions to be made. Rather, it is recommended that a sensitivity analysis should be performed to determine both the likelihood, frequency, and environmental impact of fugitive and upset condition emissions. This type of analysis was not completed as part of this study.

The form of minor or trace metals (i.e., gas or particulate) in the gas streams exiting copper smelters is not well defined, especially for elements such as arsenic, cadmium, fluorine and selenium. The same is true for the lead and zinc industry where PbO and ZnO are major emission problems. The problem is one of defining both the methods for sampling and conditions at which the samples should be taken to determine the quantity of any material present in a gas stream as vapor. A recent study at a primary copper smelter (SC-R-467) showed that the amount of condensibles between the duct temperature of 600°F and 250°F (EPA's recommended stack exit temperature) at the outlet of a hot reverberatory furnace ESP accounts for material corresponding in mass of an additional 1.0 grains/scf or 636.7 lb/hr. The same study showed only 29.8 lb/hr of material condensing in elemental form between 600°F and 32°F. Fluctuations in furnace operation accounts in part for this difference. However, it is believed that reactions occur as the gas cools which allow the hydrated sulfates to form as follows:



Thus, the metal or metal oxide vapors which pass through the ESP at 600°F are detected as heavy particulate matter as they exit the stack. Predicting the form of elements exiting the smelter as stack, fugitive, or upset condition emissions is a difficult task. Little data is available on this subject. No attempt is made to speculate on the ratio of particulate to gas emissions in the mass balances presented here.

Tables 8 and 9 are the preliminary material balances for the two smelter configurations shown in Figures 2 and 3. The data used to construct these balances is reviewed in the following section.

#### FUGITIVE EMISSIONS

In order to complete a dispersion model of the emissions from a copper/nickel smelter, an estimate of fugitive emissions must be made. To accomplish this the following assumptions were made:

- Fugitive emission gas volumes equal 10 percent of the total weak SO<sub>2</sub> gas stream volume.
- The weak SO<sub>2</sub> gas streams include: matte and slag tap ventilation gas, secondary converter hoods, electric slag cleaning off-gas, and anode furnace off-gas but do not include smelting furnace off-gases.
- Total sulfur in the fugitive emissions is 10 percent of the total in the weak SO<sub>2</sub> gas streams.
- Other elements are present in the fugitive emissions in the same proportion to sulfur as in the concentrate feed with the exception of Cu, Ni, Fe, and Co. These elements were estimated to be present in fugitive particulates at roughly half of their concentration in the concentrate.

This is a crude estimate. However, it will allow a dispersion model to be completed so that the effect of fugitive emissions on the environment can be estimated. Table 10 presents the estimate of total fugitive emissions for the Priority 1, 2A, and 2C elements.

TABLE 8. PRELIMINARY MATERIAL BALANCE FOR PRIORITY 1, 2A, AND 2C  
ELEMENTS - COPPER/NICKEL FLASH SMELTER

Element	Distribution of Elements in Smelter Exit Streams* (given as a percentage of element in the concentrate)								Estimated Accuracy** (±%)
	Waste Gas	Clarifier Acid Overflow	Sludge	Metallic Dust	Anode Copper	Cu/Ni Matte	Discard Slag		
<u>Priority 1</u>									
Arsenic	0	TR <sup>†</sup>	1	77	9	TR	1	12	20
Cadmium	0	TR	TR	7	93	TR	TR	TR	20
Cobalt	0	0	TR	TR	TR	1	49	50	20
Copper	0	0	TR	TR	1	76	22	1	10
Nickel	0	0	TR	TR	TR	1	97	2	10
Sulfur	2	93	TR	1	TR	TR	3	1	5
<u>Priority 2A</u>									
Beryllium	0	0	1	13	1	0	1	84	25
Lead	0	TR	2	21	30	TR	2	45	15
Mercury	30	12	28	28	2	0	0	0	22
Zinc	0	TR	TR	3	41	TR	6	50	15
<u>Priority 2C<sup>††</sup></u>									
Antimony	0	TR	1	11	72	TR	TR	16	20
Bismuth	0	TR	TR	6	93	TR	TR	1	10
Chlorine	1	TR	1	11	86	0	0	1	25
Fluorine	1	TR	1	11	86	0	0	1	25

\* Exit streams listed on Figure 2; Fugitive Emissions not included.

\*\* Percentage of total element flow which may be improperly distributed.

† TR = present as a trace element, <100 ppm

†† Priority 2C elements assumed to be present in trace quantities.

TABLE 9. PRELIMINARY MATERIAL BALANCE FOR PRIORITY 1, 2A, AND 2C  
ELEMENTS - COPPER/NICKEL ELECTRIC SMELTER

Element	Distribution of Elements in Smelter Exit Streams* (given as a percentage of element in the concentrate)								Estimated Accuracy** (±%)
	Waste Gas	Acid	Clarifier Overflow	Sludge	Metallic Dust	Anode Copper	Cu/Ni Matte	Discard Slag	
<u>Priority 1</u>									
Arsenic	0	TR	1	84	9	TR	1	5	20
Cadmium	0	TR	1	9	94	0	0	TR	20
Cobalt	0	0	TR	TR	TR	1	49	50	20
Copper	0	0	TR	TR	1	76	22	1	10
Nickel	0	0	TR	TR	TR	1	97	2	10
Sulfur	2	94	TR	1	TR	TR	2	1	5
<u>Priority 2A</u>									
Beryllium	0	0	2	16	2	0	1	79	25
Lead	0	TR	1	10	37	0	2	50	20
Mercury	12	25	6	55	2	0	0	0	20
Zinc	0	TR	1	10	37	0	2	50	20
<u>Priority 2C<sup>††</sup></u>									
Antimony	0	TR	1	11	74	TR	TR	14	20
Bismuth	0	0	TR	5	94	TR	TR	1	15
Chlorine	TR	TR	1	10	88	0	0	1	25
Fluorine	TR	TR	1	10	88	0	0	1	25

\* Exit streams indicated on Figure 3; Fugitive Emissions not included.

\*\* Percentage of total element flow which may be improperly distributed.

†† Priority 2C elements assumed to be present in trace quantities.

TABLE 10. ESTIMATE OF TOTAL FUGITIVE EMISSIONS OF  
PRIORITY 1, 2A, and 2C ELEMENTS

Element (Form)	Concentrate Composition (ppm)	Fugitive Emissions* (metric tons/year)	
		element	compound
S (SO <sub>2</sub> )	259,000	492	(984)
As (As <sub>2</sub> O <sub>3</sub> )	9	0.013	(0.03)
Cd (CdO)	4	0.016	(0.02)
Co (CoO)	1,284	0.99	(1.26)
Cu (Cu <sub>2</sub> O)	143,000	135	(306)
Ni (NiO)	24,457	20	(26)
Be	0.1	Not detectable	
Pb (PbO)	45	0.122	(0.13)
Hg	0.2	Not detectable	
Zn (ZnO)	905	1.76	(2.2)
Si (SiO <sub>2</sub> )	173,800**		(330)
Al (Al <sub>2</sub> O <sub>3</sub> )	40,600**		(77)
Mg (MgO)	24,800**		(47)
Ca (CaO)	19,100**		(36)
Fe (Fe <sub>2</sub> O <sub>3</sub> )	34,800**		(33)

\*Based on 492 metric tons Sulfur emitted per year as fugitive SO<sub>2</sub> gas emissions.

\*\*Oxide composition

## SECTION 5

### REVIEW OF PERTINENT LITERATURE

The literature reviewed in this section, contains both the experimental and operating data which was used to prepare the material balances in Section 4. It is important to note that only one material balance is available for a flash smelting furnace (MO-307) and none are available for a fluosolids roaster/electric furnace combination. However, there are sufficient operating data available for other similar processes to make a reasonable estimate of how each element will be distributed.

This review emphasizes operating data. The review of all the thermodynamic data available on metals would be an extremely large task and is not attempted here. Rather, only the smelter operating which is useful for indicating the path of minor elements in smelting processes is reviewed here.

Most of the operating data available is for copper smelting. Nickel is not considered as a major component in any of the literature reviewed. However, it is not expected that the metallurgy of copper/nickel smelting will affect the flow of minor elements enough to warrant a change in the priorities assigned in Section 2.

BE-A-506

This paper presents both experimental data and literature values for equilibrium vapor pressure, heat capacity, enthalpy, entropy, and free energy as a function of temperature for arsenolite [ $\text{As}_2\text{O}_3(\text{s})$ ] and  $\text{As}_4\text{O}_6(\text{g})$ . It is useful mainly as a tool for comparison. Smelter gas compositions do not represent equilibrium conditions. However, the data in this paper can be compared to smelter data to give some feel for the behavior of arsenic in the smelter gases.

Figure 6 presents the vapor pressure data given in the paper. Tables 11 and 12 list the thermodynamic functions determined for  $\text{As}_2\text{O}_3(\text{s})$  and  $\text{As}_4\text{O}_6(\text{g})$ .

GI-134

This early paper (1904) presents valuable information on the removal of impurities from copper matte. Bessemerization (converting) is compared to reverberatory furnace operation. The data are presented so that removal of impurities can be observed as a function of percent copper (or time) as the smelting process proceeds.

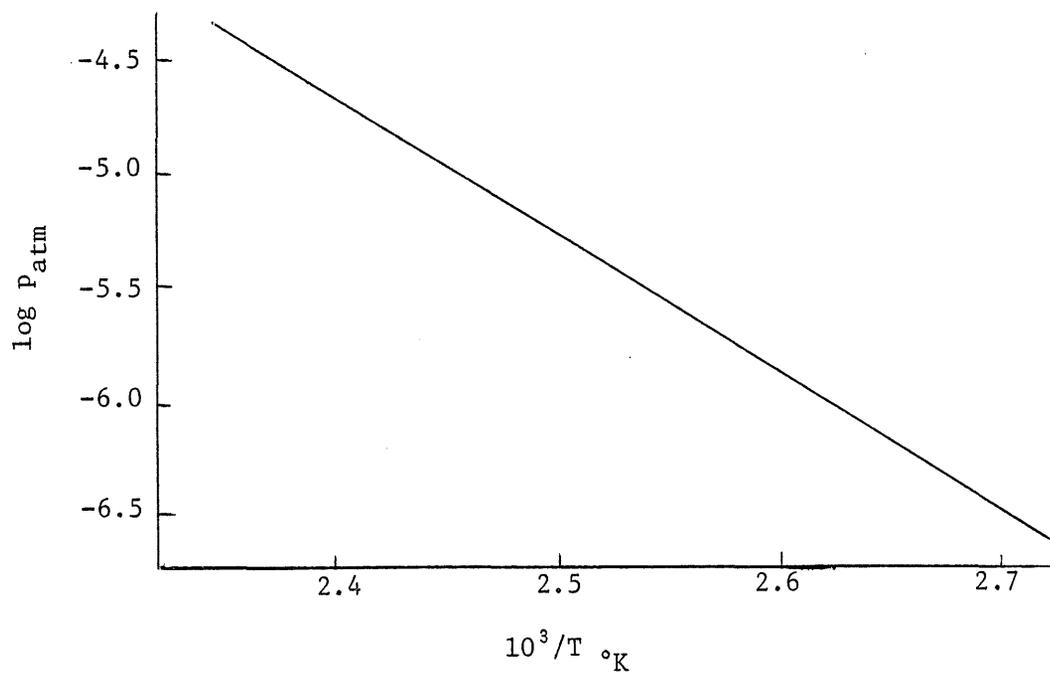


Figure 6. Vapor pressure of arsenolite.

TABLE 11. THERMODYNAMIC FUNCTIONS OF  $\text{As}_2\text{O}_3$  (ARSENOLITE)

$\frac{T}{K}$	$C$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$\frac{(H^\circ(T) - H^\circ)^a}{\text{cal}_{\text{th}} \text{mol}^{-1}}$	$\frac{S^\circ(T)}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$	$\frac{-(G^\circ(T) - H^\circ)/T}{\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}}$
298.15	22.86	0	25.67	25.67
300	22.95	42	25.81	25.67
400	27.81	2580	33.08	26.63
500	32.67	5604	39.81	28.60
600	(37.53)	(9114)	(46.19)	(31.00)
700	(42.39)	(13110)	(52.34)	(33.62)
800	(47.25)	(17592)	(58.32)	(36.33)
900	(52.11)	(22560)	(64.17)	(39.10)
1000	(56.97)	(28014)	(69.91)	(41.90)

<sup>a</sup>  $[H^\circ(298.15 \text{ K}) - H^\circ(0)] = 3923 \text{ cal}_{\text{th}} \text{mol}^{-1}$

$\text{cal}_{\text{th}} = 4.184 \text{ J}$

TABLE 12. THERMODYNAMIC FUNCTIONS OF  $\text{As}_4\text{O}_6(\text{g})$ 

$T$ K	$C$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$(H^\circ(T) - H^\circ)^a$ $\text{cal}_{\text{th}} \text{mol}^{-1}$	$S^\circ(T)$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$	$-(G^\circ(T) - H^\circ)/T$ $\text{cal}_{\text{th}} \text{K}^{-1} \text{mol}^{-1}$
298.15	$41.49 \pm 1.0$	0	$97.81 \pm 2.5$	$97.81 \pm 2.5$
300	41.61	77	98.07	97.81
400	45.56	4509	110.79	99.51
500	49.39	9318	121.51	102.87
600	51.11	14350	130.67	106.76
700	52.23	19521	138.64	110.76
800	52.98	24783	145.67	114.69
900	53.51	30109	151.94	118.49
1000	53.90	35481	157.60	122.12

$$^a [H^\circ(298.15 \text{ K}) - H^\circ(0)] = (7289 \pm 300) \text{cal}_{\text{th}} \text{mol}^{-1}.$$

$$\text{cal}_{\text{th}} = 4.184 \text{ J}$$

Although the smelting methods are different than those used today, the data on impurity removal can be applied to modern smelting practice. The results presented show that the elimination of arsenic, antimony, and bismuth depend not only on the amount originally present but also on the proportion of other impurities present. Also, the marked difference in the manner in which elimination is effected in the converter and reverberatory furnace is noted.

The following points are made which can be applied to any smelting operation:

- Bismuth is eliminated in both operations almost entirely by volatilization.
- A large portion of arsenic and antimony are eliminated by volatilization in the converter.
- A comparatively small amount of arsenic and antimony are volatilized in a furnace where the slag is highly oxidized and the copper phase is present. Rather, the As and Sb report in the slag.
- This result is due to the strong affinity of arsenic and antimonial oxides for cuprous oxide.

It must be understood that reverberatory furnace practice in 1904 was much different than current practice. Copper rather than copper matte was produced in the reverb. Therefore, the reverberatory slags were highly oxidized and contained from 6 percent(w) copper in the first stage to 40 percent(w) copper in the latter stages of production.

The reverse is true today. Flash smelting furnace and converter slags contain far more copper, 6 to 12 percent(w), than do reverb slags, 0.5 to 1.0 percent(w). Reverbs are now used to produce low grade matte, 45 percent(w) copper, whereas flash smelting furnaces produce high grade matte, 65 to 70 percent(w) copper. In some cases (HA-373) the entire converting operation is performed in a flash smelter and blister copper is produced. In either case, a highly oxidized slag containing both  $Cu_2O$  and entrained copper is produced in both the flash furnace and converter.

The behavior of As, Bi, and Sb in a flash smelter can be expected to be similar to that observed in this early work on reverberatory furnaces. The data on overall impurity removal is presented in Table 13. The data indicate that as the severity of the oxidation increases above 70 percent matte, more arsenic and antimony will be present in the slag and matte (or copper). This phenomena is explained by comparing the vapor pressure as As and Sb with their oxides at high temperatures and is discussed below (see MO-307).

TABLE 13. PATH OF As, Sb, AND Bi IN SMELTING OPERATIONS\*

	Arsenic		Antimony		Bismuth	
	Converter percent(w)	Reverber- atory percent(w)	Converter percent(w)	Reverber- atory percent(w)	Converter percent(w)	Reverber- atory percent(w)
Copper	16.0	34.0	27.0	30.0	4.0	7.0
Slag	11.0	54.2	23.0	54.0	1.0	7.6
Volatilized	73.0	11.8	50.0	16.0	95.0	85.4
TOTAL	<u>      </u>	<u>      </u>	<u>      </u>	<u>      </u>	<u>      </u>	<u>      </u>
ELIMINATED	84.0	66.0	73.0	70.0	96.0	93.0

\*Reverberatory furnace producing copper

The same is true only to a lesser extent for bismuth. Bismuth does not form compounds similar to arsenates or antimonates thus it volatilizes as it oxidizes regardless of the slag composition. The affinity that bismuth has for both the matte and slag at higher matte grades accounts for the slight decrease in volatilization.

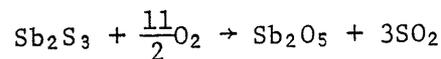
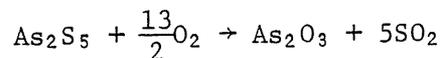
This is an earlier article (1903) by Gibb, the author of GI-134. The elimination of arsenic, antimony, and bismuth in roasting, smelting, converting, and refining processes is described. Both blast furnace and reverberatory furnace smelting are included.

The data presented show that roasting eliminates 60 to 75 percent(w) of the arsenic and 11 to 27 percent(w) of the antimony and bismuth present in the raw ore (Table 14). Of course, copper ores no longer contain 5 to 12 percent copper. However, these data do indicate that a great deal of volatilization does take place in the roasting process.

TABLE 14. ROASTING ORES - ELIMINATION OF ARSENIC, ANTIMONY AND BISMUTH

1.	Raw Ore		Calcined Ore		Elimination per 100 of Copper	Total Percentage of Elimination
	Percent Actual	Percent Relative Copper=100.	Percent Actual	Percent Relative Copper=100.		
Copper	5.55	100.00	7.68	100.00	--	--
Arsenic	1.18	21.26	0.407	5.29	15.97	75.1
Antimony	0.035	0.63	0.035	0.47	0.160	25.4
Bismuth	0.011	0.198	0.011	0.143	0.055	27.8
2.						
Copper	12.15	100.00	14.68	100.00	--	--
Arsenic	0.967	7.96	0.454	3.09	4.87	61.2
Antimony	0.046	0.378	0.045	0.307	0.071	18.8
Bismuth	0.014	0.115	0.015	0.102	0.013	11.3

Another important group of reactions may occur during the roasting process. Arsenates and antimonates may form as arsenic and antimony are oxidized and react with other metal oxides as follows:



These arsenates and antimonates will remain in the calcined ore and report in the smelting furnace slag. If the roasting step is eliminated, these arsenates will form to some extent in the smelting furnace if the furnace atmosphere is oxidizing.

It is noted that elimination of these three elements in the blast furnace occurs almost entirely by volatilization. The following conclusions can be drawn:

- The high degree of oxidation in the reverberatory furnace creates a slag rich in  $\text{Cu}_2\text{O}$  which reacts with As and Sb to form complex arsenates and antimonates.
- The reducing atmosphere in the blast furnace allows arsenates and antimonates to form arsenides and antimonides and either volatilize or report in the coarse metal (matte). Little  $\text{Cu}_2\text{O}$  is available in the blast furnace slag to react with As or Sb.

The data comparing reverb to blast furnace smelting ore are given in Tables 15 and 16.

The data presented on converting are similar to those presented for roasting white metal. These data (Tables 17 and 18) show that arsenic and antimony do not volatilize to a great extent in the converting process. Rather, they report either in the slag or, to a larger extent, in the blister copper. As mentioned earlier, bismuth does not form compounds similar to arsenates and volatilizes readily.

The data presented on refining show that virtually none of the arsenic, antimony, or bismuth remaining in the blister copper volatilize during the refining process. Whatever elimination takes place occurs by slagging with various fluxes. Table 19 presents the data on refining.

As was the case with the data in GI-134, the data presented in this paper can be applied to modern smelting processes to indicate trends in minor element flows.

MA-740

This paper presents data on observed distributions for minor elements which report in the copper, matte, slag, and offgas of the Noranda continuous smelting reactor. The data represent the dynamic state of the specific furnace being studied. However, trends in minor element behavior for other smelting furnaces can be predicted from the data presented.

TABLE 15. SMELTING CALCINED ORES IN REVERBERATORY FURNACES - ELIMINATION OF ARSENIC, ANTIMONY AND BISMUTH

1.	Calcined Ore		Coarse Metal		Elimination per 100 of Copper	Total Percentage of Elimination
	Percent Actual	Percent Relative Copper=100.	Percent Actual	Percent Relative Copper=100.		
Copper	10.60	100.00	37.0	100.00	--	--
Arsenic	0.102	0.96	0.132	0.357	0.603	62.8
Antimony	0.025	0.236	0.037	0.10	0.136	57.6
Bismuth	0.010	0.094	0.028	0.075	0.019	20.2
2.						
Copper	14.40	100.00	35.28	100.00	--	--
Arsenic	0.33	2.29	0.185	0.524	1.766	77.1
Antimony	0.050	0.347	0.04	0.113	0.234	67.4
Bismuth	0.014	0.097	0.025	0.070	0.027	27.8

TABLE 16. SMELTING CALCINED ORES IN BLAST-FURNACES - ELIMINATION OF ARSENIC, ANTIMONY AND BISMUTH

	Calcined Ore		Coarse Metal		Elimination per 100 of Copper	Total Percentage of Elimination
	Percent Actual	Percent Relative Copper=100.	Percent Actual	Percent Relative Copper=100.		
Copper	10.60	100.00	32.5	100.00	--	--
Arsenic	0.102	0.960	0.231	0.710	0.25	26.1
Antimony	0.025	0.236	0.056	0.172	0.064	27.1
Bismuth	0.01	0.094	0.015	0.046	0.048	51.0

TABLE 17. ROASTING WHITE METAL - ELIMINATION OF ARSENIC, ANTIMONY AND BISMUTH

	Weight Tons	Arsenic		Percent Relative Original Arsenic=100.
		Percent	Tons	
White metal roasted	100.0	0.089	0.089	100.0
<i>Products:</i>				
Blister-copper	70.1	0.083	0.058	65.2
Roaster-slag	16.3	0.092	<u>0.015</u>	<u>16.8</u>
Total -----			0.073	82.0
Difference due to volatilization -----			0.016	18.0

	Weight Tons	Antimony		Percent Relative Original Antimony=100.
		Percent	Tons	
White metal roasted	100.0	0.039	0.039	100.0
<i>Products:</i>				
Blister-copper	70.1	0.024	0.017	43.6
Roaster-slag	16.3	0.084	0.014	35.9
Total -----			0.031	79.5
Difference due to volatilization -----			0.008	20.5

	Weight Tons	Bismuth		Percent Relative Original Bismuth=100.
		Percent	Tons	
White metal roasted	100.0	0.015	0.015	100.0
<i>Products:</i>				
Blister-copper	70.1	0.003	0.002	13.3
Roaster-slag	16.3	0.012	0.002	13.3
Total -----			0.004	26.6
Difference due to volatilization -----			0.011	75.4

TABLE 18. CONVERTING COPPER MATTE - ELIMINATION OF ARSENIC, ANTIMONY AND BISMUTH

	Regulus		Bar Copper		Elimination per 100 of Copper	Total Per- centage of Elimina- tion
	Percent Actual	Percent Relative Copper=100.	Percent Actual	Percent Relative Copper=100.		
Copper	56.0	100.0	98.0	100.0	--	--
Arsenic	0.125	0.223	0.084	0.086	0.137	61.4
Antimony	0.043	0.077	0.022	0.023	0.054	70.1
Bismuth	0.023	0.041	0.004	0.004	0.037	90.2

The major results presented are for seven elements, lead, zinc, cadmium, arsenic, antimony, bismuth, and selenium, during both copper and matte production. The drastic difference in the distribution of the minor elements between copper and matte production is made obvious from the data presented. Tables 20, 21, and 22 present this data.

The data agree with all other sources reviewed here with the exception of that for antimony distribution as a function of matte grade. This report incorrectly states that the distribution ratio,  $C_3$  (percent(w) Sb in matte/partial pressure Sb in off gas) increases as matte grade increases. The reverse is believed to be true.

MO-307

This paper discusses the distribution of minor elements in a flash smelting furnace. A material balance around the furnace is presented for ten elements. The analyses and blending ratios of the furnace feed materials and the material balance presented are shown in Tables 23 and 24. The important point made is that the distribution of minor elements between matte, slag, and gas changes with the oxygen potential (i.e., matte grade) in the furnace.

Equilibrium calculations were completed for lead and zinc assuming that the metal, metal oxide, and metal sulfide were distributed between matte, slag, and gas as follows:

Matte:	PbS, Pb	Zn, S
Slag:	PbO	ZnO
Gas:	PbS, PbO	ZnS, Zn

The results were compared to furnace operating data which represent a dynamic system. By adjusting the values of the activity coefficients, the calculated values can be made to approximate the actual system. This is a somewhat different approach than was taken in MA-740. Comparing equilibrium

TABLE 19. REFINING BLISTER COPPER - ELIMINATION OF ARSENIC, ANTIMONY OR BISMUTH

	Weight Tons	Arsenic		Percent Relative Original Arsenic=100.
		Percent	Tons	
Blister-copper	100.0	0.452	0.452	100.0
<i>Products:</i>				
Refined copper	94.4	0.340	0.321	71.0
Refinery-slag	12.5	1.142	0.143	31.6
Total -----			0.464	102.6
Difference due to volatilization -----			Nil	Nil

	Weight Tons	Antimony		Percent Relative Original Antimony=100.
		Percent	Tons	
Blister-copper	100.0	0.037	0.037	100.0
<i>Products:</i>				
Refined copper	94.6	0.022	0.020	59.0
Refinery-slag	12.5	0.124	0.015	40.5
Total -----			0.035	99.5
Difference due to volatilization -----			Nil	Nil

	Weight Tons	Bismuth		Percent Relative Original Bismuth=100.
		Percent	Tons	
Blister-copper	100.0	0.040	0.040	100.0
<i>Products:</i>				
Refined copper	94.6	0.033	0.031	77.5
Refinery-slag	12.5	0.093	0.011	27.5
Total -----			0.042	105.0
Difference due to volatilization -----			Nil	Nil

TABLE 20. OBSERVED DISTRIBUTION OF MINOR ELEMENTS IN NORANDA PROCESS MAKING COPPER<sup>1</sup> (30% OXYGEN-ENRICHED AIR)

Element	Fractional Distribution in Reactor Streams <sup>2</sup>		
	Offgas (Dust) (D <sub>1</sub> )	Tapped Slag (D <sub>2</sub> )	Reactor Copper (D <sub>3</sub> )
Pb	0.21	0.77	0.02
Zn	0.14	0.858	0.002
Cd	0.95	0.045	0.005
As	0.39	0.14	0.47
Sb	0.18	0.52	0.30
Bi	0.43	0.42	0.15
Se	0.60	0.21	0.19

<sup>1</sup>Test Conditions - Copper concentrate analysis: 24.6% Cu, 28.9% Fe, 32.5% S, Fe/SiO<sub>2</sub> ratio in slag: 1.5

$$D_1 = \frac{\text{tons of X in offgas (dust)}}{\text{tons of X in reactor feed}}$$

$$D_2 = \frac{\text{tons of X in tapped slag}}{\text{tons of X in reactor feed}}$$

$$D_3 = \frac{\text{tons of X in reactor copper}}{\text{tons of X in reactor feed}}$$

TABLE 21. DISTRIBUTION OF MINOR ELEMENTS IN NORANDA PROCESS MAKING COPPER<sup>1</sup> (NORMAL CONVERTING AIR)

Element	Fractional Distribution in Reactor Streams					
	Offgas (Dust) (D <sub>1</sub> )		Tapped Slag (D <sub>2</sub> )		Reactor Copper (D <sub>3</sub> )	
	Observed	Projected	Observed	Projected	Observed	Projected
Pb	0.24	0.26	0.74	0.72	0.02	0.02
Zn	0.21	0.29	0.789	0.708	0.001	0.002
Cd	0.955	0.964	0.04	0.03	0.005	0.006
As	0.19	0.22	0.27	0.23	0.54	0.55
Sb	0.29	0.19	0.36	0.42	0.35	0.39
Bi	0.52	0.56	0.30	0.28	0.18	0.16
Se	0.78	0.69	0.07	0.16	0.15	0.15

<sup>1</sup>Test Conditions - Copper concentrate analysis: 25.3% Cu, 28.9% Fe, 31.7% S, Fe/SiO<sub>2</sub> ratio in slag: 1.7

TABLE 22. DISTRIBUTION OF MINOR ELEMENTS IN NORANDA PROCESS MAKING 70% Cu MATTE<sup>1</sup> (NORMAL CONVERTING AIR)

Element	Fractional Distribution in Reactor Streams		
	Offgas (Dust) (D <sub>1</sub> )	Tapped Slag (D <sub>2</sub> )	Reactor Copper (D <sub>3</sub> )
Pb	0.74	0.13	0.13
Zn	0.27	0.68	0.06
As	0.85	0.07	0.08
Sb	0.57	0.28	0.15
Bi	0.70	0.21	0.09

<sup>1</sup>Conditions - Copper concentrate analysis: 25% Cu, 28% Fe, 32% S, Fe/SiO<sub>2</sub> ratio in slag: 1.6

data to dynamic operating data has limitations but is a useful tool for indicating trends in minor element behavior.

One important observation is made to explain why at matte grades near 70%, a reduction in the volatility of arsenic is observed. At temperatures near 1300°C the vapor pressure of arsenic metal is greater than the vapor pressure of As<sub>2</sub>O<sub>3</sub>. Presumably, the affinity of As metal for both the Cu<sub>2</sub>O in the slag and the Cu<sub>2</sub>S in the matte is great enough to reduce the overall volatility in the furnace system.

SC-R-467

The study describes results obtained by sampling at a primary copper smelter with a production rate of 200 tons Cu/day. Concentrate, matte and slag streams of the reverberatory furnace were analyzed. The main effort of the study, however, focused on the electrostatic precipitator (ESP) controlling particulate emissions from the reverberatory furnace. The main findings of the study are presented below.

Titanium, potassium, magnesium, and sodium enter the smelter as major components besides the elements of importance in the smelting operation itself (Cu, Fe, Si, Ca, and Al). Minor elements of environmental concern are: arsenic, cadmium, molybdenum, lead, antimony, selenium, zinc, and fluorine. The rest of the elements surveyed enter in the low ppm concentration range or were not detected by spark source mass spectrometry analysis. Molybdenum entering the reverberatory furnace with the concentrate is almost completely discharged in the reverberatory furnace slag.

TABLE 23. ANALYSES AND BLENDING RATIOS OF THE FEED MATERIALS FOR THE FLASH FURNACE

Feed Material	Blend Ratio (mtons)	Au	Ag	Cu	Pb	Zn	As	Bi	Sb	Cd	Se
		g/t g	g/t Kg	% mtons	% mtons	% mtons	% mtons	% mtons	% mtons	% mtons	% mtons
Copper Concentrates	1000	2.6 2635	307 307	21.10 211	2.69 26.92	4.07 40.74	0.123 1.23	0.107 1.07	0.072 0.72	0.019 0.187	0.002 0.024
Cement		47.6	1550	74.50	1.00	0.58	0.10	0.501	0.048		0.088
Copper	20	951	31	14.9	0.20	0.11	0.02	0.10	0.01		0.02
Copper Sulfide	50	0.3 15	78 4	25.41 12.7	2.17 1.1	2.00 1.00	1.52 0.76	0.09 0.04	0.066 0.03	0.213 1.06	0.009 0.004
Copper Cake	40	21.0 840	5809 232	21.05 8.4	8.42 3.4	5.97 2.4	0.713 0.3	0.166 0.07	0.680 0.3	0.107 0.04	
Dross	6	32.7 196	822 5	53.58 3.2	30.19 1.8		1.74 0.1	0.041 0.002	1.5 0.09		
Brass Powdered	10			32.23 3.2	1.71 0.2	24.93 2.5					
Converter Slag Conc.	70	4.8 336	629 44	35.73 25	8.99 6.3	3.77 2.6	0.271 0.2	0.024 0.01	0.510 0.3	0.009 0.006	
Dusts Recycled	100	4.0 400	491 49	19.94 19.9	10.73 10.7	5.18 5.2	1.213 1.2	0.163 0.2	0.268 0.3	0.267 0.3	0.010 0.01
Sand	185		6 1	0.04 0.07	0.06 0.1	0.20 0.4					
Total	1481	3.63 5373	454 673	20.12 298	3.42 50.7	3.71 55.0	0.257 3.81	0.100 1.49	0.118 1.75	0.107 1.59	0.004 0.058

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TABLE 24. MATERIAL BALANCE OF THE MINOR ELEMENTS AT KOSAKA FLASH FURNACE

Material	Amount mton/mo	Au	Ag	Cu	Pb	Zn	As	Bi	Sb	Cd	Se
		g/t g mton/mo	g/t Kg mton/mo	% t mton/mo	% t mton/mo	% t mton/mo	% t mton/mo	% t mton/mo	% t mton/mo	% t mton/mo	% t mton/mo
Feed	24,332	2.9 70,117 100	408 9,927 100	20.49 4,986 100	3.36 817 100	3.32 808 100	0.296 72 100	0.051 12 100	0.128 31 100	0.051 12 100	0.004 1 100
Matte	8,849	7.1 62,828 89.6	984 8,703 87.7	50.55 4,473 89.7	3.56 315 38.5	2.50 221 27.4	0.046 4 5.6	0.030 3 25.0	0.090 8 25.8	0.016 1 8.3	0.001 0.1 10.0
Slag	9,438	0.1 944 1.4	9 85 0.8	0.59 56 1.1	0.95 90 11.0	4.47 422 52.2	0.064 6 8.3	0.025 2 16.7	0.139 13 41.9	0.003 0.3 2.5	0.001 0.1 10.0
Boiler & Cyclone Dusts	1,556	3.3 5,135 7.3	483 751 7.6	21.13 329 6.6	10.49 163 20.0	4.97 77 9.5	1.029 16 22.2	0.144 2 16.7	0.236 4 12.9	0.176 3 25.0	0.016 0.2 20.0
Cottrell Dust	756	1.6 1,210 1.7	374 283 2.9	14.91 113 2.3	21.21 160 19.6	4.97 37 4.6	3.18 24 33.3	0.444 3 25.0	0.427 3 9.7	0.562 4 33.4	0.020 0.1 10.0
Humidifier Sludge	--	--	105 1.1	15 0.3	89 10.9	51 6.3	22 30.6	2 16.6	3 9.7	3.7 30.8	0.5 50.0

Nearly 50 percent of the selenium and 30 percent of the fluorine are discharged together with the reverberatory furnace off gases. Nearly all of the fluorine escapes in the gaseous state.

The arsenic flows found were compared to tests made by smelter personnel. In addition, integral arsenic balances were established from the plant data. The findings were as follows:

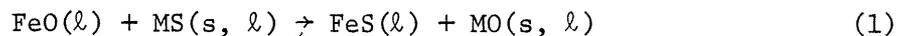
- 1) Approximately 50 percent of the arsenic entering the smelter leaves in the reverberatory furnace off-gas based on both plant and Radian sampling data.
- 2) Data gathered during this sampling study indicate that as much as 90 percent of the arsenic entering the reverberatory furnace ESP may leave in the off-gas.
- 3) Arsenic and selenium escaping the electrostatic precipitator are partly in the vapor state.
- 4) The arsenic concentration in the reverberatory furnace feed varies within a few days from 700 ppm to 7000 ppm. This variation is not only a function of the arsenic concentration in the ore, but also depends on the amount of electrostatic precipitator dust recycled.
- 5) The arsenic detected was present as arsenolite,  $As_2O_3$ . This was determined by X-ray diffraction.

ESP temperature ( $600^{\circ}F$ ) and gas flow rate (160,000 acfm) correspond to design parameters. ESP inlet grain loading determined at duct temperature is 0.60 grains/scf, and the outlet grain loading is 0.020 grains/scf. The overall particulate collection efficiency is calculated to be 96.7%. Design efficiency was 96.8%. The amount of condensibles between duct temperature  $600^{\circ}F$  and  $250^{\circ}F$  (EPA recommended) accounts for material corresponding in mass to an additional 1.60 gr/scf at the inlet and 1.0 gr/scf at the outlet.

YA-078

This article provides a great deal of insight into the behavior of minor elements during copper smelting. Thermodynamic data are presented which help describe both the distribution of impurities between matte and slag and impurity elimination via slagging and volatilization.

The distribution of metals between matte and slag is discussed using the following equilibrium relation:



$$K_1 = \frac{a_{FeS} a_{MO}}{a_{FeO} a_{MS}} \quad (2)$$

By making the approximation that the activities,  $a$ , of FeS and FeO are equal to 0.4, equation 2 reduces to:

$$K_2 = a_{MO}/a_{MS} \quad (3)$$

$$K_2 = (\gamma_{MO}/\gamma_{MS}) (N_{MO}/N_{MS}) \quad (4)$$

where:  $a_i$  is the activity of component  $i$   
 $\gamma_i$  is the activity coefficient component  $i$   
 $N_i$  is the mole fraction component  $i$

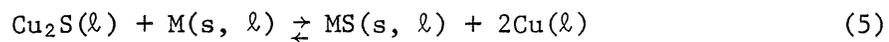
Values for the activity coefficients are then estimated and values for  $K_2$  are calculated. The  $K_2$  values are an indication of the tendency of the metal to enter either the slag or matte phase. Table 25 lists the values of  $K_2$ . Elements with small  $K_2$  values tend to stay in the matte. High  $K_2$  values indicate that the metal will tend to oxidize and dissolve in the slag.

TABLE 25. THERMODYNAMIC DATA FOR THE DISTRIBUTION OF IMPURITIES BETWEEN MATTE AND SLAG (1200°C)

Element	$\Delta F_2^\circ$	$K_2$	$\gamma_{MO}/\gamma_{MS}$	$N_{MO}/N_{MS}$
Ag	45,400	$1.7 \cdot 10^{-7}$	1	$2 \cdot 10^{-7}$
Na	29,440	$4.3 \cdot 10^{-5}$	$\sim 10^{-7}$	$\sim 10$
Cu	27,600	$8.0 \cdot 10^{-5}$	1	$8 \cdot 10^{-5}$
Pb	12,350	$1.5 \cdot 10^{-2}$	$\sim 0.3$	$\sim 0.05$
Co	10,000	$3.3 \cdot 10^{-2}$		
Ni	9,220	$4.3 \cdot 10^{-2}$	$\sim 5$	$\sim 0.01$
Ba	5,800	0.14		
Ca	2,980	0.36		
Bi	1,140	0.68		
Zn	750	0.77	0.5	2
Mn	- 3,030	2.8		
Sn	- 7,510	13		
Al	- 8,770	20		
Sb	-10,550	37		
Mg	-17,320	$3.7 \cdot 10^2$		

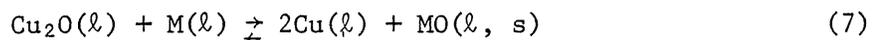
Similar calculations were made both for the distribution of metals between matte and copper and for the elimination of impurities from copper. The following are the equations describing each case:

Matte/Copper Distribution



$$K_5 = \frac{a_{\text{Cu}}^2 a_{\text{MS}}}{a_{\text{Cu}_2\text{S}} a_{\text{M}}} \quad (6)$$

Impurity Elimination



$$K_7 = \frac{a_{\text{Cu}}^2 a_{\text{MO}}}{a_{\text{Cu}_2\text{O}} a_{\text{M}}} \quad (8)$$

Values for  $K_5$  and  $K_7$  are presented in Tables 26 and 27.

TABLE 26. THERMODYNAMIC DATA FOR THE REMOVAL OF IMPURITIES FROM MOLTEN COPPER (1200°C)

Element	Content ***	$K_7$	$\gamma_M^\circ$	(Ref.)	$P_M^\circ$
	(%)				(atm)
Au	0.0003	$1.2 \cdot 10^{-7}$	0.34	(17)	$4.9 \cdot 10^{-7}$
Hg		$2.5 \cdot 10^{-5}$			$5.2 \cdot 10^2$
Ag	0.1	$3.5 \cdot 10^{-5}$	4.8	(12)	$2.2 \cdot 10^{-4}$
Pt		$5.2 \cdot 10^{-5}$	0.03	(18)	$6.4 \cdot 10^{-13}$
Pd		$6.2 \cdot 10^{-4}$	0.06	(18)	$8.5 \cdot 10^{-7}$
Se	0.04	$5.6 \cdot 10^{-4}$	<<1		66
Te	0.01	$7.7 \cdot 10^{-2}$	0.01 ?		3.9
Bi	0.009	0.64	2.7	(14)	$4.2 \cdot 10^{-2*}$
Cu	~ 99	-	1		$4.5 \cdot 10^{-6}$
Pb	0.2	3.8	5.7	(13)	$1.9 \cdot 10^{-2}$
Ni	0.2	25	2.8	(19)	$2.8 \cdot 10^{-8}$
Cd		31	0.73	(16)	32
Sb	0.04	50	0.013	(14)	$7.9 \cdot 10^{-2**}$
As	0.04	50	0.0005	(15)	$5 \cdot 10^2 ?$
Co	0.001	$1.4 \cdot 10^2$	10 ?		$3.2 \cdot 10^{-8}$
Ge		$3.2 \cdot 10^2$			$4.2 \cdot 10^{-7}$
Sn	0.005	$4.4 \cdot 10^2$	0.11	(12)	$6.5 \cdot 10^{-6}$
In		$8.2 \cdot 10^2$	0.32	(15)	$8.1 \cdot 10^{-4}$
Fe	0.01	$4.5 \cdot 10^3$	15	(20)	$7.8 \cdot 10^{-8}$
Zn	0.007	$4.7 \cdot 10^4$	0.11	(16)	10
Na		$1.1 \cdot 10^5$			8.7
Cr		$5.2 \cdot 10^6$			$3.2 \cdot 10^{-7}$
Mn		$3.5 \cdot 10^7$	0.80	(21)	$9.3 \cdot 10^{-4}$
Si	0.002	$5.6 \cdot 10^8$	0.1	(22)	$1 \cdot 10^{-6}$
Ti		$5.8 \cdot 10^9$			$6.3 \cdot 10^{-10}$
Al	0.005	$8.8 \cdot 10^{11}$	0.008	(18)	$1.3 \cdot 10^{-5}$
Ba		$3.3 \cdot 10^{12}$			$6.3 \cdot 10^{-2}$
Mg		$1.4 \cdot 10^{13}$	0.067	(18)	2.1
Be		$5.4 \cdot 10^{13}$			$9.5 \cdot 10^{-6}$
Ca		$4.3 \cdot 10^{14}$			0.13

\*  $P_{Bi}^\circ = P_{Bi} + P_{Bi_2}$       \*\*  $P_{Sb}^\circ = P_{Sb} + P_{Sb_2} + P_{Sb_4}$

\*\*\* Typical blister copper from Japanese smelter.

TABLE 27. DATA FOR THE DISTRIBUTION OF METAL IMPURITIES  
 BETWEEN MOLTEN COPPER AND COPPER SULFIDE  
 (1200°C)

Element	$\Delta F^\circ_5$	$K_5$	Distribution Ratio	
			$N_{MS}/N_M$	Experimental Data*
Bi	27,780	$6.6 \cdot 10^{-5}$	$1.8 \cdot 10^{-4}$	0.13
Sb	26,700	$1.1 \cdot 10^{-4}$	$1.4 \cdot 10^{-6}$	0.072
Sn	19,140	$1.4 \cdot 10^{-3}$	$1.7 \cdot 10^{-4}$	
Ag	13,060	$1.2 \cdot 10^{-2}$	$3.7 \cdot 10^{-2}$	
Pb	11,370	$2.1 \cdot 10^{-2}$	0.12	0.1 ~ 0.2
Ni	9,580	$3.8 \cdot 10^{-2}$	0.11	0.33
Co	7,190	$8.6 \cdot 10^{-2}$	0.86	
Cd	4,790	0.20	0.15	
Fe	3,010	0.36	5.4	
Zn	- 4,950	5.4	0.60	0.67, 1.0
Mn	-20,190	$9.9 \cdot 10^2$	$7.9 \cdot 10^2$	
Na	-37,880	$4.2 \cdot 10^5$		

\* Distribution ratio = % in  $Cu_2S$  / % in Cu.

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