

MINOR ELEMENTS IN COPPER
SMEETING AND ELECTROREFINING

by

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To my parents

ABSTRACT

Minor element (As, Sb, Bi, Pb, Ni) behavior, control and removal techniques in the conventional copper smelting/electrorefining process was studied. The analysis was based on the information collected from an exhaustive literature review, the visit of 23 smelters, 14 electrorefineries and consultations at 15 different institutes specialized in the field.

Data was collected for several types of matte smelting furnaces such as Outokumpu flash, INCO flash, Mitsubishi S-furnace, Teniente Converter, Noranda Process Reactor, Isasmelt and reverberatory. Behavior in Peirce-Smith converting furnaces, Mitsubishi C-furnace, Noranda Continuous Converter and Kennecott-Outokumpu Flash Converting Furnace was also discussed.

The effect of various matte smelting furnace operating parameters such as matte grade, oxygen enrichment, concentration in feed, other minor constituents and temperature on minor element partition to gas and distribution coefficient (wt% matte / wt% slag) was analyzed theoretically and validated with industrial data when possible. Because fewer data were available, only a brief comparison between the elimination in traditional batch converting and new continuous converting processes was performed. The behavior of minor elements in electrorefining was described from a theoretical viewpoint.

In the matte smelting furnaces, the volatilization of As, Sb, Bi, Pb, Ni averaged respectively 66%, 22%, 46%, 22% and 2% of the total input to the furnace. Volatilization was found to depend mainly on oxygen enrichment and matte grade (%Cu) in addition to feed content for As. Deportment to slag in the matte smelting furnaces for As, Sb, Bi, Pb, Ni averaged 17%, 49%, 11%, 36%, and 27% of the input. It was found to vary mainly with matte grade and to a lower extent with oxygen enrichment. The effect of the smelting furnace type and design on minor element behavior was found to be low as compared to the influence of operating parameters.

Elimination of Bi and Pb in batch converting were better than in the new continuous processes. The elimination of As and Sb in continuous processes using calcium ferrite slag and high oxygen partial pressure were higher than for converting furnaces with silicate slag.

In electrorefining, Pb was found to report predominantly to anode slimes while Ni was largely dissolved in the electrolyte. As, Sb and Bi behavior depended primarily on anode composition for given electrorefining conditions.

A description and brief analysis of major techniques used industrially for control and removal of minor elements was performed. Feed pre-treatments, removal from molten matte or copper, dust bleed and treatment, anode doping and electrolyte purification techniques were considered. The use of vacuum for minor element removal (pre-treatment, matte or molten copper) and hydrometallurgical feed pre-treatment appear to be the most promising options not to have reached industrial application yet.

Finally, a desire to increase the knowledge on minor element removal was encountered within the industry especially because of the gradual exhaustion of 'clean' natural resources from which copper is extracted. Therefore, it is believed that the future of copper smelting and refining developments will go hand-to-hand with improved control over minor elements.

RÉSUMÉ

Une augmentation du traitement de matériaux riches en éléments mineurs, sans pour autant affecter la qualité du produit, peut représenter un avantage économique important pour un producteur de cuivre. Ceci peut être fait par une optimisation du procédé pour favoriser l'élimination ou encore par l'utilisation de technologies spécialisées.

Le comportement des éléments mineurs (As, Sb, Bi, Pb, Ni) dans le procédé traditionnel de production du cuivre (fonderie/électro-affinerie) a été étudié. De plus, les méthodes courantes de contrôle et les techniques permettant leur élimination ont été décrites et évaluées sommairement. L'analyse a été basée sur l'information recueillie suite à une recherche littéraire exhaustive, la visite de 23 fonderies et 14 électro-affineries de cuivre et les consultations effectuées auprès de 15 instituts spécialisés dans le domaine.

Les données furent compilées pour plusieurs types de vaisseaux de smeltage tels que le four flash Outokumpu, le four flash INCO, le réacteur Noranda, le vaisseau de smeltage du procédé Mitsubishi, la technologie Isasmelt et le four à réverbère. Les partitions entre les phases dans les convertisseurs Peirce-Smith, le vaisseau de convertissage du procédé Mitsubishi, le convertisseur continu Noranda et le four de convertissage flash Kennecott-Outokumpu furent également recueillies.

Les effets de divers paramètres d'opération des vaisseaux de smeltage sur la partition au gaz et le coefficient de distribution (%M matte / %M scorie) des éléments mineurs tels que la teneur en cuivre de la matte, l'enrichissement en oxygène, la concentration dans l'alimentation, la présence d'autres constituants mineurs et la température ont été évalués théoriquement et industriellement lorsque c'était possible. Étant donné que moins de données furent acquises pour les convertisseurs, seulement une brève comparaison entre l'élimination entre le procédé traditionnel 'batch' et les convertisseurs continus a été faite. De plus, le comportement des éléments mineurs dans le procédé d'électro-affinage a été discuté théoriquement.

Dans les fours de smeltage, la volatilisation de l'As, Sb, Bi, Pb, Ni a atteint respectivement, en moyenne, 66%, 22%, 46%, 22%, et 2% de l'alimentation totale au four selon les données industrielles. L'enrichissement en oxygène et la teneur en cuivre de la matte ont été identifiés comme ayant le plus d'impact sur la volatilisation. À cela s'ajoute la teneur dans l'alimentation pour l'As. Les éliminations dans la scorie du four de smeltage pour l'As, Sb, Bi, Pb, Ni sont respectivement en moyenne de 17%, 49%, 11%, 36% et 27% de l'alimentation. La teneur en cuivre de la matte et, dans une plus faible mesure,

l'enrichissement en oxygène ont été démontrés comme ayant un impact sur la scorification des éléments mineurs.

L'élimination du Bi et Pb dans le procédé de convertissage 'batch' a été identifiée comme étant supérieure à celle dans les nouveaux procédés continus. Cependant, l'utilisation de la scorie calcaire (Ca-Fe) et la pression partielle d'oxygène plus grande permettraient une meilleure élimination dans la scorie de l'As et Sb dans les convertisseurs continus.

Dans le procédé d'électro-affinage, le Pb se retrouve principalement dans les boues anodiques tandis que le Ni est dissous dans l'électrolyte. La portion d'As, Sb et Bi qui se retrouve dans les boues anodiques et l'électrolyte dépend principalement de la composition des anodes.

Les principales techniques utilisées industriellement pour contrôler les éléments mineurs ont été décrites et brièvement analysées. Le pré-traitement de l'alimentation, l'enlèvement des éléments mineurs de la matte ou du cuivre en fusion, le 'saignage' et le traitement des poussières, le 'dopage' des anodes et les techniques de purification de l'électrolyte ont été considérés. La purification sous-vide (pré-traitement, matte ou cuivre en fusion) pour enlever les éléments mineurs de même que le pré-traitement hydrométallurgique de l'alimentation sont deux technologies prometteuses qui ne sont pas encore utilisées industriellement.

Finalement, les consultations et visites industrielles ont permis de constater que l'importance accordée au traitement des éléments mineurs ira en augmentant dans le futur à cause de l'épuisement graduel des ressources 'propres'. Ceci laisse croire que les développements futurs dans l'industrie du cuivre devront être faits de pair avec un contrôle amélioré des éléments mineurs.

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CHAPTER 1

INTRODUCTION

The key judge of quality of the final product, cathode copper in the copper industry, is chemical composition. Nowadays, the production of high purity copper at a competitive production cost is increasingly challenging because the purity of the mineral resources is slowly decreasing. Ore bodies with low levels of impurity (often called 'clean') have become rare after several decades of intense extraction. In addition, recent developments in the copper production technology to increase productivity as well as environmental compliance, are often unfavorable to impurity elimination.

Iron and sulphur are the principal impurities in the copper concentrates comprising on average as much as 60% by mass of the concentrate. Pyrometallurgical vessels used for smelting, converting and fire-refining are specially designed to efficiently remove Fe and S with the result that they presently offer no significant problems to the industry. Another group of impurities present at lower concentrations (often only few ppm in feed) are referred to as '**MINOR ELEMENTS**'. Their detrimental impact on quality of the copper requires a special attention to limit their presence at low levels in the final cathode. Removal of minor elements might be extremely difficult even at low concentration because of their thermodynamic and electrochemical properties similar to copper. In addition, some have been found to be toxic (e.g., arsenic and lead) so their removal might present environmental and health and safety challenges.

The simplest strategy to control the levels of minor elements in the product copper is to limit the feed content of minor elements. However, it is not always possible due to the absence of high-purity feed materials or unfavorable economics. In consequence, the optimization of minor element elimination in the conventional smelting/electrorefining flowsheet or development of special removal treatments are important for the copper industry.

1.1. OBJECTIVES

The present study is undertaken with the global objective of identifying factors critical to minor element control and different techniques to permit their removal in the pyrometallurgical/electrorefining copper production flowsheet. In order to achieve this purpose the following sub-objectives are covered:

- 1- To describe the thermodynamic and electrochemical behavior of specific minor elements (As, Sb, Bi, Pb, Ni) in the copper smelting/electrorefining process;
- 2- To describe the theoretical effect of various operating parameters on distributions;
- 3- To compare theoretical behavior with industrial data;
- 4- To provide a descriptive analysis of specific operating practices and technologies for the control and removal of minor elements.

At the end of the thesis, the reader should be able to understand the effect of the major thermodynamic and operating factors on the behavior of As, Sb, Bi, Pb and Ni. In addition, the reader should be familiar with the industrial technologies used for the removal of these elements from the conventional copper smelting/electrorefining flowsheet.

1.2. LIMITATIONS

The scope of the thesis is limited to **arsenic, antimony, bismuth, lead and nickel**. These were selected by the sponsor (Noranda Inc. - Horne smelter), the research supervisor and the author because of their significance to the Canadian copper industry.

The thesis covers the behavior of these elements from the reception of the concentrate at the smelter to cathode plating in electrorefining. Therefore, mineral processing of the ore to produce the concentrate as well as post-treatment of the copper product are beyond the limits of the present work.

On environmental issues, gas treatment and effluent stabilization are beyond the scope of this thesis. In summary, the focus of this work is the extractive metallurgy associated with minor element treatment in the conventional copper production flowsheet.

1.3. DIFFERENCES FROM FUNDAMENTAL M.ENG. PROJECT

The methodology in this work was slightly different from most conventional M.Eng. projects, in that no laboratory experiments were performed. The data was collected by an exhaustive literature review coupled with industrial visits and discussions at copper smelters and refineries treating various levels of minor elements. This methodology was employed because of the nature of the subject treated and the objectives that were established. Discussion with the smelters/refineries was used to obtain data regarding the different practical aspects related to minor element treatment in the industry.

1.4. STRUCTURE OF THE THESIS

The final section of Chapter 1 presents a general portrait of the economics of minor element treatment. It will help the reader to understand the driving force behind the desire to gain a better knowledge in order to maximize the treatment of more minor elements.

An introduction, giving a background on the modern copper production processes, is presented in Chapter 2. The reading of this section can be omitted by a reader familiar with the copper industry.

The methodology of the present project is described in Chapter 3. Chapter 4 establishes the anticipated relationship between the behavior of minor elements in copper smelting against various factors (e.g. matte grade, oxygen enrichment, initial content in feed, etc.). Industrial data collected in industrial visits are compared to anticipated theoretical behavior. In Chapter 5, the theoretical behavior of minor elements in electrorefining is discussed briefly.

The various operating practices and technologies available for minor element removal and control in the conventional smelter/refinery flowsheet are described and evaluated in Chapter 6. Conclusions follow in Chapter 7. The complete list of references in alphabetical order is given in Chapter 8.

Appendix A contains the Table of Results with information collected from plant visits and literature on the distribution of As, Sb, Bi, Pb and Ni in copper smelting. In Appendix B, the References are classified accordingly to the sections of the thesis to help the interested reader to locate more information on a specific subject.

1.5. ECONOMICS OF MINOR ELEMENT TREATMENT

The simplest and oldest way to control the impurities reporting to copper is to limit their content in the feed to the smelter. However, this option has limited application as it is often unprofitable or simply impossible to treat clean concentrates only. The economics of minor element treatment are completely different between a 'captive' smelter (mine-smelter complex) and 'custom' smelter (concentrate treatment on a toll basis).

For a captive smelter, revenues are generated by selling copper on the market as the mine-smelter complex owns the ore body. Therefore, the presence of technologies dedicated to minor element control, removal, and environmentally friendly discharge are required if the ore body contains levels of impurities above process limits. This might require a company to not exploit a part of valuable copper reserves contaminated with minor elements to avoid the extra capital and operating costs required. A good example is the 'CODELCO-Mansa Mina' deposit in Chile, rich in copper which has been left unexploited for decades because of anticipated treatment costs associated with high arsenic levels (Cu is mainly present as enargite - Cu_3AsS_4).

On the other hand, a custom smelter-refinery generates its revenues mainly from three sources:

- 1- **Treatment/refining charges:** fix charges are paid by the mine (or material owner) in return for concentrate treatment at the smelter and refinery. The charges strongly depend on the market (world independent mining production vs. custom smelters' capacity – Lesemann, 1995) and varies from contract to contract.
- 2- **Metal gain:** recovery of copper and precious metals to be paid to the client are pre-determined in the contract. Recoveries above contract specifications represent a source of revenue that can be substantial.
- 3- **Penalty charges:** this revenue is directly related to minor element concerned and is described in more detail below:

In theory, the penalty charges paid by the owner of the material to be smelted exist to cover the extra costs for processing contaminated materials. However, in practice, the penalty charges are set by the market. The difference between the actual incremental treatment costs incurred by the smelter and the market penalty charges represents additional smelter revenue. This gives rise to specialization of certain custom smelters to take advantage of those penalties. Noranda Inc. - Horne smelter / CCR refinery and Dowa - Kosaka smelting and refining are excellent

examples. For them, penalty charges are as important as treatment charges for their profitability.

Table 1.1. gives typical penalty charges for the treatment of dirty concentrates gathered from various sources. As a general structure, a custom smelting contract usually identifies a No Charge Maximum (NCM) specifying levels for minor elements under which no penalty has to be paid. Above NCM, a penalty per discrete increment in the level of minor element is generally charged. Wide variations exist as a consequence of the independence and privacy of smelting contracts and market fluctuations. They are site specific due to specific smelting process limits (product limits, environmental regulations, labor costs, etc.) and can even vary from contract to contract for a particular site.

Table 1.1. Typical penalty charges for the treatment of 'dirty' copper concentrates [Robilliard and Mounsey, 1995 ; Diaz et al., 1997; Godbehere, 1999; Davenport, 2000]

Element	No Charge Maximum (NCM - wt% in dry feed)	Penalty (US\$/MT of dry concentrate)
Arsenic	0.1-0.3%	\$1.5-4 / 0.1% above NCM
Antimony	0.1-0.3%	\$1.5-4 / 0.1% above NCM
Bismuth	0.01-0.03%	\$1.5-4 / 0.01% above NCM
Lead	0.5-2%	\$1.5-3 / 1% above NCM

No penalty charge is given for nickel in Table 1.1. Nickel sulfate is usually a value added by-product in electrolytic refining offsetting partly or completely for nickel's extra processing costs. In addition, most smelters with high levels of Ni are captive (e.g., INCO – Copper Cliff). At very high levels of nickel (e.g., above 0.5% Ni in feed), it can be presumed that penalty would be charged to treat the concentrate in a custom smelter but no information was obtained in relation to their magnitude.

It can also be observed from Table 1.1. that penalties for Bi are about ten times greater than those for As and Sb and 100 times greater than those for Pb. This is attributable to the dramatic effect of Bi on product quality and also to the relatively higher cost of removing this element from the system. It should be emphasized that these penalties are not fixed but change with time from the market supply/demand curve and technology development.

To give an order of magnitude for revenue from penalty charges to the reader, they can quickly reach U.S.\$5-10 M for a custom smelter of medium size (750,000 tpy of concentrate) with a moderate ability to treat minor elements. The revenue can be higher for smelters specialized in minor element treatment. However, costs related to the development and operation of dedicated removal and control techniques have to be subtracted from this additional income.

CHAPTER 2

COPPER PRODUCTION PROCESSES

A general description of copper production process is presented in this chapter*. It gives the background information necessary on modern copper production for a better understanding of the thesis as well as defining the industrial jargon used in the following chapters. The description is brief and references can be consulted for more details. In particular, '*Extractive Metallurgy of Copper*' by Biswas and Davenport, 1994, is a complete source for information.

Both pyrometallurgical and hydrometallurgical processes are used for copper production. As most copper in the earth's crust is present in copper-iron sulfide form, the pyrometallurgical production is by far the most extensive. Approximately 90% of copper is produced via copper smelting [Biswas and Davenport, 1994]. At the moment, the application of hydrometallurgical processes is limited to copper oxide ores. The leaching thermodynamics and kinetics as well as precious metal recovery are still obstacles to a wider application of hydrometallurgy on copper sulfide ores.

Typically, copper sulfide ores contain from 0.5% Cu (open-pit mine) to 1-2% Cu (underground mine). In these deposits, most of the copper is present as copper-iron sulfide minerals such as chalcopyrite (CuFeS_2), bornite (Cu_5FeS_4) and chalcocite (Cu_2S). Complex sulfide ores contain various other metal sulfides (ZnS , PbS , AsS , etc.) in a copper-iron sulfide matrix and represent great reserves of copper. The exploitation of these deposits is presently limited as it usually requires the application of specialized removal techniques for impurities to produce quality copper at low cost and an environmentally stable residue. More details on selected techniques for removal of As, Sb, Bi, Pb and Ni to produce copper from complex sulfides are given in Chapter 6.

A general flowsheet of pyrometallurgical copper production follows in Figure 2.1.

* This chapter can be skipped by the reader with a good knowledge of the operations involved in the pyrometallurgical copper production.

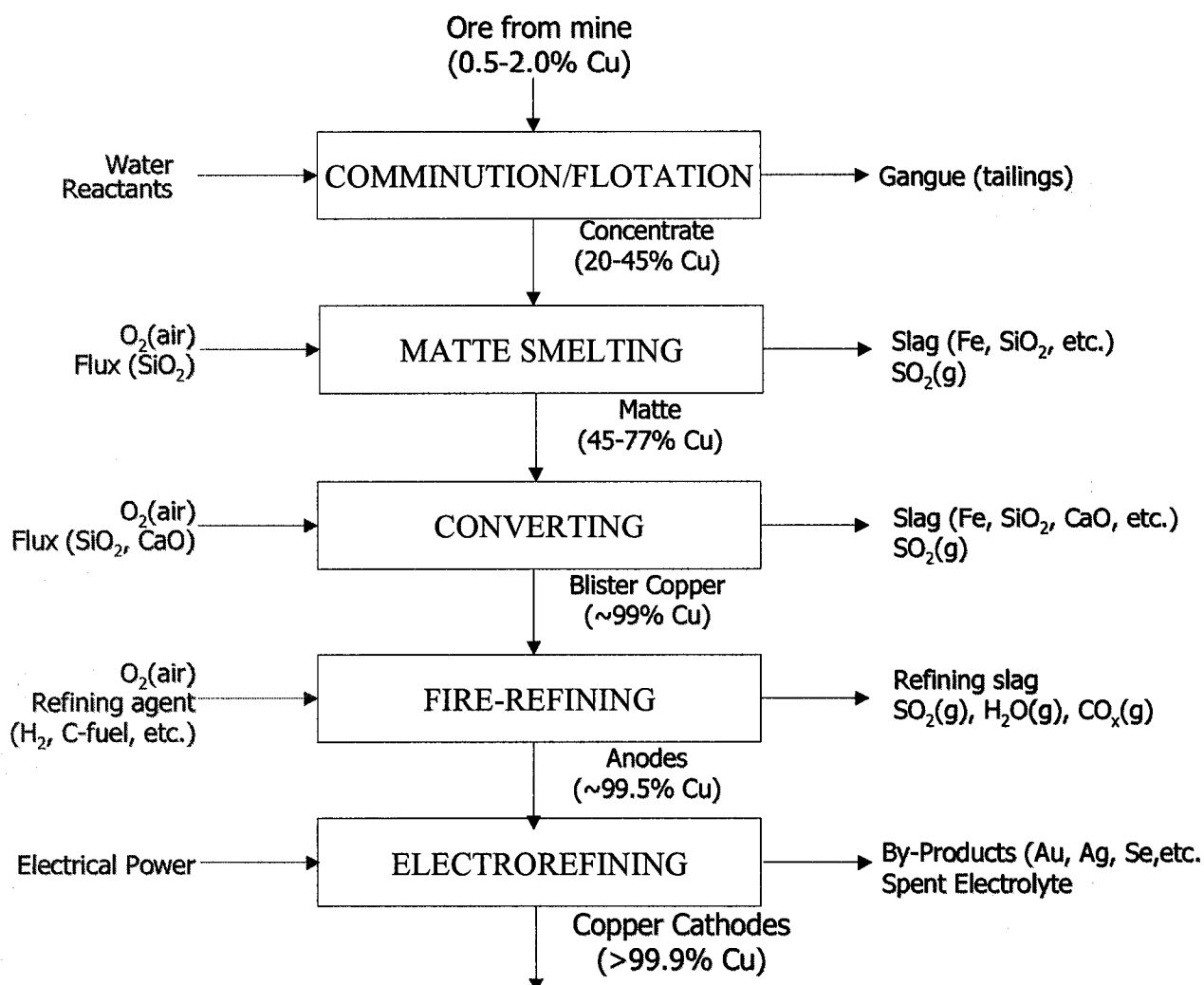


Figure 2.1. General flowsheet of conventional copper production process

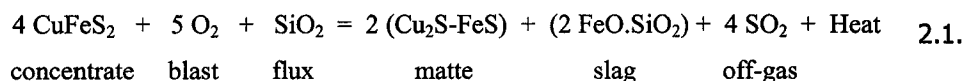
2.1. CONCENTRATION BY FROTH FLOTATION

The copper level in a typical deposit (0.5-2.0% Cu) is generally low, with the result that copper production requires 'concentration' prior to smelting of the ore to be economical. Concentration is the physical separation of copper-sulfide minerals from a residue (also called 'gangue') using mineral processing techniques. Without going into the details, chemical reagents (collectors, frothers and modifiers) can selectively modify the properties of the copper sulfide minerals in aqueous slurry to render them hydrophobic. By injecting air at the bottom of a flotation cell, the hydrophobic copper sulfide minerals attach to the rising air bubbles and are carried to the surface

from where they are collected as a temporary froth. This froth is dewatered to become a concentrate with a copper content between 20 to 45%.

2.2. MATTE SMELTING

The first stage of pyrometallurgical copper production is usually matte smelting. On occasion, some concentrates are roasted for impurity elimination (Chapter 6) or smelted directly to blister copper known as direct-to-copper smelting. In matte smelting, the copper concentrate is melted and part of the sulphur and iron is removed by oxidation. The inputs to the smelting furnace are the copper concentrate, silica-based flux, air or oxygen-enrich air, recycled dust, reverts and sometimes carbonaceous and/or inert materials to balance the heat requirements. Modern smelting is carried out in furnaces at a temperature of around 1200°C under oxidizing atmospheres. The smelting reaction for a chalcopyrite concentrate can be written as:



The operation of the furnace is usually semi-continuous, using tapholes/ladles to transfer the products of smelting or fully continuous using launders for the same purpose. The products of matte smelting are molten sulfide matte (45-77% Cu), molten oxide slag and a SO₂ rich off-gas. The matte is transferred to another vessel for copper converting (Section 2.3.). Slag is either discarded directly if the copper content is low (generally < 1% Cu) or re-processed by mineral processing or pyrometallurgically for copper and precious metals recovery and then discarded. The off-gas, rich in SO₂, is first cleaned for dust removal before being converted to sulfuric acid or on occasion, to liquid sulphur dioxide in associated chemical plants. When environmental regulations permit, the off-gas and associated SO₂ is emitted directly into the atmosphere. This practice is no longer allowed by the law in most developed countries.

Matte smelting is performed in different types of furnaces depending on the needs of the smelter, the environmental regulations in place and the company expertise. Industrial smelting furnaces can be categorized in three types: flash, bath and lance smelting. Flash smelting furnace is designed so that predominant smelting reactions occur directly between oxygen-bearing gas and concentrate particles dispersed in the gas phase. In bath smelting furnaces, the oxygen-bearing gas is injected in the bath via submerged tuyeres. The concentrate is enveloped and smelting reactions occur in the turbulent bath of matte, slag and gas. Finally, in lance smelting furnaces, the oxygen-bearing gas is added by lance(s) at the top of the bath. The

reactions mainly happen in the bath but there are also some flash reactions before concentrate melting giving a mix behavior. Melting furnaces such as reverberatory or electric vessels were the dominant smelting vessels three decades ago. However, today their use is limited due to high energy cost and environmental regulations.

In 1999, about 50% of the copper concentrates were smelted in Outokumpu Flash Smelting Furnaces [Hanniala et al., 1999]. A schematic representation of an Outokumpu FSF is included in Figure 2.2. The other half of the copper concentrate is treated with technologies such as El Teniente Converter (bath – Morales and Mac-Kay, 1999), Mitsubishi S-Furnace (lance – Goto et al., 1998), reverberatory furnace (Biswas and Davenport, 1994), INCO Flash Furnace (Butler, 1992), Noranda Process Reactor (bath – Prévost, 1992), Isasmelt Furnace (lance – Binégár and Tittes, 1994), Vanyukov (bath – Tarasov and Kovgan, 1995). A picture of the Noranda Process Reactor is shown in Figure 2.3. A complete discussion on the similarities and differences between the processes is beyond the scope of this introductory chapter and can be found elsewhere [c.f. Appendix B for references specific to chapter].

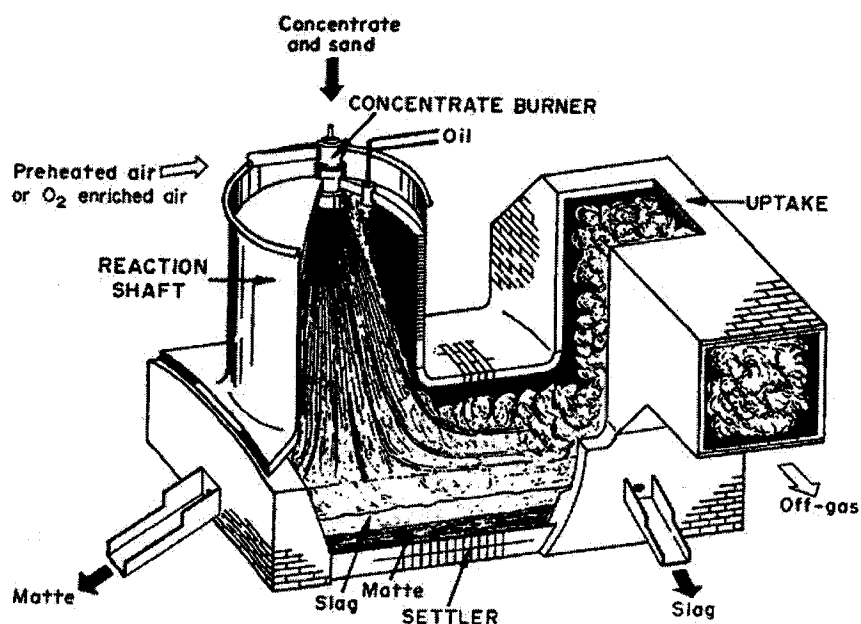


Figure 2.2. Schematic representation of an Outokumpu Flash Smelting Furnace reproduced from Biswas and Davenport, 1994

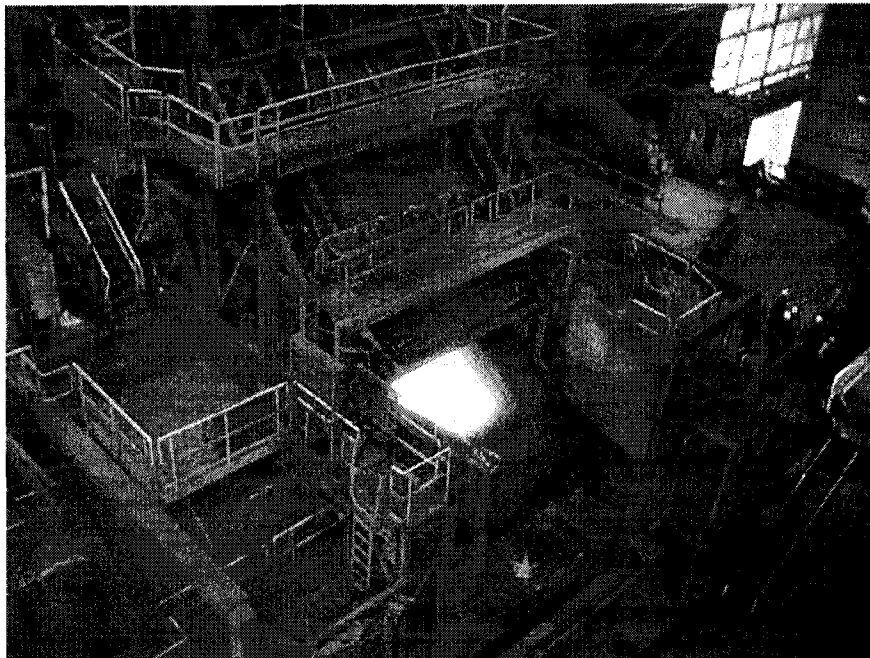
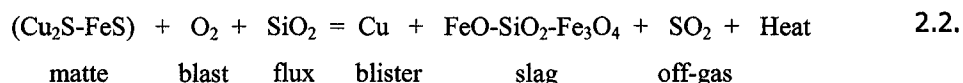


Figure 2.3. Noranda Process Reactor at the Horne Smelter from Larose, 2001

2.3. CONVERTING

Converting is the oxidation of the copper matte with air (or oxygen-enriched air) in the presence of a flux. The objective of copper converting is to transfer the remaining iron in the matte to a slag and sulfur to a rich SO₂ off-gas stream. Matte is transferred from the smelting furnace to the converting furnace(s) in large ladles, launders or granulated matte via pneumatic conveying. The products of converting are crude molten metallic blister copper (~99% Cu), Fe-rich slag and SO₂-rich off-gas. A general, unbalanced, converting reaction can be written as:



The above equation is highly simplified, as in reality, a set of simultaneous chemical reactions occur. Converting is also carried out at a temperature around 1200°C similar to the smelting temperature. It is autothermal because the heat generated from the iron and sulphur oxidation is more than sufficient to balance the heat losses and other heat demands of the process. The excess heat generated often permits the melting of cold concentrates by injection or other copper bearing materials as coolant referred to as 'cold dope' (secondary materials or internal reverts). In some converting processes, the silica slag is replaced by calcium-ferrite slag to allow operation at higher oxygen potentials due to greater magnetite solubility in this type of slag.

Because of the high agitation and the strong oxidizing conditions prevailing in converting, the slag produced has a high copper content (3-10% Cu). This requires the recirculation of converting slag to the smelting vessel or re-processing for copper recovery (slag cleaning furnace or mineral processing). Similar to smelting, the converting off-gas is cleaned for dust removal and SO_2 is often converted to sulfuric acid in an associated acid plant.

Today, most copper converting (~80%) is carried out in Peirce-Smith converters (Figure 2.4. and 2.5.). This mature technology has been used for about one century. The Peirce-Smith converter is operated in batch mode. Because of long process time, complex scheduling and material handling, it is usually necessary to have several Peirce-Smith vessels operating independently to sustain the matte smelting vessel(s) production rate. In preparation for the batch converting cycle in the Peirce-Smith, the liquid matte is transported by large ladles and is charged through the central mouth. When the converter is filled, it is rotated to submerge the tuyeres and the air or oxygen enriched-air blowing starts.

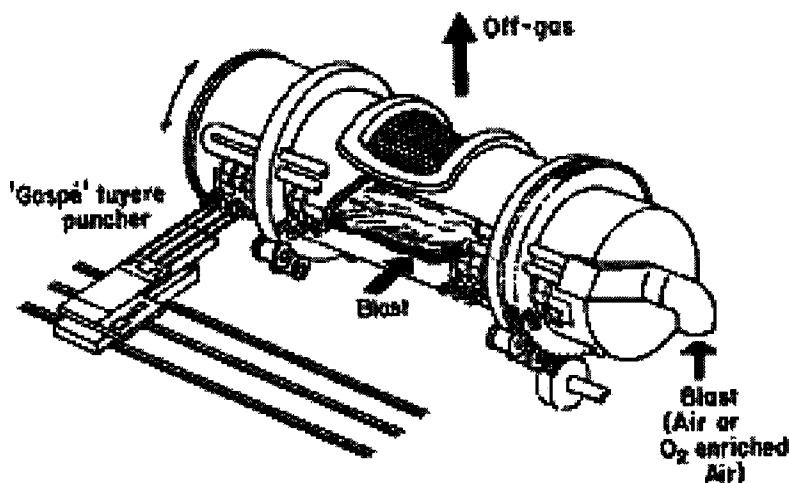


Figure 2.4. Schematic representation of a Peirce-Smith converter reproduced from Biswas and Davenport, 1994

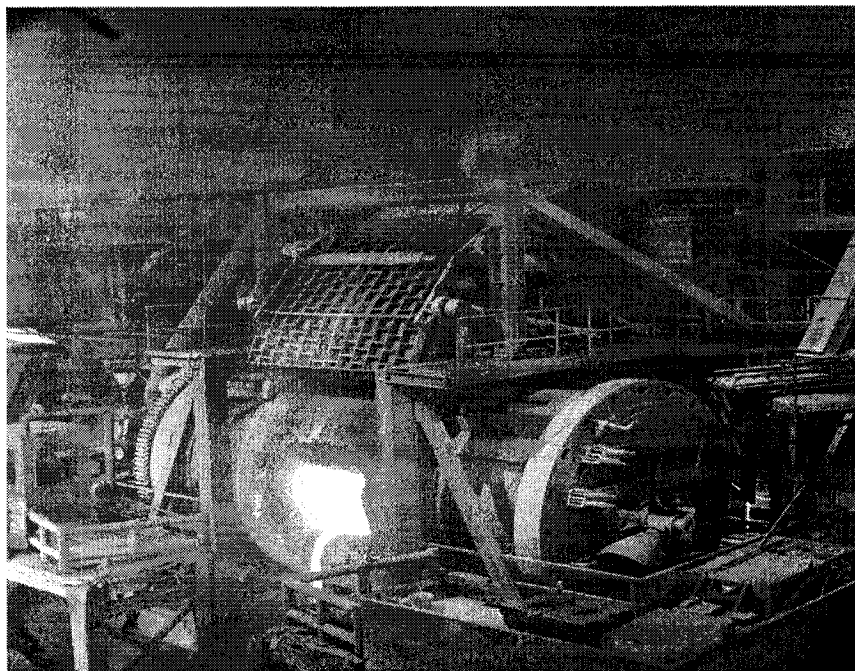
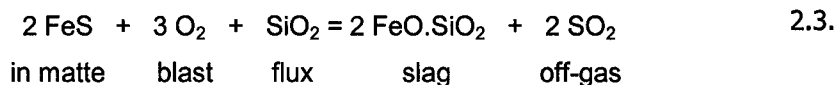


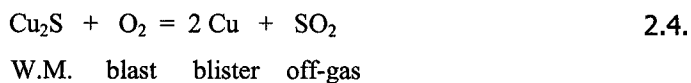
Figure 2.5. Peirce-Smith Converter during skimming from Noranda Inc., Horne smelter

The batch operation comprises two sequential chemically distinct stages. First, iron elimination occurs in the slag-forming stage ('slag blow'):



Often, multiple (2 to 4) slag-forming cycles are performed on the same converter charge to maximize productivity whereby after skimming the slag from a first blowing cycle, more molten matte is added to the converter and blowing is repeated. The result is a gradual accumulation of Cu_2S (white metal).

The second converting stage is the oxidation of white metal with air (or oxygen-enriched air) to form blister copper. This stage is called 'copper blow':



In the Peirce-Smith converter, the copper blow follows the slag blow as it starts only when the matte contains less than about 1% Fe. Moreover, thermodynamics predict that significant copper oxidation does not occur until the sulphur content of the copper falls below approximately 0.02 wt. % S. This is the point at which the converting operation is terminated.

The major disadvantage of the Peirce-Smith converter is the difficulty to comply with strict environmental regulations. This is caused by the batch operation of several vessels simultaneously that requires a complex schedule for the production of a constant strength off-gas. Moreover, significant leakage of SO₂ into the atmosphere during molten matte transport, charging, roll-in and roll-out and skimming creates environmental challenges. To reduce this environmental problem as well as increase productivity and automation, several new converting processes have been developed recently. The industrial operation of these new processes is still very limited but it is believed that it will expand significantly in the near future, as the environmental regulations are tightening.

In 1999, industrial options to Peirce-Smith converting are the Hoboken converter (batch similar to P-S but with modified off-gas), the Mitsubishi C-Furnace (lance – Goto et al., 1998), the Kennecott-Outokumpu Flash Converting Furnace (continuous – Hanniala et al., 1998), the Noranda Continuous Converter (bath – Prévost et al., 1999) and the INCO MK-Converter (lance – Queneau and Marcuson, 1996). Again, a complete discussion is beyond the scope of this project. More details can be found in the References or (Chapter 8 or Appendix B).

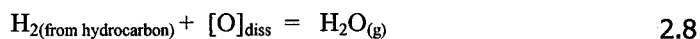
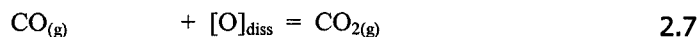
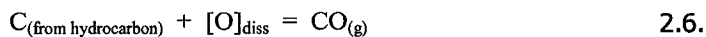
2.4. FIRE-REFINING AND CASTING

The dissolved sulphur and oxygen present in the blister copper after converting operations would react upon cooling and solidification to form SO₂ bubbles (blisters) and affect the physical quality of the cast anode. Therefore, final polishing by fire-refining is required to remove most of the sulphur and oxygen dissolved in the copper. Fire-refining removes sulphur and oxygen from the melt in two distinctive stages.

1. Air-oxidation to remove sulphur as SO₂ ('desulfurization'):



2. Hydrocarbon-reduction to remove the dissolved oxygen as CO/CO₂/H₂O ('poling'):



Industrially, fire-refining is achieved in an 'anode furnace'. The vessel is very similar but larger than a Peirce-Smith converter. A tap-hole is included in the design for anode casting, fewer tuyeres (generally only 2) are mounted on the vessel permitting lower flowrate of injection for more precise control of the oxidizing conditions. In addition, the mouth is smaller because of the lower volume of gaseous emissions and to minimize heat losses, and burners are required to maintain the temperature of the melt during casting. Fire-refining is carried out at temperatures around 1200°C. Air-oxidation (Equation 2.5.) is done by blowing air through one or two tuyeres to lower the sulphur content to approximately 0.001% S in the copper melt. For the hydrocarbon-reduction (Equations 2.6.-2.8.), the choice of a reducing agent is diversified. Gas and liquid hydrocarbons (natural gas, reformed hydrocarbon gas, petroleum gas, propane, bunker oil, kerosene, butanol, naphtha, wooden poles, ammonia, etc.) are injected directly via the tuyeres sometimes with steam. Concentrations below 0.15% O are desirable in the melt for anode casting.

Fire-refining is the last chance to treat the copper melt before its solidification. If the copper contains excessive impurity levels, special treatments might be introduced at this point. This is especially true for arsenic, antimony and lead that can be removed pyrometallurgically by fluxing during fire-refining. More details will be given on this removal technique in Chapter 6.

The copper is finally cast into anode-shaped molds to be inserted in the electrolytic tankhouse. Most copper smelters use a large horizontal rotating 'casting-wheel' with twenty to thirty anode moulds. Automation and precise control over the anode weight is now standard in the industry. Continuous casting of anodes using a Hazelett twin-belt casting machine is also used in limited applications.

2.5. ELECTROREFINING

The fire-refined cast anode produced is not of a purity suitable for most applications, especially for electrical conduction. Final purification is via electrorefining. Electrorefined copper usually contains less than 20 parts per million impurities [Biswas and Davenport, 1994].

In electrorefining, the copper present in the impure anode from the smelter (99.0-99.5% Cu) is electrochemically dissolved into an $\text{CuSO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ electrolyte to be plated onto copper or stainless steel cathodes. Many impurities are insoluble (Ag, Au, Pb, Pt, Sn, etc.) in the electrolyte and report to a 'mud' at the bottom of the cell. This 'mud', also called 'anode slimes', is sent to a by-product plant for precious metals recovery. Other impurities (As, Sb, Bi, Ni, Fe, etc.) are partially or fully soluble in the electrolyte. Because their electrochemical potential is lower than the voltage of the electrorefining cell, they do not plate. However, their level in the electrolyte must be carefully controlled below specific limits that depend on tankhouse practice to avoid physical contamination by various mechanisms as discussed in Chapter 5. This is achieved by continuously bleeding a part of the electrolyte to a purification circuit. More details on the different type of purification circuits are given later in Chapter 6 as they have a strong impact on the tolerance of the refinery for minor elements. A typical electrorefinery flowsheet is reproduced in Figure 2.6 and a general view of CODELCO-Potrerrillos refinery is shown in Figure 2.7.

Industrially, electrorefining is carried out in large electrolytic cells containing between 35 to 60 cathodes interleaved with anodes. The cell is filled with electrolyte at a temperature around 65°C. Typical electrolyte composition is 40-50 kg/m³ Cu, 160-200 kg/m³ H₂SO₄, and additives such as glue, thiourea and Cl⁻ are added to improve plating morphology and precious metal recovery. The cathodes are made of copper or stainless steel blanks (ISA or Kidd process). Typically, copper is deposited on the cathode for 7 to 14 days depending on the current density and technology used and on the anode/cathode spacing. After washing, the cathodes are sold or remelted and cast as a final product.

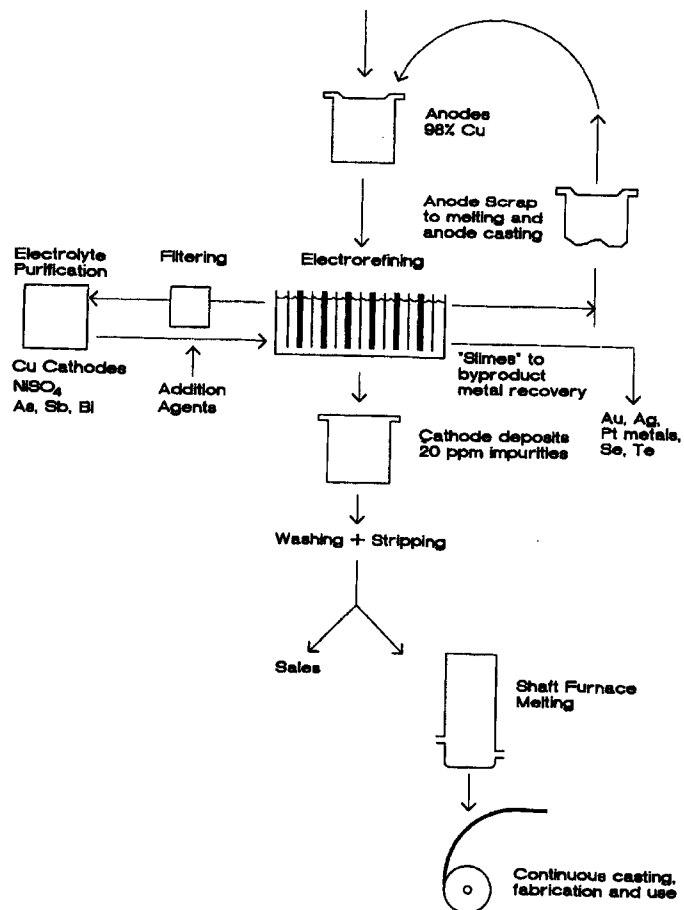


Figure 2.6. Typical Copper Electrefinery Flowsheet reproduced from Biswas and Davenport, 1994

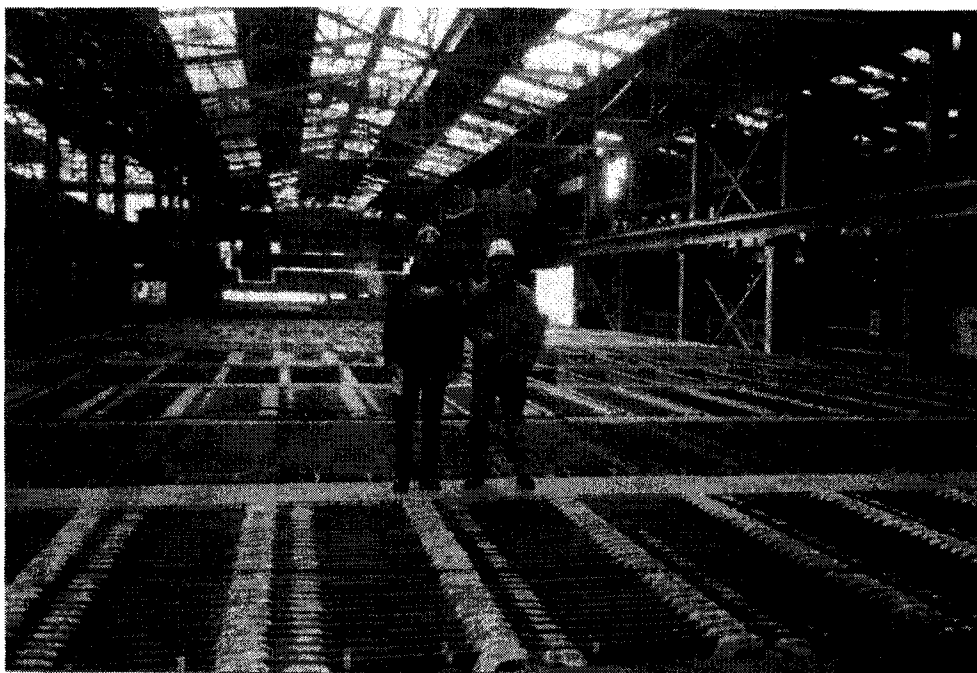


Figure 2.7. General view of CODELCO - Potrerillos Refinery (Chile)

2.6. CATHODE QUALITY

A unique combination of properties such as electrical and thermal conductivity, resistance to corrosion and ease of fabrication gives copper an important place in the world metal market. The chemical composition of copper has a great influence on its properties. Electrical and thermal conductivity of copper, as in all pure metals, is significantly affected by the presence of other impurity elements. Similarly, the impurities in the cathode directly affect the castability and rolling of copper as well as the anneability of the final rod [Adams and Sinha, 1990; Dennis, 1965; Hoffmann, 1994].

As a result of the detrimental effects related to the presence of impurities, the chemical composition of copper sold on the market is controlled to certain maximum values. Specifications from the American Society for Testing and Materials (ASTM) for cathode copper are given in Table 2.1. as an example. It should also be noted that most cathodes are significantly purer than ASTM specifications with less than 20 ppm impurities plus oxygen [Biswas and Davenport, 94]. Many producers try to have their cathode certified by the London Metal Exchange (LME) or Commodity Exchange Incorporated (COMEX) where they are required to meet stringent standards for physical, chemical and physico-chemical specifications. Premiums are also obtained for registered brands [Baboudjian et al., 1995].

Table 2.1. Grade 1, ASTM B115-95 electrolytic copper specifications [ASTM, 1996]

Element	Allowance (ppm)
Selenium	2
Tellurium	2
Bismuth	1.0
<i>Group Total</i>	<i>3</i>
Antimony	4
Lead	5
Arsenic	5
Iron	10
Nickel	10
Tin	5
Sulphur	15
Silver	25
Allowable Total	65

CHAPTER 3

METHODOLOGY

Data gathering consisted of industrial visits, consultations with specialists as well as an extensive review of the information published both related to fundamental of minor element behavior and industrial practices. This approach was chosen to obtain an up-to-date portrait of minor element control. The different components of the methodology employed are described below.

Literature Review:

The literature on minor elements' fundamental research and industrial control is abundant. It contains valuable information such as experimental results, computer simulations, industrial distributions, and description of removal technologies. On the other hand, the information is often presented fragmentally, i.e., specific to a unique element or unit operation. In addition, except for few exceptions, there is a general lack in the literature for relative comparison of industrial minor element distributions and control practices. It is an objective of this thesis to regroup the information on As, Sb, Bi, Pb and Ni and compare industrial distributions scattered in the literature with those gathered from industrial visits.

Search engines (METADEX and SCIFINDER SCHOLAR) have been used to identify related literature. In terms of presentation, it should be noted that there is no dedicated section for literature review as the information is presented throughout the thesis when related. For the convenience of the reader interested in obtaining more information on a specific subject, Appendix B presents the references classified by chapter/section treated in the thesis.

Consultations with experts:

Various academic research groups, consultants and industrial research centers were visited as part of this work to identify and analyze key concepts related to minor elements in the copper industry. Table 3.1. presents a summary of consultations undertaken.

Table 3.1. Summary of consultations with experts performed in this project

Name	Key subject discussed
Noranda Inc. – NTC	Thermodynamics
Falconbridge – FTC	M.E. in the copper circuit of Ni production
CODELCO – IM2	M.E. challenges for the Chilean industry
SUMITOMO – Research Institute	Sumitomo past and present experience with M.E.
Kvaerner Metals	M.E. considerations in the design of a smelter
CADE-IDEPE	M.E. projects with Chilean copper industry
McGill University	Vacuum refining
University of Utah	Thermodynamics
University of Arizona	Thermodynamics
Universidad Catolica del Norte	Hydrometallurgical processing
Universidad de Santiago de Chile	M.E. in electrorefining
Universidad de Chile	Soda fluxing
Tohoku University	Thermodynamics
IWATE University	Thermodynamics
Nagoya University	Thermodynamics

Industrial visits/consultations:

Data collection for minor element behavior was carried out throughout industrial visits. In the visits, discussions with technical and process engineers permitted the author to learn about the problematic of minor elements in the industry. In addition, consultations were critical to develop the analysis of removal techniques in smelters and refineries presented in Chapter 6. Table 3.2. summarizes the industrial visits/consultations performed during this project.

Table 3.2. Industrial visits/consultations performed in this project

	Smelter	Refinery
Noranda – Horne	X	
Noranda – CCR		X
INCO – Copper Cliff	X	X
Falconbridge – Sudbury	X	
Falconbridge – Kidd Creek	X	X
Stelco – Lake Erie Works	Vacuum Degasser*	
Kennecott Utah Copper Corporation	X	X
Cyprus Miami Mining Corporation	X	X
ASARCO – Hayden	X	
Phelps Dodge – Hidalgo	X	
Phelps Dodge – Chino	X	
Mexicana de Cobre – La Caridad	X	X
CODELCO – El Teniente	X	
Disputa – Chagres	X	
ENAMI – Las Ventanas	X	X
CODELCO – Chuquicamata	X	
Noranda – Altonorte	X	
CODELCO – Potrerillos	X	X
ENAMI – Hernan Videla Lira	X	
DOWA – Kosaka	X	X
MITSUBISHI/DOWA – Onahama	X	X
MITSUI – Tamano	X	X
MITSUBISHI – Naoshima	X	X
SUMITOMO – Toyo and Niihama refinery	X	X
NMM – Saganoseki	X	X

*Steel producer was visited to see industrial equipment for vacuum metallurgy as it is included in Chapter 6.

PRIVACY OF DATA COLLECTED:

Because this thesis is in the public domain, privacy was a significant issue in data gathering. In the competitive world of copper production, minor element is usually not an open subject of discussion. To respect the desire of companies not to have sensitive information published, the compromise was to obtain raw information from them and publish only calculated ratios. Without this agreement, very little data would have been obtained. The present objectives can be fulfilled nevertheless with calculated ratios as they are useful tools to discuss of minor element behavior.

CHOICE OF INDUSTRIAL/EXPERT VISITED

The producers and experts visited were selected to acquire as much data and knowledge on minor element behavior and treatment in the copper industry given the limited timeframe and budget of this work. It is recognized that other regions of the world such as Europe and Australia have an expertise in this field but consultation in these regions were not possible for the above reasons.

CHAPTER 4

BEHAVIOR IN COPPER SMELTING

The behavior of minor elements in copper smelting has been the subject of much experimental and industrial research in the last century. With the advancement of scientific knowledge as well as the development of sophisticated analytical tools, a better understanding of the key parameters affecting the minor element distributions became possible.

In this chapter, the behavior of As, Sb, Bi, Pb and Ni in copper smelting is discussed. General considerations such as the form (i.e., species or ions) of the minor elements in concentrates, matte, slag, and anode copper are presented at the beginning of the chapter. Following this, the behavior of minor elements with changes in various operating parameters is discussed. When possible, theoretical influence of these parameters, described in the literature, is validated with industrial data.

The discussion in this chapter includes all five minor elements (As, Sb, Bi, Pb, Ni). When volatilization is evaluated, Ni is left outside as its elimination in the gas phase is negligible. However, the literature and industry usually focus only on one or two of these elements at the time. Smelters have representative data related only for the elements which are problematic in their system. The same situation applies to the literature as the research is often financed by the industry to solve a specific problem. As a consequence, it is sometimes difficult to develop a complete description for all elements. In general, the literature and the industry are more concerned with As, Sb and Bi than with Pb and Ni as the former have been more problematic in the last few decades.

Thermodynamics can be used to predict and/or explain minor element behavior in copper smelting. The use of these equilibrium sciences requires that numerous assumptions be taken. The most significant is to assume that chemical equilibrium conditions are prevailing. In modern copper smelting processes, this assumption can be taken with reasonable confidence due to the high operating temperature and large turbulence that promotes fast process kinetics.

4.1. FORMS OF MINOR ELEMENTS IN COPPER SMELTING PHASES

4.1.1. MINOR ELEMENTS IN THE CONCENTRATES

Minor elements are usually present as sulfides in copper concentrates according to the structure of the ore deposit. Frequently occurring mineralogical species of As, Sb, Bi, Pb, and Ni in copper concentrates are presented in Table 4.1. Outside of these major species, minor elements can also be introduced in the elemental form or in various oxides with the concentrate or secondary materials treated in the smelter.

Table 4.1. Common mineralogical forms of As, Sb, Bi, Pb and Ni in copper concentrates

Arsenic		Antimony		Bismuth	
Arsenopyrite	FeAsS	Tetrahedrite	$(\text{Cu,Fe})_{12}\text{Sb}_4\text{S}_{13}$	Wittichenite	Cu_3BiS_3
Enargite	Cu_3AsS_4	Famatinite	Cu_3SbS_4	Emplectite	CuBiS_2
Lautite	CuAsS	Chalcostibite	CuSbS_2	Aikinite	PbCuBiS_3
Tennantite	$(\text{Cu,Fe})_{12}\text{As}_4\text{S}_{13}$	Polybasite	$(\text{Ag,Cu})_{16}\text{Sb}_2\text{S}_{11}$	Bismuthinite	Bi_2S_3
Pearceite	$(\text{Ag,Cu})_{16}\text{As}_2\text{S}_{11}$	Stibinite	Sb_2S_3	Tetradymite	$\text{Bi}_2\text{Te}_2\text{S}$
Cobalite	CoAsS	Pyrargyrite	Ag_3SbS_3		
Lead		Nickel			
	Galena	PbS	Pentlandite	$(\text{Fe,Ni})_9\text{S}_8$	
	Jordanite	$\text{Pb}_{14}\text{As}_6\text{S}_{23}$	Heazlewoodite	Ni_3S_2	
	Cosalite	$\text{Pb}_2\text{Bi}_2\text{S}_5$	Millerite	NiS	

4.1.2. MINOR ELEMENTS IN COPPER MATTE

The composition of industrial copper matte is very close to the Cu_2S -FeS line across the ternary Cu-S-Fe system often leading to the misconception that copper matte is covalently bounded. Thermodynamic behavior of high grade (%Cu) molten copper matte is better explained by ionic melt theory. The ionic theory was used with success to explain laboratory and industrial observations in modern copper smelting systems [Roine and Jalkanen, 1985]. This postulate will be assumed for the present discussion. In practice, it seems like copper matte has a mixed behavior (covalent and ionic) but phenomena related to minor element distributions are better explained with the ionic theory.

In the ionic theory, a structural representation of molten copper matte as a complex ionic network consisting of large S^{2-} ions and small Cu^+ and Fe^{2+} ions has been adopted. Figure 4.1. is a comparative representation of the ionic sizes of major constituents in copper matte at different valences.

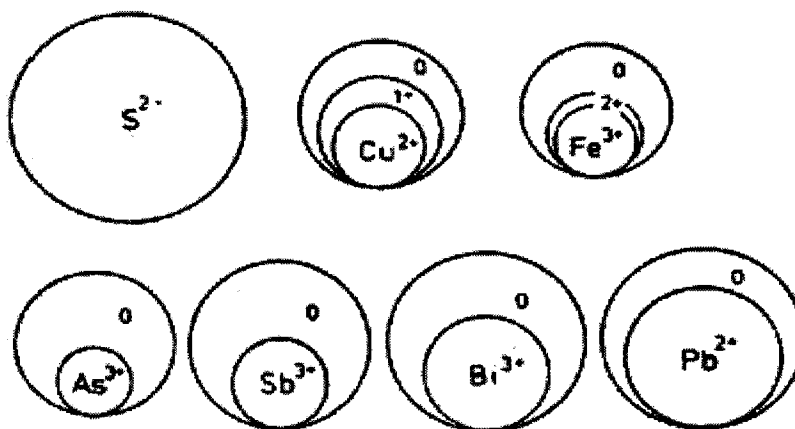


Figure 4.1. The effect of valence on ionic sizes reproduced from Roine and Jalkanen, 1985

For high grade matte similar to the operation of most modern industrial smelting furnaces, arsenic and antimony are believed to exist mainly in the molecular state in copper matte [Roine and Jalkanen, 1985]. Due to the relatively large size (Figure 4.1) of these molecules compared with Cu^+ and Fe^{2+} ions, they should substitute for S^{2-} ions in the melt.

The state of bismuth in copper matte has not been clearly identified in the literature and is believed to depend on the nature of the smelting system as follows. Under oxidizing conditions (low sulphur partial pressure) as observed in modern copper smelting systems, Bi is most likely present in the molecular state. This phenomena can be explained from the interpretation of the author by the hypothesis that the fewer sulfur ions (higher p_{O_2}) would preferentially bound with Cu^+ and Fe^{2+} ions leaving less to stabilize Bi^{3+} . Comparable sizes of molecular bismuth permit the substitution for sulphur in the ionic melt. In fact, a mixed behavior is more realistic (Bi and Bi^{3+} ions) from which the predominance of Bi and Bi^{3+} ions would be determined by the sulfur and oxygen partial pressures. Under oxidizing conditions (e.g. Noranda reactor, flash furnaces, etc.), the molecular state is dominant and the Bi^{3+} ions prevalence is believed to increase in vessels with a high sulphur partial pressure (e.g., reverberatory furnace).

For lead, it was found that Pb^{2+} ions are more stable than molecular Pb in the matte smelting system. Because of their positive charges, Pb^{2+} ions substitute for Cu^+ and Fe^{2+} ions in the melt even if significantly larger in size. Similarly, but to a lower extent than Bi, Pb is believed to exist in the molecular state in the molten copper matte under highly oxidizing conditions (low sulphur partial pressure).

Nickel has a similar behavior to copper and Ni^+ ion is the major state of Ni in molten copper matte. Ni^+ ion should substitute for copper and iron ions in the ionic melt.

Often it has been said that lead or nickel are present as PbS or Ni_3S_2 in the molten copper matte. At this point, a parenthesis should be opened to clarify terminology which have been used. Strictly speaking, the sentence above does not have the same meaning as having Pb^{2+} and Ni^+ ions in the molten melt. However, for convenience and simplicity, it is often used in industry and even in the research with the same meaning.

In the copper smelting flowsheet, the ionic description of the melt is valid both for high grade matte smelting and the first stage of copper converting ('slag blow'). The behavior of minor elements during the 'slag blow' where residual Fe is oxidized can be described as a matte approaching white metal (apparent Cu_2S) composition. It is similar to matte smelting with gradually increasing $p\text{O}_2$ and decreasing $p\text{S}_2$. Therefore, molecular Pb and Bi will gradually replace Pb^{2+} and Bi^{2+} (if present) ions in the melt as the 'slag blow' proceeds. Once all Fe has been eliminated and only white metal (Cu_2S) is present the oxygen partial pressure of the system increases and solubility of the minor element oxides in the white metal is also believed to be significant. The solubility of oxides in high grade copper matte is thought to be in the form of covalently bonded oxides which would be 'physically dissolved' [Flengas, 1973].

4.1.3. MINOR ELEMENTS IN COPPER

As soon as the Cu-Fe-S melt, undergoing oxidation converting, reaches about 1% Fe (i.e. ~ 77-78% Cu), metallic copper starts to precipitate. The electronic structure of this copper is drastically different from copper matte. The matte has an ionic structure while the copper has a metallic structure. In the copper melt, all minor elements are believed to exist in the metallic state, i.e., molecular state, to integrate the metallic matrix.

Table 4.2. shows numerical values of the activity coefficient of minor elements in copper and matte after the work of Kim and Sohn, 1998, and Nagamori and Chaubal, 1982. The smaller the

activity coefficient is, the stronger the bounding forces between the element and the melt are (increased stability). Numerical values confirms the greater stability of all elements but Pb in matte than in metallic copper. The exceptional behavior of lead is probably due to the fact that Pb^{2+} ion is very stable in copper matte.

In practice, it means that as soon as metallic copper appears in the process at the end of the 'slag blow' or in continuous converting operations, it will act as a sink for As, Sb, Bi and Ni because of the high stability of the metallic bonds in comparison with the attractions of the ionic matte melt.

Table 4.2. Raoultian activity coefficients in dilute solutions at 1523 K (calculated from expressions given for matte by Kim and Sohn, 1998 and Nagamori and Chaubal, 1982)

Substance	$\gamma_i^0(\text{matte})^*$	$\gamma_I^0(\text{copper})$
As	0.71	0.0007
Sb	2.8	0.02
Bi	12.3	2.3
Pb	1.85	4.9
Ni	4.06	2.5

* Values were calculated corresponding to a matte grade of 65% Cu

4.1.4. MINOR ELEMENTS IN SLAG

For copper matte smelting and copper converting, the slag phase is mainly ionic, i.e., made up of cations and anions. In the matte smelting furnace, the slag largely consists of iron cations and silica connected anionic rings [Biswas and Davenport, 1994]. This slag which has an apparent composition around $2 \text{ FeO} \cdot \text{SiO}_2$ is also called fayalite slag from the name of this specie. For converting, both the fayalite system and calcium ferrite (mainly for continuous converting) are used. More details are given later in this chapter on the influence of slag type on minor element distributions (Section 4.2.5).

The dominant mechanism by which minor elements are transferred to the slag phase is oxidation. Equations 4.1. and 4.2 are the overall and observable reactions. In reality, it is a combination of multiple chemical reactions that can involve intermediate species such as copper oxide,

magnetite, copper (matte smelting), and other minor element oxides formed locally in the reaction zone.

$$M_{(concentrate / matte / blister)} + \frac{y}{2} O_{2(gas)} = MO_{y(slag)} \quad 4.1.$$

$$MS_{x(concentrate / matte)} + \frac{y}{2} O_{2(gas)} = MO_{(y-2x)(slag)} + xSO_{2(gas)} \quad 4.2.$$

Metallic or sulfidic species can also report to the slag due to the limited physical solubility of these forms of the minor elements or by mechanical entrapment of matte or blister in the slag. Entrapment is not negligible as it can account for more than 25% of the presence of minor elements to slag in industrial smelting and converting furnaces. This phenomena is greatly affected by the degree of turbulence of the process resulting from the design and operation of the furnace. Nagamori and Mackey, 1978, have proposed a correction to the distribution coefficients considering the suspensions in the case of the Noranda Process Reactor. Their correction is an engineering approach specific to the design of the Noranda Reactor not really related to fundamental or thermodynamic. In the present work, this correction parameter will not be used as distribution coefficients in several smelting technologies are evaluated without enough information to compute an appropriate value for every type of furnace. To determine the value of this correction parameter, the thermodynamic conditions of the furnace have to be precisely simulated in the laboratory where quiescent equilibrium between matte (or metallic phase) and slag can be obtained. It is also possible to evaluate the level of mechanical entrapment by a microscopic analysis of the slag.

4.1.5. MINOR ELEMENT REMOVAL TO GAS

Transfer of minor elements to the gas phase is possible via vaporization of metallic, sulfidic or oxidic species. Removal to gas is a simple process involving mass transfer of a specie from the melt to the gas phase. Thermodynamics can be used to quantify the potential of a specie to evaporate. The potential for transfer of the species to the gas phase is directly proportional to the vapor pressure of the species in the melt evaluated as follows*:

$$p_i = \gamma_i x_i P_i^o \quad 4.3.$$

* It is assumed that only the monoatomic metallic form and the dimeric form of the sulfidic or oxidic form evaporates
[Allaire and Harris, 1989]

where i is the metallic, sulfidic or oxidic form of the minor element, γ_i is Raoultian activity coefficient of i in the phase of interest (matte or copper) and P_i^o is the vapor pressure of pure i .

The potential to lower the concentration of minor elements by volatilization in a bulk solution depends upon the relative volatility of the minor elements with respect to the bulk phase. Olette, 1961, expressed this relative volatility with the volatilization coefficient and criterion for refining following this inequality:

$$\phi_i = \frac{\gamma_i P_i^o}{P_B^o} \left[\frac{MW_B}{MW_i} \right]^{1/2} \geq 1 \quad 4.4.$$

where i is the specie to be separate from specie b , MW_i and MW_b are the molecular weights and P_i^o and P_B^o are the vapor pressure of the specie of interest and the bulk specie, respectively.

For numerical simulations, kinetics including mass transfer coefficients and the dynamic change in composition have to be used (differential equations). This discussion is beyond the scope of the present work. Examples of numerical simulations for copper smelting and converting exist in the literature [Chaubal et al., 1989; Kylo and Richards, 1998].

For a given element, taking the P_M^o to be the total vapor pressure of all species of M and assuming ideal gas law is valid, the concentration (units depend on the gas constant used) in the gas phase (R) can be represented by:

$$C_{M(gas)} = \frac{(x_M)(\gamma_M)(P_M^o)}{RT} \quad 4.5.$$

It can be observed that the 'driving force' for minor element volatilization is not only a function of the vapor pressure of the pure substance but also depends on the solution thermodynamics. The influence of solution thermodynamics is represented by the activity coefficient term. As an example, lower activity coefficient of arsenic in copper than in matte (Table 4.2) can explain the to a large extent the higher volatilization during matte smelting as compared to during the 'copper blow'.

Vapor pressures of pure solids and liquids depend on temperature and numerical correlation can be found in Section 4.2.6.3. or in the literature [Nagamori and Chaubal, 1982; Chaubal et al., 1989; Kim and Sohn, 1991; Kylo and Richards, 1998].

The composition of dust collected from industrial smelting furnaces is usually not a good indication of the species volatilized. This is because high temperature oxidation with oxygen from infiltrated air occurs in the furnace off-gas system to produce mainly sulfates and oxides collected in the dust collecting devices

In smelting vessels like the Noranda Reactor (feed from slinger), Mitsubishi S-Furnace and reverberatory furnaces, volatilization of a part of the impurity as sulfide directly from the concentrate is possible. This is due to a partial roasting (heating of the concentrate temporarily suspended in a low oxygen environment) above the bath as a result of contact between the concentrate and gas phases at high temperature prior to melting. Flash or injection vessels do not permit this partial roasting as melting and reactions are almost instantaneous. More importantly, the concentrate in these furnace is not submitted to low oxygen environment at high temperature because the oxidant is supplied in the immediate vicinity of the concentrate.

4.2. PARTITIONS AND DISTRIBUTIONS OF MINOR ELEMENTS IN MATTE SMELTING

The removal of impurities in copper smelting can only be carried out by transfer to the slag and gas phases. The total elimination (or recovery) of an element depends to some extent on the operating practices with respect to slag processing, off-gas capture, dust treatment, and special removal treatments used (Chapter 6).

However, the elimination of minor elements can be significantly influenced by the operating conditions prevailing in pyrometallurgical furnaces. All copper smelters have developed their own optimum set of operating parameters. This leads to different minor element distributions. The objective of this section is to discuss the effects of selected operating parameters on theoretical and industrial (when possible) minor element behavior.

Definition of parameters used for evaluation

Two distinct approaches have been used to quantify the distribution of minor elements in a smelting furnace, the partition and distribution coefficients.

Partition coefficient:

The partition is the fraction of an element in a given phase based on the total input. It can be defined as:

$$P_M^{\text{phase } j} = \frac{\text{mass } M \text{ in phase } j}{\text{mass } M \text{ in input}} = \frac{(\text{wt } \% M)_j (\text{mass phase } j)}{(\text{wt } \% M)_{\text{input}} (\text{mass input})} \quad 4.6.$$

where the partition is evaluated for phase j (e.g., matte, copper, slag or gas) and $M = \text{As, Sb, Bi, Pb, Ni}$ in the present thesis. Its use is often referred to as an engineering approach to look at minor element distributions. On the other hand, it does not relate easily to thermodynamics and for that, the distribution coefficient is a better tool.

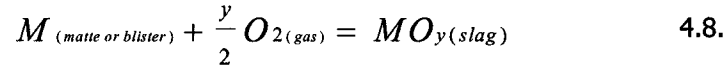
Distribution coefficient:

Distribution coefficient is the ratio of metal composition between two phases at equilibrium.

$$D_M^{i/j} = \frac{(\text{wt } \% M)_{\text{phase } i}}{(\text{wt } \% M)_{\text{phase } j}} \quad 4.7.$$

where i, j are matte, copper, slag, metal, gas in the copper smelting system and $M = \text{As, Sb, Bi, Pb, Ni}$ in the present work.

For a discussion on equilibrium systems such as matte/slag or copper/slag, the distribution coefficient is more precise than the partition coefficient as it relates to the thermodynamics of the system. As an example, consider the following equilibrium for minor element M between matte or copper and slag:



The equilibrium constant (K_T) at temperature T is given by:

$$K_T = \frac{(a_{MO_y})_{slag}}{(a_M)_{matte\ or\ blister} (pO_2)^{y/2}} \quad 4.9.$$

where 'a' stands for the activity of the specie and ' p_{O_2} ' is the oxygen partial pressure at the matte/slag interface. By definition the activity of the specie M is given by:

$$a_M = (\gamma_M)(x_M) \quad 4.10.$$

and the mole fraction can be transformed to mass fraction by:

$$x_M^i = \frac{(\text{mole } M)_i}{\text{mole } i} = \frac{\frac{(\text{mass } M)_i}{MW_M}}{\frac{(\text{mass } i)}{MW_i}} \approx \frac{(\text{wt } \% M)_i MW_i}{(100)MW_M} \quad 4.11.$$

The distribution ratio $D_M^{\text{matte or copper/slag}}$ (which means it can be used either for matte/slag or copper slag equilibrium) for an element M can be derived by combining Equations 4.9, 4.10 and 4.11 (also note that $[\%M]_{slag} = [\%MO]_{slag} * MW_M/MW_{MO}$):

$$D_M^{\text{matte, copper/slag}} = \frac{1}{(K_T)(pO_2)^{y/2}} \left(\frac{\gamma_{MO}}{\gamma_M} \right) \left(\frac{MW_{slag}}{MW_{matte, copper}} \right) \quad 4.12.$$

At a given temperature, K_T of the reaction is fixed and known. Therefore, this ratio varies only with the oxygen partial pressure and activity coefficients for a given matte and slag system. If these are constant, the distribution coefficient should be fixed. In matte smelting, the activity coefficient of the element in the slag is determined by the chemistry of the slag (e.g., type, Fe/SiO₂, etc.). On the other hand, for a given system, the oxygen partial pressure and activity

coefficient in the matte depends on operating parameters such as oxygen enrichment and matte grade.

It can be seen that the distribution coefficients are not affected by external factors such as the mass of slag and matte as the partition coefficients might be (Equation 4.6). To illustrate this phenomena, consider the example of a decrease in the concentrate copper grade for a given furnace. As a result, the amount of slag will be increased and amount of matte decreased for the same feed throughput. The minor element equilibrium between matte and slag would be thermodynamically readjusted to maintain chemical equilibrium in the furnace. By keeping all other parameters identical, the partition coefficients $P'_M{}^{\text{matte}}$ and $P'_M{}^{\text{slag}}$ after the change would be significantly different from $P_M{}^{\text{matte}}$ and $P_M{}^{\text{slag}}$ before the decrease in concentrate grade because of the change in matte and slag tonnage. On the other hand, the $D_M{}^{\text{matte/slag}}$ would not be affected unless melt chemistry, i.e., thermodynamics changed. This is a hypothetical example as often, if the concentrate grade changes, other operating parameters (blowing, oxygen enrichment, fuel ratio) would also be adjusted as a response to compensate for a change in the heat balance. However, it is found that, in general, the effect would be less noticeable on the distribution coefficients than on the partition coefficients. Thus, distribution coefficient should always be used when possible to evaluate the impact of process variables on minor element elimination.

In theory, the distribution coefficients could be used to evaluate the equilibrium between a metal phase and the gas. However, in copper smelting, the composition of off-gas in equilibrium with the slag and matte is practically impossible to be obtained. The use of partition coefficient is more convenient when dealing with the gas. In practice, the partition coefficient to gas can be calculated by the difference from total feed of a given element (including internal recirculations) and fraction reporting to matte and slag for which more precise estimate of weight and chemical assays are available. Partition to the gas phase can also be estimated and/or confirmed from the mass and assay of the dust and by gas sampling of the ducts.

In this work, the distribution coefficients will be used to describe the matte/slag and copper/slag equilibrium whereas the partition coefficients will be used to quantify minor element volatilization.

Transformation between partition and distribution coefficients in matte smelting:

For the matte smelting three-phase equilibrium (matte, slag and gas) the partition coefficients can be transformed to a distribution coefficient if the relative masses of the two molten phases is known. The formula is obtained by combining Equations 4.6 and 4.7:

$$D_M^{matte/slag} = \frac{P_M^{matte}}{P_M^{slag}} (\text{mass slag} / \text{mass matte}) \quad 4.13.$$

By definition, the sum of partition coefficients is equal to unity. For the matte smelting furnace, it can be written as:

$$P_M^{matte} + P_M^{slag} + P_M^{gas} = 1 \quad 4.14.$$

If the partition to gas (P_M^{gas}) is known or assumed and slag and matte assays are available, it is possible to obtain partition to matte. The following equation is found by combining Equation 4.13 and 4.14:

$$P_M^{matte} = \frac{D_M^{matte/slag} (1 - P_M^{gas})}{(D_M^{matte/slag} + \frac{\text{mass slag}}{\text{mass matte}})} \quad 4.15.$$

The P_M^{slag} can be calculated using Equation 4.13. when P_M^{matte} and P_M^{gas} are known.

4.2.1. DISCUSSION OF THE RESULTS

As described in Chapter 3 - Methodology, several copper producers were visited as part of data collection. The distribution and partition coefficients for As, Sb, Bi, Pb, Ni for matte smelting furnaces over various parameters are presented in a table format in **Appendix A**. The blanks in the table of results indicate that no value was collected. Often, in a smelter visit, the data for only few elements were available. This is especially true for Ni for which only few data was supplied. Values collected from literature are also reported with their source.

Data were rarely given as partition and distribution coefficients. In most cases, raw tonnage of feed to furnace (often blended concentrates, which includes secondary and recycled materials and flux), matte, and slag were given with typical chemical assays for these streams. Because this is proprietary information for many smelters, it was transformed to partition and distribution coefficients and only these ratios are published. Equations 4.13 and 4.15 were used for the purpose of transforming the data. P_M^{gas} was usually calculated by difference from the feed information given. In certain circumstances, it was also given by the smelter.

Assays in the blended feed to furnace are used for plotting graphs ($D_M^{matte/slag}$ and P_M^{gas} versus wt% M in feed) in this thesis. However, numerical values are not given in Appendix A as it was a sensitive issue for some smelters. Typical anode assays are also shown in the same table.

As part of the industrial visits, partitions and distribution coefficients in copper converting were also sought. Unfortunately, limited data was collected for converting. It can be understood as in most cases, batch converting is used where partition and distribution coefficients change dynamically with the progression of cycle. Also, it is common in industry to have the converting cycles changed as a response to the events happening on a given day which also change the partition coefficients. Moreover, the smelters usually do not have all assays and tonnage of intermediate phases to compute the distribution coefficients. Consequently, data for converting are not included in the Table of Results in Appendix A.

PRECISION AND REPRODUCIBILITY OF $D_M^{i/j}$ AND P_M^i FROM INDUSTRIAL VALUES

A comment is necessary on the precision and reproducibility of data. From the upcoming graphs plotted with industrial data, a large scatter was obtained in $D_M^{i/j}$ and P_M^i values. A part of this scatter is certainly due to the level of precision of the data gathered. However, it is the opinion of the author that most of the scatter is due to variations in operating parameters of the furnaces all included on the same graph. In an ideal situation, only smelters operating within a certain range of various operating parameters would have been placed on the same graph to confirm the last statement. This approach was not possible given the number of operating parameters having an effect on minor element distribution and the limited number of smelters surveyed.

The $D_M^{i/j}$ is generally calculated from raw assays of the different phases given at the smelter. When possible, averaged values over long periods of time (e.g., yearly composites) were sought to reduce the error from only a single assay of both phases. Analytical methods used for the chemical assay and representativity of the samples are potential source of errors. The effect of analytical error is especially important at low values (e.g., 0.001%) which were common (e.g., for As and Bi in slag). In addition to the greater impact of small imprecision at these low levels, the analytical equipment was probably close to its detection limit where the level of precision is reduced. Because a ratio is used, the effect of a drift in the reading of the analytical equipment would be lowered given that both samples are analyzed using the same equipment.

On the other hand, the P_M^i was mostly calculated by difference and a larger uncertainty exists. There is a potential error in the tonnage and assays of feed, matte and slag given at the smelter. This is mainly true for matte and slag tonnage as approximates (e.g., # of ladles per day * average weight per ladles) were often best values available. This uncertainty is lowered for smelters having weighting devices on their cranes. The analytical error discussed above is also to be considered for calculated P_M^i values.

Obviously, it would have been excellent to compare the reproducibility of data by comparing a few smelters with the same operating conditions but it was not possible. As part of this limited M.Eng. project, it was not possible to perform an evaluation of the precision of each laboratory from which assays were obtained and to force the smelters to validate weight given for calculation of partition coefficients. The author recognizes that an inherent error might be associated with data presented which is probably higher than for a typical laboratory project but the best available data from industry were used.

A comment that came across often in my discussions about the project is the possibility of obtaining false information given on-purpose by the companies because of the sensibility of the subject for the business. It is a possibility which cannot be totally eliminated but the collaboration from the industry was outstanding and there is no reason to believe that false information was given to mislead the conclusions of the project.

4.2.2. EFFECT OF MATTE GRADE

Increased productivity motivates the industry to operate at high matte grade (weight % Cu in matte). Besides the benefits of the use of high matte grade on productivity, other effects should be considered such as minor element behavior. Industrially, Noranda pioneered the evaluation of minor element behavior at different matte grades as part of their evaluation of the performance of the Noranda Process Reactor [Mackey et al., 1975, Persson, et al., 1986]. Later, experiments and numerical simulations permitted a better understanding of the behavior of minor elements as a function of matte grade [c.f. Appendix B for related literature].

Effect of matte grade on $D_M^{\text{matte/slag}}$

$D_M^{\text{matte/slag}}$ values for As, Sb, Bi, Pb, and Ni collected from industrial visits and literature are plotted against matte grade (% Cu) in Figure 4.2. It should be reminded that the limited size of the population were forced to use data for different types of furnaces and operating conditions (oxygen enrichment, level of minor element in the feed, reducing agent for thermal balance, etc.) on the same graph. This causes the scatter observed.

Nevertheless, clear tendencies can be observed in Figure 4.2. for arsenic, bismuth and lead. $D_{\text{As}}^{\text{matte/slag}}$ increases with matte grade. On the other hand, $D_{\text{Bi}}^{\text{matte/slag}}$ and $D_{\text{Pb}}^{\text{matte/slag}}$ decrease. $D_{\text{Sb}}^{\text{matte/slag}}$ is not greatly affected by matte grade although it is slightly lower at high matte grades. Finally for nickel, the scatter does not permit identification of a clear trend for industrial results.

Theoretically, the effect of matte grade on the matte/slag equilibrium in a matte smelting furnace can be discussed in terms of Equation 4.12., presented earlier.

$$D_M^{\text{matte,copper/slag}} = \frac{1}{(K_T)(pO_2)^{y/2}} \left(\frac{\gamma_{MO}}{\gamma_M} \right) \left(\frac{MW_{slag}}{MW_{matte,copper}} \right) \quad 4.12.$$

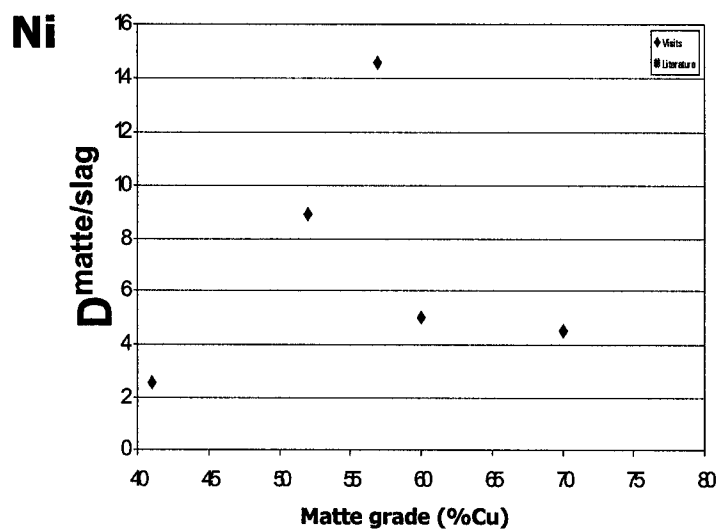
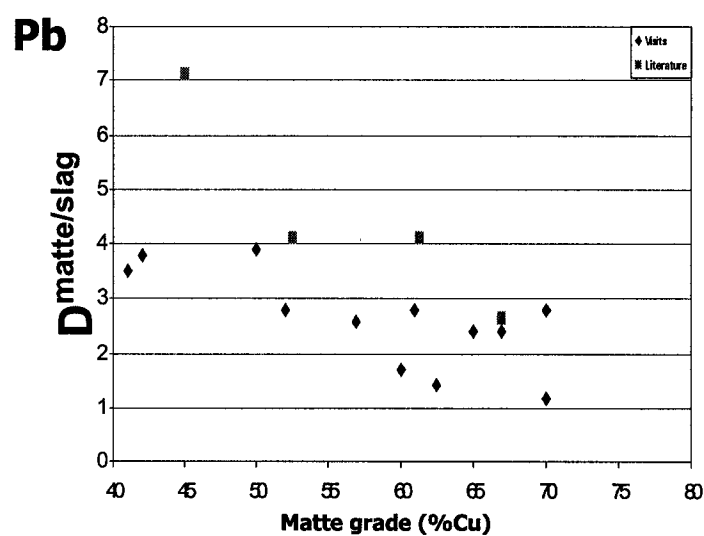
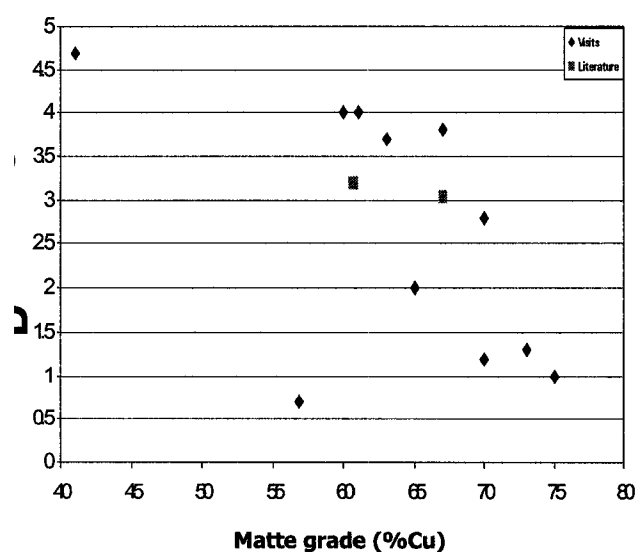
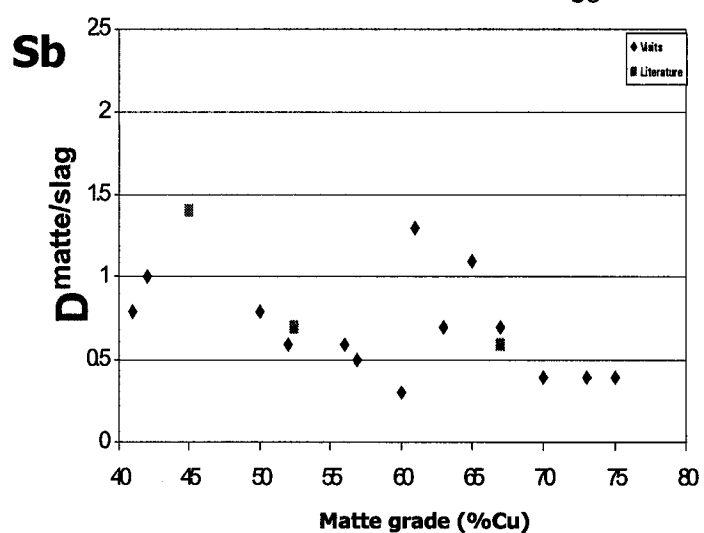
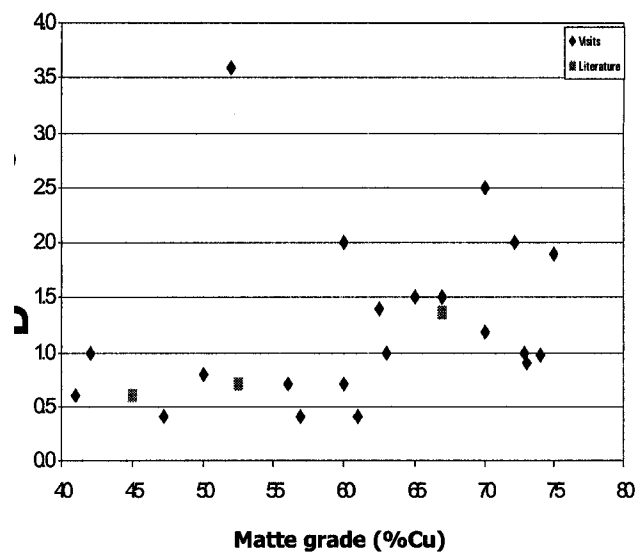
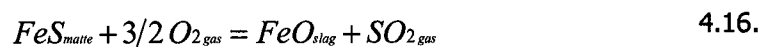


Figure 4.2. Effect of matte grade on distribution coefficient

The oxygen partial pressure at the reaction interface and γ_M in matte are the main variables affected by the matte grade in Equation 4.12. K_T is fixed at a certain temperature and γ_{MO} is specified by the slag system used. For all data plotted in Figure 4.2, the fayalite slag system was used. The effect of minor constituents and Fe/SiO₂ ratio on activity coefficient in slag (γ_{MO}) implies a secondary effect which is beyond the scope of this work.

The oxygen partial pressure in the matte smelting system is set by the FeS/FeO equilibrium:



The equilibrium constant of Equation 4.16 is:

$$K_T = \frac{(a_{FeO})_{slag} (p_{SO_2})}{(a_{FeS})_{matte} (p_{O_2})^{3/2}} \quad 4.17.$$

From Equation 4.17, the oxygen partial pressure (or potential) can be isolated:

$$(p_{O_2}) = \left[\frac{(a_{FeO})_{slag} (p_{SO_2})}{(a_{FeS})_{matte} (K_T)} \right]^{2/3} \quad 4.18.$$

The iron matte grade ($\%Fe$)_{matte} has a direct impact on the oxygen potential of the system via a_{FeS} as observed in Equation 4.18 ($a_{FeS} = \gamma_{FeS(matte)} * [\%Fe * MW_{matte} / MW_{Fe}]$). Iron content in the matte is probably the best indication of oxygen partial pressure as discussed by Sridhar et al. 1997. Nevertheless, the oxidation of the melt is controlled industrially principally with Cu matte grade ($\%Cu$ in matte). It is not as precise as $\% Fe$ but gives a good approximation as copper is the other main metallic element of the melt and its content can be related to iron assuming a Cu₂S-FeS binary melt. The oxygen potential increases with copper matte grade as presented in Figure 4.3.

The use of copper matte grade has limitations to represent oxygen partial pressure in equilibrium with the melt when high levels of minor elements such as Pb and Zn are present along with Cu and Fe in the matte. As an example, a matte grade of 70% with high levels (e.g. >2%) of impurities would probably have the oxygen potential of a matte with a matte grade around 72-73% Cu and no impurity. This is perceivable mainly at high matte grades due to the large change of oxygen partial pressure with matte grade in that region as shown by large steep slope the PO₂ vs $\%Cu_{matte}$ in Figure 4.3. For this reason, some smelters with high levels of these

elements such as Noranda Inc. – Horne smelter, use % Fe for matte grade control. However, iron matte grade was not widely available from the industrial visits and for this reason, copper matte grade is used for the rest of this section.

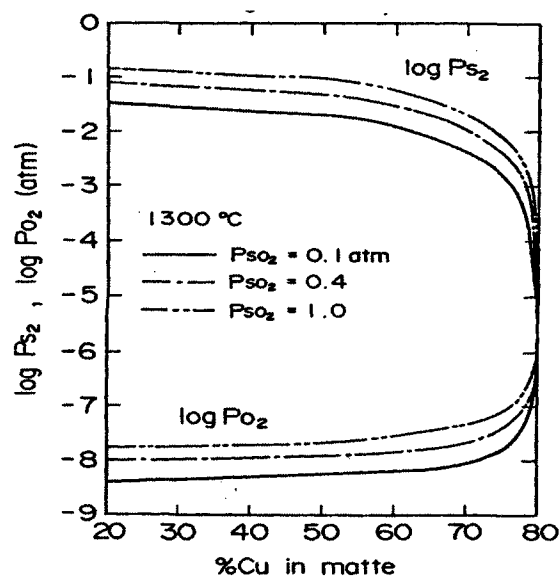


Figure 4.3. Relation between oxygen and sulphur partial pressure and copper content at 1523K reproduced from Itagaki, 1986

The variation in the Henrian activity coefficient of arsenic, antimony and bismuth as a function of matte grade is reproduced from Itagaki in Figure 4.4.

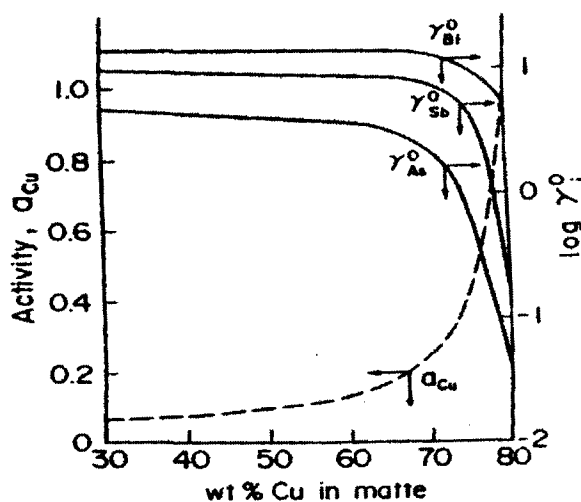


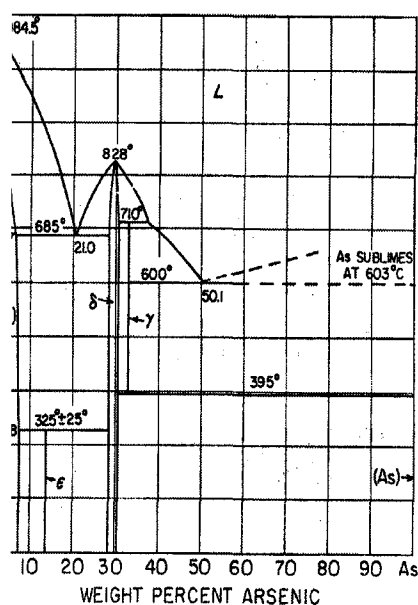
Figure 4.4. Changes in the copper activity and the activity coefficients of arsenic, antimony, and bismuth in matte smelting process from Itagaki and Yazawa, 1983

From Figure 4.4. the Henrian activity coefficients of As, Sb and Bi are roughly constant at matte grades below 60% Cu. Above this value, γ_{As}^0 and γ_{Sb}^0 decrease dramatically as the copper activity (represented by the dashed line) increases. On the other hand, γ_{Bi}^0 is less affected. The greater affinity of As and Sb for copper than Bi underlies this difference.

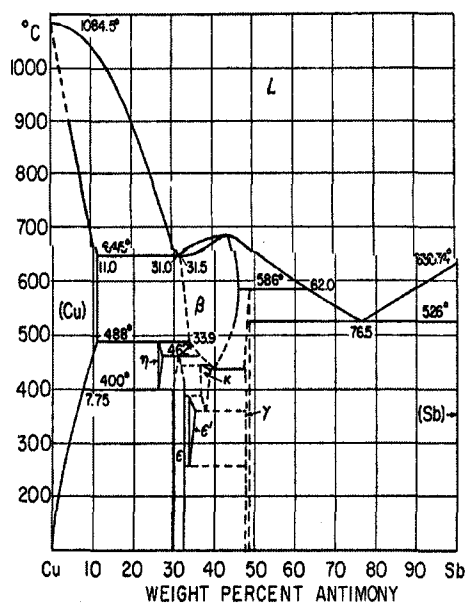
Affinity of an element for Cu can be qualitatively evaluated by looking at the binary phase diagrams. In the low concentration region, the presence of several possible stable phases indicates high affinity existing between two metals. The binary phase diagrams with copper of the minor elements studied are reproduced in Figure 4.5. It can be observed that several stable phases exist for Cu-As and Cu-Sb systems indicating that strong chemical affinity prevails. The opposite is true for Cu-Bi, Cu-Pb and Cu-Ni. From that, it is reasonable to expect that γ_{Pb}^0 and γ_{Ni}^0 will be less affected by the matte grade than γ_{As}^0 and γ_{Sb}^0 . However, as discussed in Sections 4.1.2. and 4.1.3., lead changes from the ionic to the less stable molecular form in matte with increasing oxygen potential. Therefore, an increase in γ_{Pb}^0 at high Cu matte grade can be expected. No thermodynamics data were located to confirm this postulate.

The low impact of matte grade on γ_M^0 for Bi, Pb and Ni, implies that $D_M^{matte/slag}$ should decrease with increasing matte grade because of the dominance of pO_2 in Equation 4.12. This is in accordance with industrial results reported in Figure 4.2. For arsenic, the increase in $D_{As}^{matte/slag}$ is caused by the dominant effect of the decrease in γ_{As}^0 over the increase in oxygen partial pressure. Finally, industrial results show that the effect of these two parameters is roughly balanced for antimony.

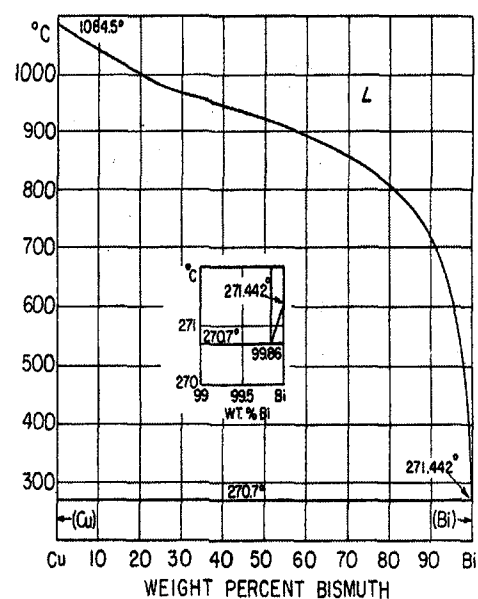
To decrease the noise arising in the comparison of various industrial furnaces, a laboratory evaluation was carried out by Roghani et al., 1997. Their results are reproduced in Figure 4.6. It should be noted that $L_M^{s/m}$ used by Roghani et al. is simply the inverse of $D_M^{matte/slag}$.



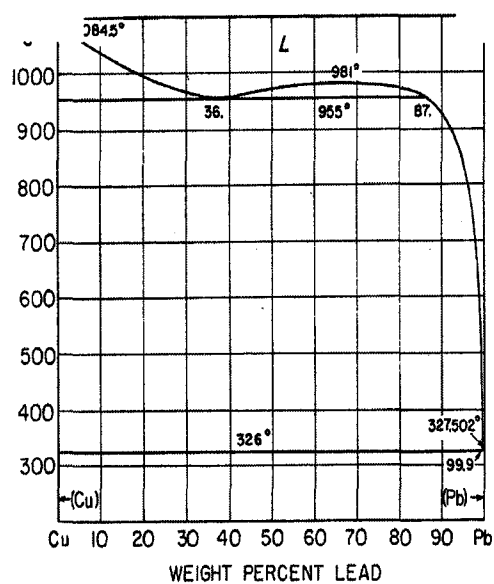
(A)



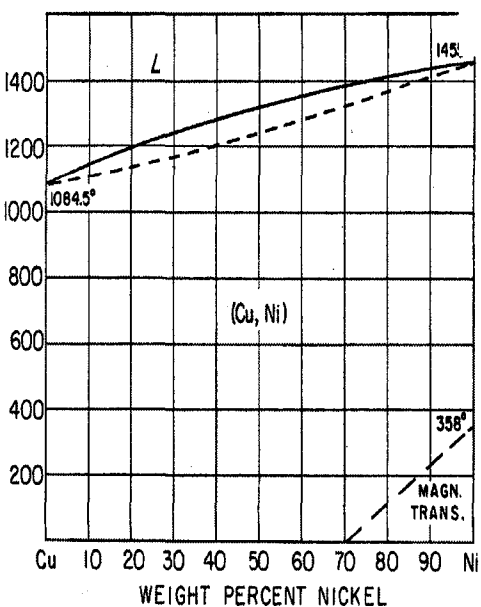
(B)



(C)

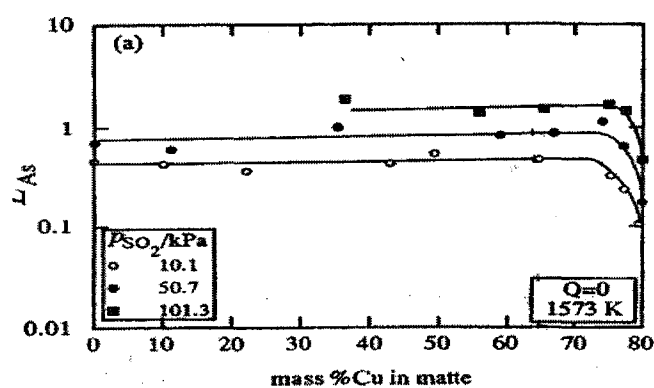


(D)

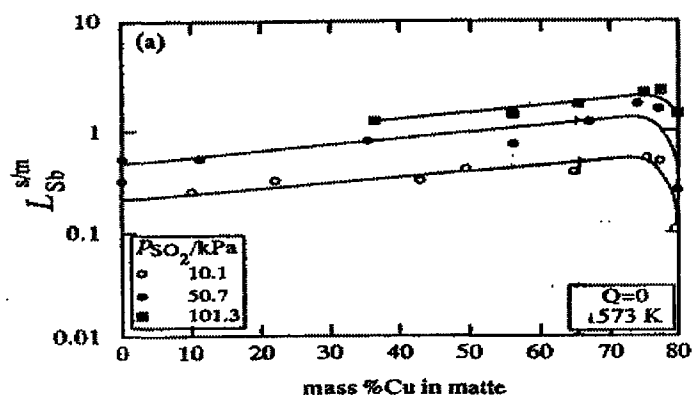


(E)

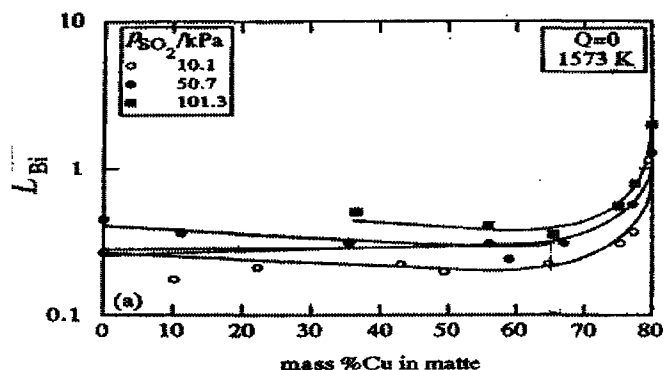
Figure 4.5. Binary phase diagrams Cu-M reproduced from Phase diagrams for ceramists, 1964-83; (A) Cu-As; (B) Cu-Sb; (C) Cu-Bi; (D) Cu-Pb; (E) Cu-Ni



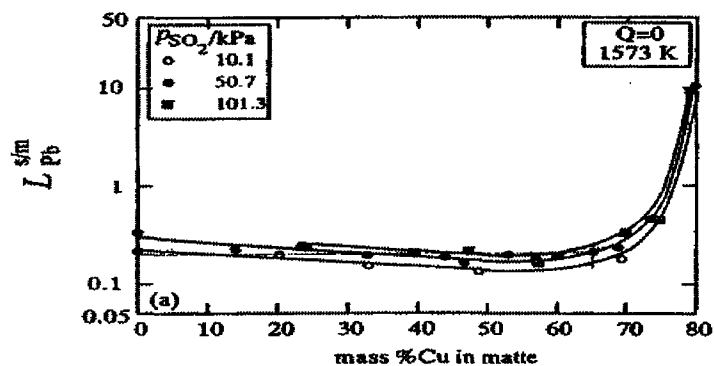
(A)



(B)



(C)



(D)

Figure 4.6. Experimental distribution ratio between slag and matte against matte grade for $\text{SiO}_2\text{-FeO}_x$ slag system at 1573K reproduced from Roghani et al., 1997.

(A) M=As; (B) M=Sb; (C) M=Bi; (D) M= Pb.

Results of Roghani et al. are in general accordance with industrial data presented in Figure 4.2. It should be noted that the sharp decrease in $L^{s/m}$ of antimony at very high matte (78-80% Cu) was reported. However, no industrial matte smelting furnaces operate above 75-77% Cu on a regular basis and thus it is difficult to comment on experimental results in that range. Moreover, except for some reverberatory furnaces operating around 40% Cu in matte, most industrial results are for matte grades greater than 50% Cu and only that portion of the graph in Figure 4.6. should be compared with Figure 4.2.

Effect of matte grade on P_M^{gas}

Figure 4.7 presents the partition of minor elements to the gas phase, P_M^{gas} as a function of matte grade for industrial matte smelting furnaces. For arsenic, between 60% and 80% of the feed is usually volatilized in the smelting furnace. Matte grade has little impact on P_{As}^{gas} . In looking at the graph, low P_{As}^{gas} occurs for some smelters at a matte grade around 60% Cu. Values below 0.5 are for flash smelters (e.g. Hayden, Saganoseki, etc.) characterized by high oxygen enrichment (>50 % O₂ V/V). The effect of oxygen enrichment is discussed in Section 4.2.3.

For antimony, volatilization is usually below 20%. Caletones, Chuquicamata and Miami smelters all have very low levels of antimony and imprecision in the chemical assays probably explains the 50% volatilization of Sb. Bismuth volatilization is usually above 50%. Literature values (■ in Figure 4.7) indicate that the partition to gas decreases at high matte grades. Care must be taken in interpreting these values from literature as they are all for Chilean's Teniente converters in which input levels of bismuth are low and highly sensitive to analytical errors. P_{Pb}^{gas} clearly increases with matte grade. From industrial visits, volatilization around 20% occurred at low matte grades. At high matte grades, volatilization is as high as 35-40%.

The matte grade affects the activity coefficient of the minor elements in Equation 4.5 presented earlier. The partial pressure of pure substances (P_M^0) over the melt will not be affected by a change of matte grade for molecular species ($M_{(g)}$, $M_{2(g)}$, $M_{3(g)}$, $M_{4(g)}$, etc.). For oxide and sulfide species, the volatilization reaction will be affected by the change of sulphur and oxygen partial pressures in the system since the effective vapor pressure of the oxide and sulfide species depends on the partial pressure of oxygen and sulfur that is in effect in the melt. Figure 4.8. reproduced from Itagaki illustrates the effect of matte grade on the partial pressure of selected species of arsenic, antimony and bismuth for a fixed activity of $a_M=0.01$. It should be noted that the effect of the change in γ_M is not included in this graph as the activity is fixed and only the effects of p_{SO_2} , p_{S_2} and p_{O_2} are being represented. The variations in partial pressures are small below 70% Cu in matte. Above this level of Cu in matte, the effect of large increases and decreases in oxygen and sulphur partial pressures, respectively with matte grade (Figure 4.3), are perceptible on the P_M^0 for oxides and sulfides.

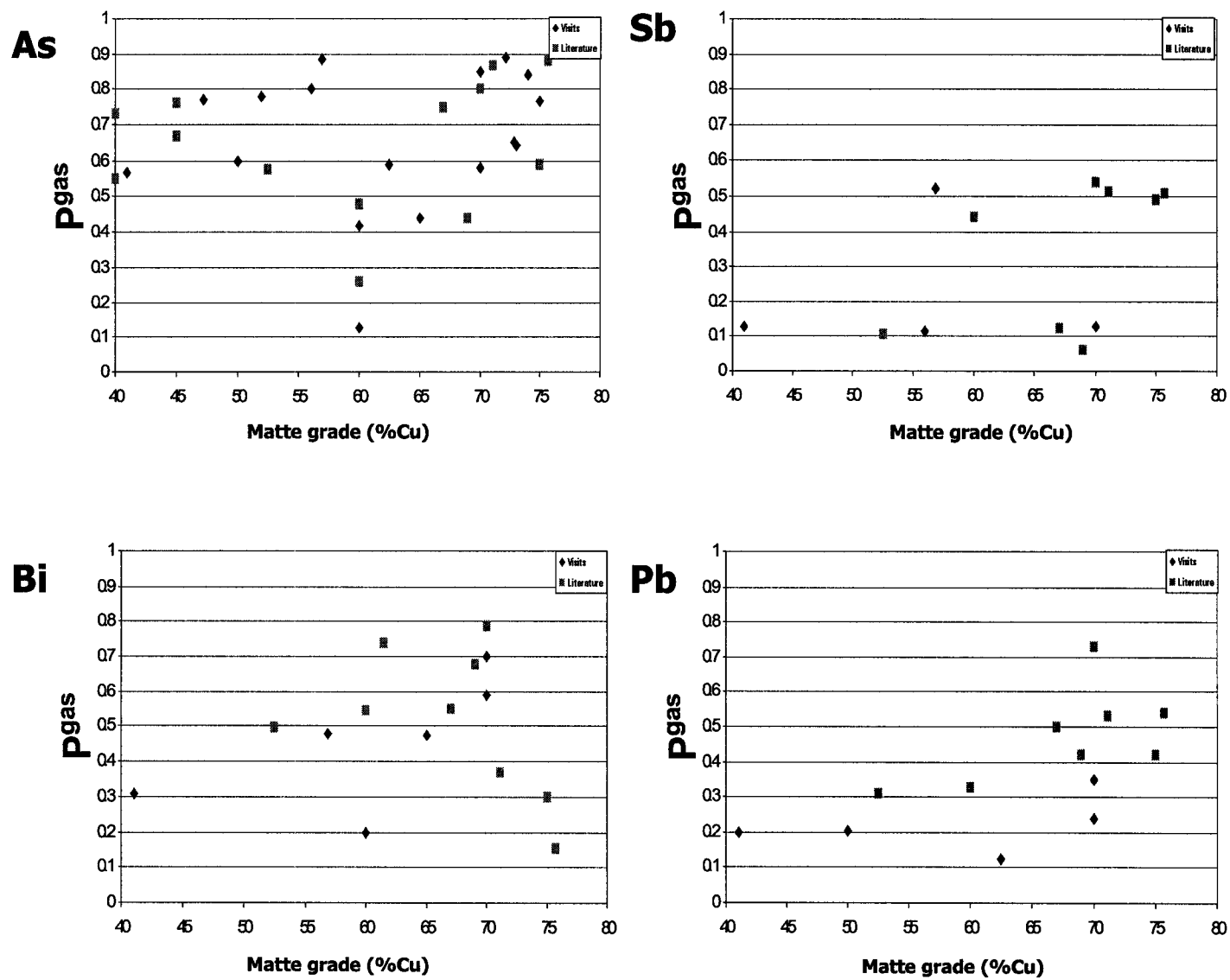


Figure 4.7. Effect of matte grade on partition to gas

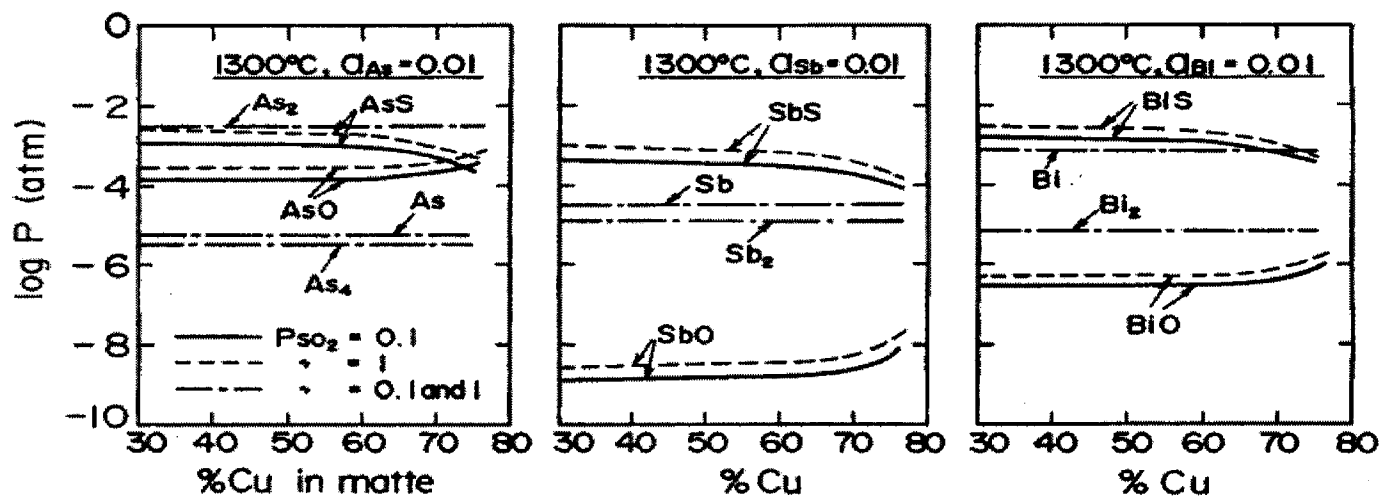
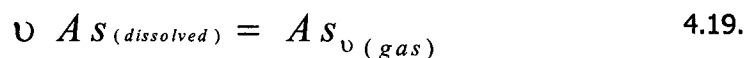


Figure 4.8. Vapor pressure of As, Sb, and Bi and their compounds as a function of the matte grade at 1300°C and $a_M=0.01$ reproduced from Itagaki, 1986.

The dependence of the activity coefficients of minor elements on matte grade was discussed for As, Sb, Bi, Pb and Ni earlier in this section. For the elements that can volatilize as polymetallic species, the effect of a change in the activity coefficient is amplified. As an example, for arsenic, As₂ and As₄ are volatile species. The volatilization reaction can be written as:



The equilibrium constant is:

$$K_T = \frac{p_{As_{\nu}}}{(x_{As} \gamma_{As})^{\nu}} \quad 4.20.$$

The dependence of volatilization on the activity coefficient is exponential (power ν) for polymetallic species as illustrated in Equation 4.20. The effect is believed to be marked particularly for arsenic for which the activity coefficient can be as low as 10^{-3} and as high as 4. For other elements (Sb, Bi, Pb, Ni), the polymetallic species have lower partial pressures than the sulfides, oxides and monatomic elemental form and the effect should be less significant.

In summary, a simultaneous analysis of Figures 4.4 and 4.8 permits a qualitative estimation of the volatilization behavior of As, Sb, Bi as a function of matte grade. For As, the volatilization is expected to decrease at high matte grades (>65% Cu) as a consequence of the decrease in the activity coefficient and the amplified effect on polymetallic species (As_{2(g)} and As_{4(g)}) volatilization.

For Sb, a decrease of volatilization is expected with increasing matte grade because of the decrease in $\gamma_{\text{Sb}}^{\circ}$ in addition to the dominance of SbS in the gas phase. For Bi, BiS is the dominant gaseous form and the decrease in $\gamma_{\text{Bi}}^{\circ}$ is relatively small at high matte grade. For these two reasons, volatilization is expected to decrease only slightly above 65-70% Cu in matte. For Pb, volatilization is believed to increase at high matte grade because of the increase in oxygen partial pressure which lowers the stability of Pb^{2+} ions in the matte and the enhanced volatilization of PbO. For Ni, volatilization is lower than 5% at all matte grades and for this reason results are not presented.

Theoretical predictions are in agreement with the results presented in Figure 4.7. for lead and bismuth. However, for arsenic and antimony, the predicted trend is not observed. It is believed that other factors such as oxygen enrichment which has a large impact on volatilization since overall off-gas volume is reduced has a greater influence on volatilization and masked the effects postulated here.

4.2.3 EFFECT OF OXYGEN ENRICHMENT

Modern copper smelters enrich the air with oxygen in the blowing gas. Oxygen-enriched blast permits an increase in the productivity, reduces energy consumption and produces lower volumes of more concentrated SO₂ gas for further fixation to H₂SO₄ as compared to non-enriched blast. Oxygen enrichment is carried out by mixing a high purity oxygen stream (usually >90%v/v O₂) to blast air supply. Beside all the benefits on productivity associated with the use of oxygen enrichment, it also affects the behavior of minor elements.

Effect of oxygen enrichment on $D_M^{\text{matte/slag}}$

The effect of oxygen enrichment on $D_M^{\text{matte/slag}}$ is plotted in Figure 4.9. A small decrease in $D_{Pb}^{\text{matte/slag}}$ is observed for lead with increasing oxygen enrichment. For other elements, no marked effect is observed. However, it does not necessarily imply that oxygen enrichment is not affecting the minor element distribution of As, Sb, Bi, and Ni. It is the opinion of the author that its effect is masked by the greater impact of other factors such as matte grade. The theoretical impact of an increase of oxygen enrichment on the thermodynamics is on local oxygen partial pressure of the system which is mainly damped by the matte grade as stated in the last section but oxygen enrichment has a small impact also. As seen in Equation 4.18, the oxygen partial pressure in the bulk matte or metal depends on p_{SO_2} and p_{S_2} prevailing at that location. For a matte of a given composition, p_{S_2} is fixed. Similarly, for a given smelting system, P_{SO_2} at the reaction zone can be written as:

$$p_{SO_2} = \frac{V_{SO_2}}{V_{SO_2} + V_{N_2} + V_{O_2}} \quad 4.21.$$

where V_{SO_2} is the volume of SO₂ produced per tonne of concentrate. Because modern smelting furnaces have oxygen efficiency, P_{O_2} would be relatively small. On the other hand, V_{N_2} , the volume of nitrogen per tonne of concentrate, can be approximated by:

$$V_{N_2} = \frac{(100 - \% O_{2 \text{ blast}})}{100} (V_{\text{blast}}) \quad 4.22.$$

By looking at Equations 4.21. and 4.22., it can be seen that P_{SO_2} increases with oxygen enrichment as V_{N_2} decreases per tonne of oxygen reacting. Therefore, the local equilibrium oxygen partial pressure (Equation 4.18) is higher if the other smelting parameters are kept to the same levels. This should favor the deportment to slag by Equations 4.1. and 4.2. presented earlier in Section 4.1.4. Therefore, it would be expected that if the effect of other changes did not hide it, oxygen enrichment would have decreased $D_M^{\text{matte/slag}}$ for all elements by driving the oxidation reaction.

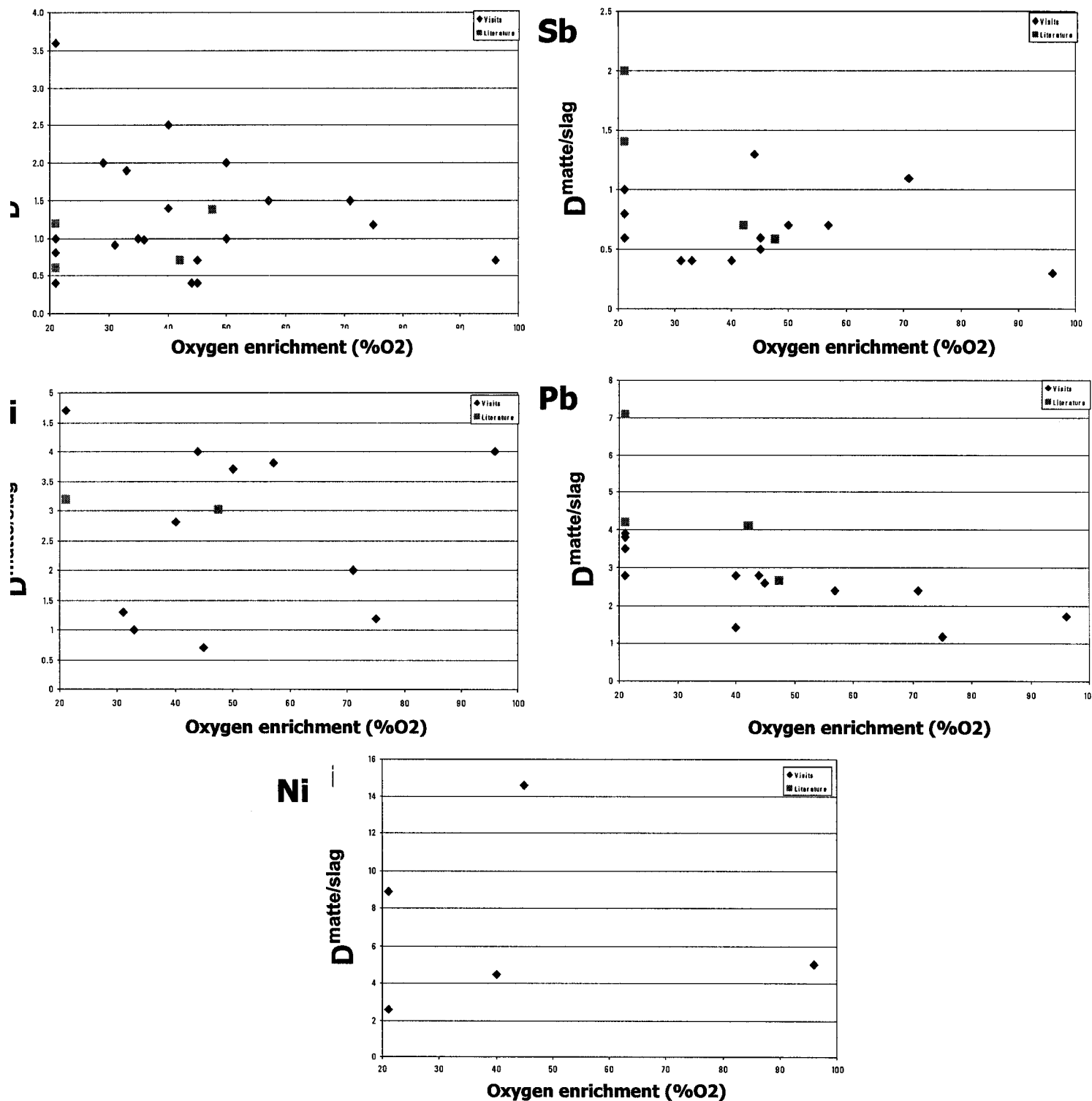


Figure 4.9. Effect of oxygen enrichment on distribution coefficient

Effect of oxygen enrichment on P_M^{gas}

Figure 4.10. presents the effect of oxygen enrichment on P_M^{gas} . It is observed, as a general trend, that volatilization is higher at low oxygen enrichment. There is an exception in this trend for values at 21% O_2 for which volatilization is lower than what can be anticipated by the trends. All these values are for reverberatory furnaces. The poor contact between the gas and the melt in reverberatory smelting is at the origin of this lower volatilization. The efficiency of the contact was discussed by Itagaki, 1986 as vapor saturation concept. Vapor saturation should be high for all modern copper smelting processes (flash, bath and lance) as good gas/melt contact is observed.

Volatilization of arsenic is decreased significantly with oxygen enrichment. For bismuth, the three points on Figure 4.10. from literature data (■) around 30% O_2 showing volatilization below 40% seem imprecise. They are for Teniente converters operating at high matte grade (low γ_{Bi}) with low input levels of bismuth (analytical error ?). Removing these three points from the analysis for bismuth, a decrease in P_{Bi}^{gas} is observed with oxygen enrichment. From Figure 4.10, no clear trends in the volatilization of antimony or lead with oxygen enrichment were observed but a decrease is to be expected as follows.

The consequence of enrichment is that the oxygen concentration increases in the overall blast and smaller non-reacting gas volumes are used to oxidize the same quantity of concentrate. Inert N_2 and other air constituents are the principal non-reacting gases in copper smelting. These gases are also called 'washing gas' as they flow through the molten phases helping volatilization. Enrichment also helps to reduce the thermal demands of the furnace. As a consequence, less fuel is required producing smaller volumes of CO and CO_2 in the off-gas that can also be seen as 'washing gas'. Lower volumes of 'washing gas' will increase the concentration of minor element in the off-gas reducing the driving force and hence, the tendency for volatilization.

A simulation of the theoretical effect of oxygen enrichment on the partitions of As, Sb, and Bi has been performed by Itagaki, 1986 on a typical copper matte of 60% Cu. The results are reproduced in Figure 4.11. They are in rough agreement with industrial results.

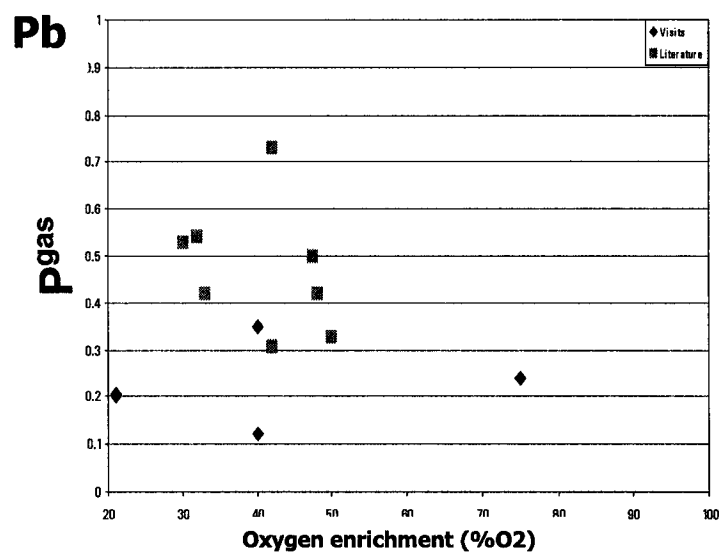
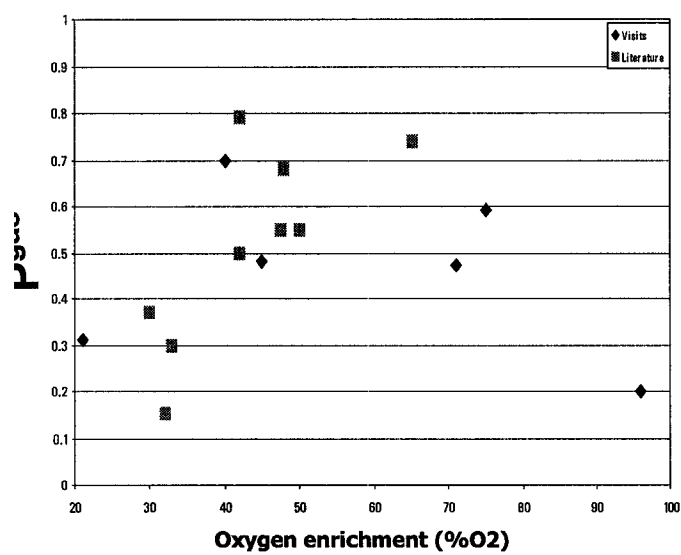
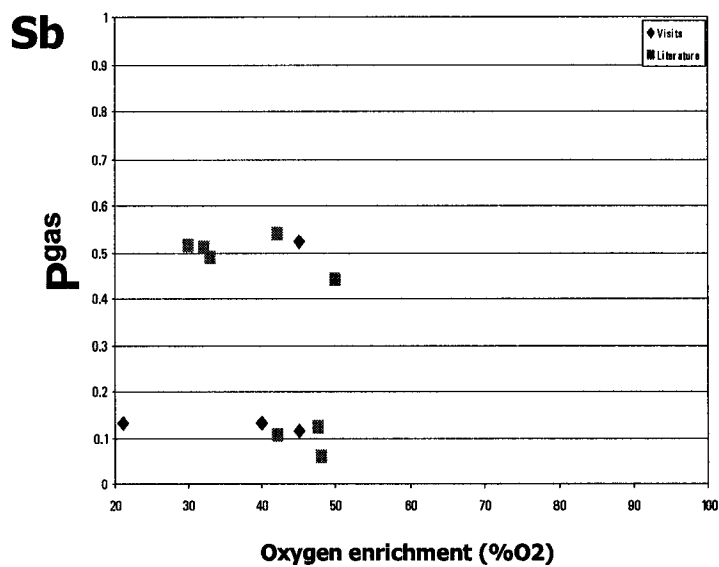
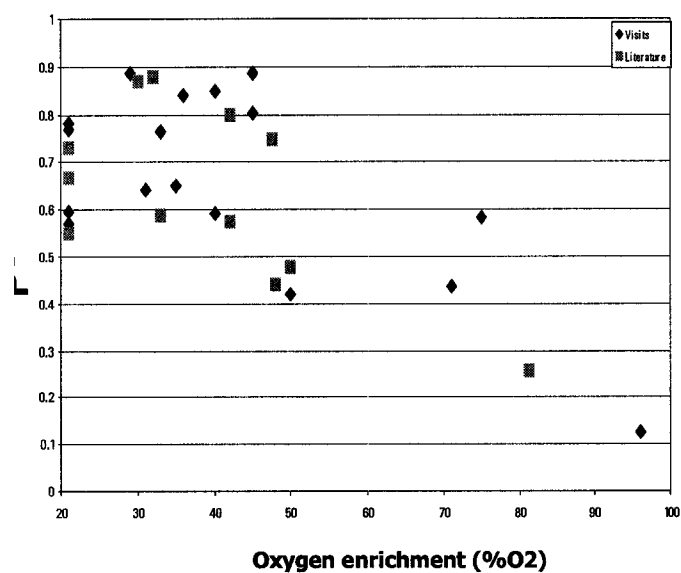


Figure 4.10. Effect of oxygen enrichment on partition to gas

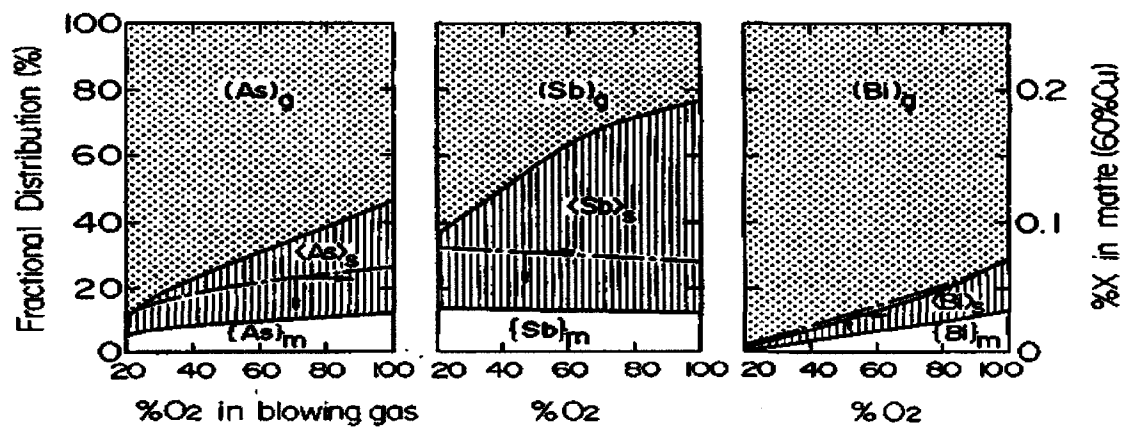


Figure 4.11. Relation between oxygen-enrichment in blowing gas and partitions for 60 % Cu matte, vapor saturation ($S=1$), 1300°C and 0.3% M in charge reproduced from Itagaki, 1986

4.2.4. EFFECT OF MINOR ELEMENT CONCENTRATION IN FEED

Effect of minor element concentration on $D_M^{\text{matte/slag}}$

The effect of concentration of minor elements in the feed to the smelting furnace on $D_M^{\text{matte/slag}}$ is presented in Figure 4.12. No clear relationship is observed for any element from that figure. This was expected from theory as the concentration does not appear in Equation 4.12. defining the matte/slag equilibrium. The scatter observed on this figure is believed to be mainly due to the effect of other operating parameters.

Effect of minor element concentration on P_M^{gas}

The effect of minor element in the feed to the smelting furnace on volatilization is shown in Figure 4.13. It can be seen that for arsenic, $P_{\text{As}}^{\text{gas}}$ might increase with the concentration in the feed. The trend is uncertain because of the scatter. The two points with lower volatilization ($0.4 < P_{\text{As}}^{\text{gas}} < 0.5$) in the 0.9-1% As in the feed are for the Outokumpu flash furnace at CODELCO-Chuquicamata and the high oxygen enrichment ($> 50\% \text{ O}_2$) is probably at the origin of this phenomena as discussed in the last section. If these two points are removed, the trend for As becomes more apparent. For Sb, Bi, and Pb, no relationship is evident.

From a theoretical point of view, the concentration difference between the molten phases and the gas is the driving force for volatilization. The exception is for elements having volatile polymetallic species. This is the case for arsenic where As_2 and As_4 are volatile. As seen from Equations 4.19. and 4.20., presented earlier, the volatilization of polymetallic species dependency on concentration (x_M) is raised to the exponent ν . Therefore, an increase in $P_{\text{As}}^{\text{gas}}$ with initial arsenic concentration in feed is expected which is partly confirmed by industrial data.

To confirm the higher volatilization of arsenic with an increase of its level in concentrate, data from Mendoza et al., 1995 are reproduced in Figure 4.14. They permit us to look at this effect without having the influence of other operating parameters (matte grade, oxygen enrichment, etc.). From Mendoza's data, it is observed that the matte and slag assays in both furnaces are usually following the same pattern. It shows that $D_{\text{As}}^{\text{matte/slag}}$ does not vary with initial content of As ($\text{wt\% As}_{\text{matte}}/\text{wt\% As}_{\text{slag}}$). On the other hand, the slope in both graphs is smaller than unity indicating that the partition to gas increased with initial content of As in feed.

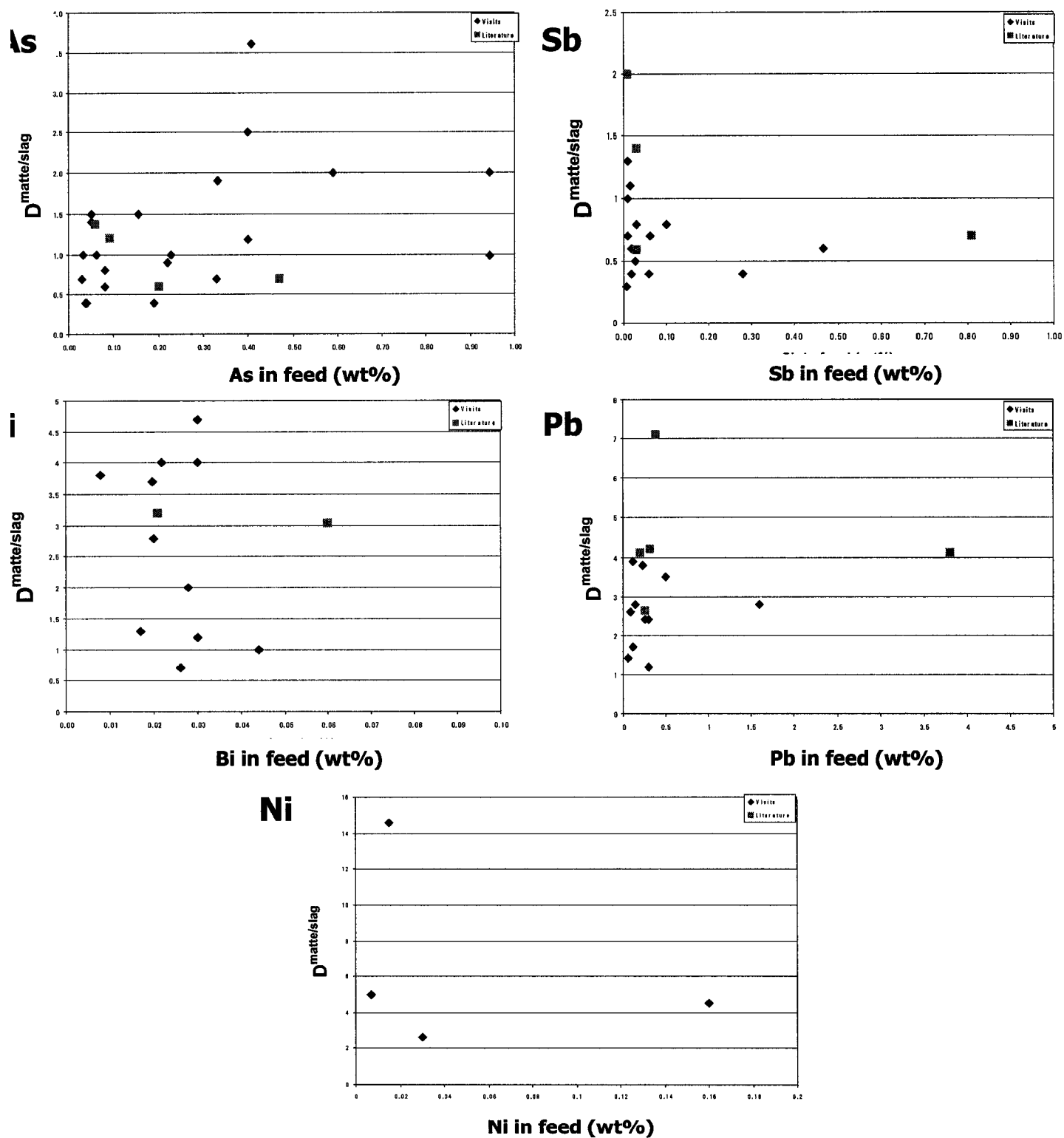


Figure 4.12. Effect of initial content on distribution coefficient

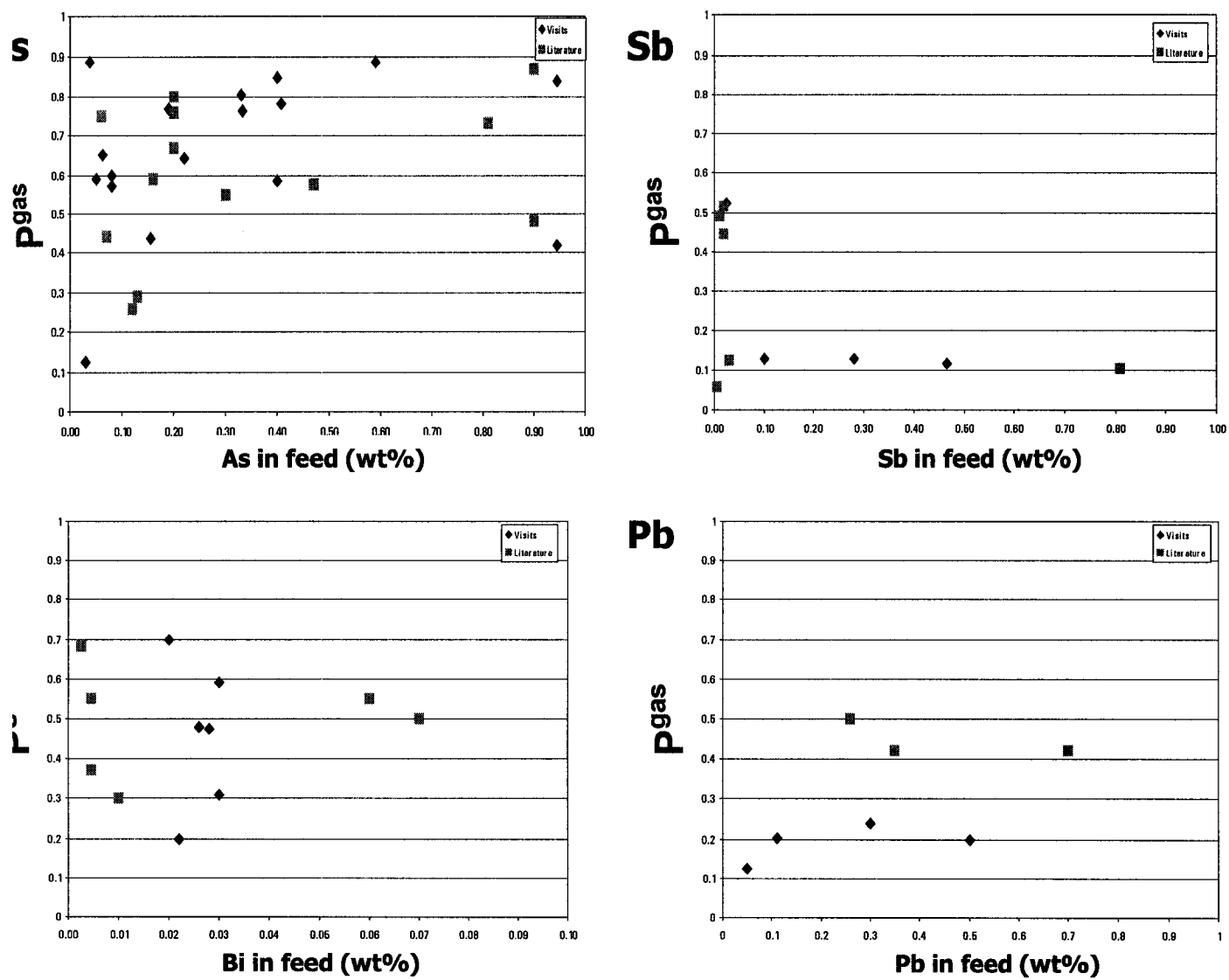


Figure 4.13. Effect of feed composition on partition to gas

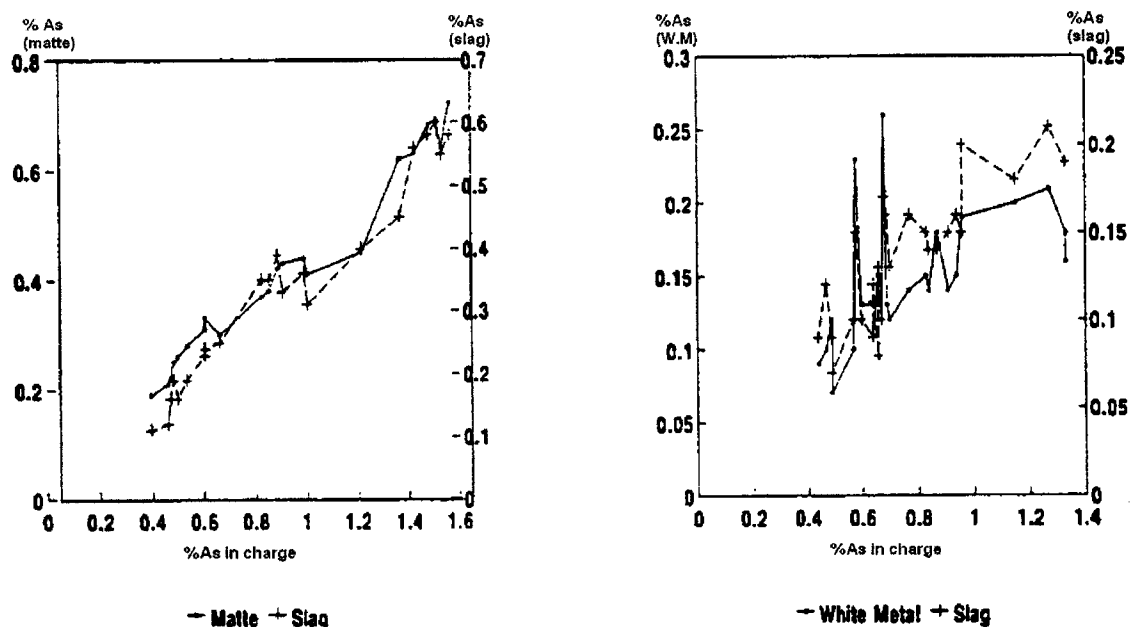


Figure 4.14. Empirical distributions of Arsenic at Chuquicamata as a function of arsenic concentration in feed reproduced from Mendoza et al., 1995 (left is for Outokumpu flash smelting furnace and right for Teniente converter)

Itagaki computed the behavior of minor element as a function of feed content in his simulation work reproduced in Figure 4.15.. Dependence of arsenic on feed content is confirmed and it indicates that volatilization of Sb and Bi are independent of the feed content [Itagaki, 1986].

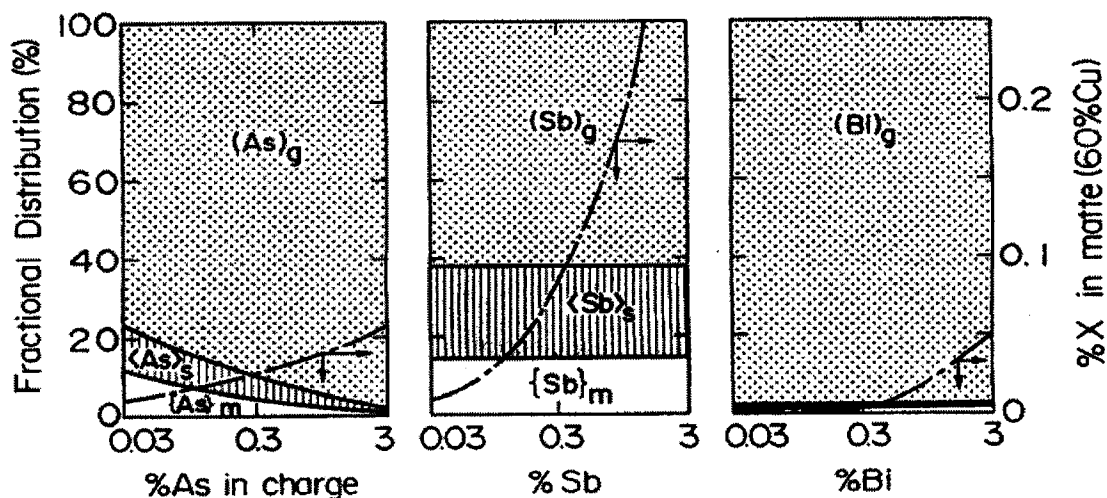


Figure 4.15. Relation between initial concentration of X (M in the present notation) and fractional distributions of As, Sb, Bi at 60% Cu matte for air blowing (1300°C and S=1) reproduced from Itagaki, 1986

4.2.5. EFFECT OF SLAG COMPOSITION

The slag composition affects the stability of the minor elements in slag. Mathematically, it can be translated as a change in the activity coefficient of the element in slag. The dominant species of most minor elements in copper smelting slag are the oxides. Therefore, a change in slag composition will directly affect (γ_{MO}). $D_M^{\text{matte/slag}}$ defined for the oxidation reactions (4.1.-4.2.) by Equation 4.12 obtained earlier is affected by this change in γ_{MO} .

$$D_M^{\text{matte,copper/slag}} = \frac{1}{(K_T)(pO_2)^{v/2}} \left(\frac{\gamma_{MO}}{\gamma_M} \right) \left(\frac{MW_{slag}}{MW_{matte,copper}} \right) \quad 4.12.$$

Matte smelting furnaces

As all industrial matte smelting furnaces use silica based slag, the change in stability of the oxides in slag will mainly come from variation in the silica content and the influence of minor oxides such as CaO, Al₂O₃, MgO, etc. From industrial visits, it was not possible to collect enough information to discuss the influence of these factors on $D_M^{\text{matte/slag}}$. Very little literature exists on the subject. In the opinion of the author, it is a field that should be exploited to improve deportment of minor elements to slag in matte smelting furnaces.

From a scientific point of view, the changes in the activity coefficients can be explained by the acid-base interactions between the minor element oxide and the slag system. As for aqueous solutions, a basic molten compound has the tendency to donate an electron pair whereas acid compounds are more electronegative and seek electrons. As presented by Peacey et al., 1980, a relative measure of this tendency is the strength of the metal-oxygen bond presented qualitatively in Figure 4.16.

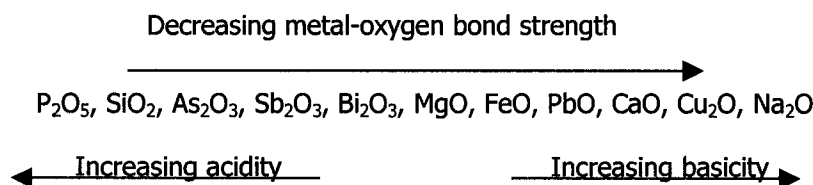


Figure 4.16. Relative strength of the metal-oxygen bond of major oxides in copper smelting system from Peacey et al., 1980

Increasing basic minor oxide constituents in matte smelting slag should decrease the $D_M^{\text{matte/slag}}$ of arsenic and antimony since their oxides are acidic. Acidic constituents should help for the deportment to slag of lead and nickel because their oxides are basic. Bismuth should not be affected to a great extent by minor oxide constituents as Bi_2O_3 is not having a clear acidic or basic behavior.

Converting furnaces

Peirce-Smith converters use silica slag. Therefore, the minor element distribution coefficients will be affected mainly by silica saturation and minor oxide constituents as for matte smelting vessels.

For new continuous converting furnaces, the possibility exists to evaluate quantitatively different slag systems. The Mitsubishi C-furnace and Kennecott-Outokumpu Flash Converting Furnace (K-O FCF) use calcium-ferrite slag (Ca-Fe-O). Originally, calcium-ferrite slag was developed as a response by the industry to the need to carry out converting at ever increasing degrees of oxygen enrichment without precipitation of magnetite (Fe_3O_4). For the Noranda Continuous Converting Furnace (NCV), the silica slag is used similarly to smelting. Table 4.3. presents the $D_M^{\text{Cu/slag}}$ for continuous converting furnaces.

Table 4.3. $D_M^{\text{Cu/slag}}$ in various continuous copper converting furnaces

	Type of slag	Data source	$D_{\text{As}}^{\text{Cu/slag}}$	$D_{\text{Sb}}^{\text{Cu/slag}}$	$D_{\text{Bi}}^{\text{Cu/slag}}$	$D_{\text{Pb}}^{\text{Cu/slag}}$
Naoshima C-F	Ca-ferrite	Ajima et al., 1995	0.53	0.53	1.4	0.37
Kennecott K-O FCF	Ca-ferrite	Calculated from partition coefficients given at visit	0.49	-	1.7	0.23
Horne NCV	Fayalite	Levac et al., 1995 + visit	50	2.5	8.5	0.10

As expected, a significant difference in $D_M^{\text{Cu/slag}}$ is observed due to a change in the type of slag. It can largely be explained by the acid-base theory presented in Figure 4.16. The greater deportment of arsenic and antimony to slag with calcium-ferrite slag can be explained by the greater stability (lower activity coefficient) of As_2O_3 and Sb_2O_3 in the basic Ca-Fe-O slag system. On the other hand, the elimination of lead to slag is improved with fayalite slag which is to be expected from the greater stability of PbO in the acidic SiO_2 slag system. For bismuth, the greater deportment to slag with calcium-ferrite slag is difficult to explain and probably depends

on other factors as follows. The presence of a matte phase in the NCV and the lower oxygen enrichment have the consequence of decreasing the equilibrium oxygen partial pressure of the system to 10^{-7} atm while the K-O FCF and Mitsubishi C-Furnace operate with a p_{O_2} around 10^{-5} - 10^{-6} atm [Levac et al., 1995]. This higher p_{O_2} will reduce the $D_M^{Cu/slag}$ in Ca-ferrite industrial furnace compared to the NCV but also has other disadvantages (e.g., higher Cu content of slag, higher refractory wear, etc.). At the Horne smelter, the semi-blister copper (1-1.3% S) from the NCV is desulfurized in a dedicated vessel [Prévost et al., 1999] where significant deportment of minor elements to slag also occurs.

The thermodynamical quantities related with distribution equilibrium between copper and slag for the minor elements have been studied by Takeda et al., 1983 and are reported in Table 4.4.

Table 4.4. Thermodynamic data related with distribution equilibrium of minor elements between copper and slag at 1523K from Takeda et al., 1983

Element	γ_M^0	γ_{MO_2}		$D_M^{Cu/slag}$
		Fayalite	Ca-ferrite	(calcium-ferrite system)
				$D_M^{Cu/slag}$ (fayalite system)
Cu	1.0	2.8-3.3	3.5-5	1.4
As	0.004	0.07-0.3	0.006-0.06	0.02-0.86
Sb	0.03	2	0.15-0.6	0.08-0.30
Bi	2.3	0.5	0.1-1	0.2-2.0
Pb	4.8	0.4	3.2	8
Ni	2.2	5-11	3-12	0.27-2.4

Table 4.4 confirms the industrial observations that deportment of As and Sb is significantly improved with calcium-ferrite slag. Lead elimination is better with the use of fayalite slag. For bismuth and nickel, the large range of γ_{MO_2} , reported in the experimental results of Takeda does not give a clear indication which slag system is better for the deportment to slag of these elements. Yazawa et al. recently suggested a new chemistry of slag, ferrous-calcium-silicate (Fe-Ca-Si-O) which is believed to make the best of the two existing slag systems. Even though it is promising, this slag has not been used yet either in copper smelting or converting industrial operations and literature should be consulted for more details [Yazawa et al., 1999].

4.2.6. THEORETICAL EFFECT OF OTHER FACTORS ON MINOR ELEMENT DISTRIBUTION

For the following parameters, it was not possible to obtain sufficient representative data from industrial visits to compare theoretical background with industrial behavior. Therefore, only theory will be discussed.

4.2.6.1. Effect of Sulfur Content of the Copper Matte:

The Cu-Fe-S phase stability diagram presented in Figure 4.17 shows that even if matte is assumed to lie on the pseudo-binary composition line of Cu_2S -FeS, matte can be stable over a range of Cu-Fe-S compositions not on the line.

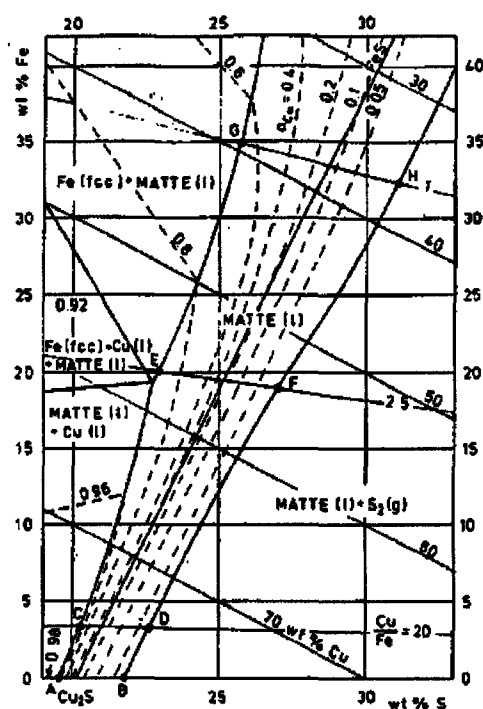


Figure 4.17. Cu-Fe-S phase diagram at 1200°C reproduced from Roine and Jalkanen, 1985

However, for the present purpose, if it is assumed that matte is a binary mixture of Cu_2S -FeS, it is possible to evaluate quantitatively the influence of the metal to sulphur ratio with the following expression:

$$\text{Free S} = X_S - \frac{X_{\text{Cu}}}{2} - X_{\text{Fe}} \quad 4.23.$$

When this quantity is negative, the matte is sulfur deficient and if it is positive, there is excess sulfur with respect to the $\text{Cu}_2\text{S}-\text{FeS}$ pseudo binary composition line. The effect of this parameter on the activity of As, Sb, Bi, and Pb has been addressed by Akagi in his Master's thesis, 1988 and is represented in Figure 4.18. It is observed that As and Sb respond differently from Bi and Pb to a change in metal to sulfur ratio. γ_{As} and γ_{Sb} decreased drastically in sulfur deficient matte. On the other hand, γ_{Bi} is maximized around stoichiometric sulfur composition and γ_{Pb} increases in sulfur deficient matte. This will have an impact both on $D_{\text{M}}^{\text{matte/slag}}$ and $P_{\text{M}}^{\text{gas}}$ from Equations 4.12 and 4.5. It can be seen, due to the interaction of S and O to form SO_2 , that mattes deficient in S will have a high p_{O_2} relative to mattes of the same $\text{Cu}_2\text{S}/\text{FeS}$ having an excess S. It is hard to quantify industrially but it is believed that this effect can be as important as the influence of matte grade.

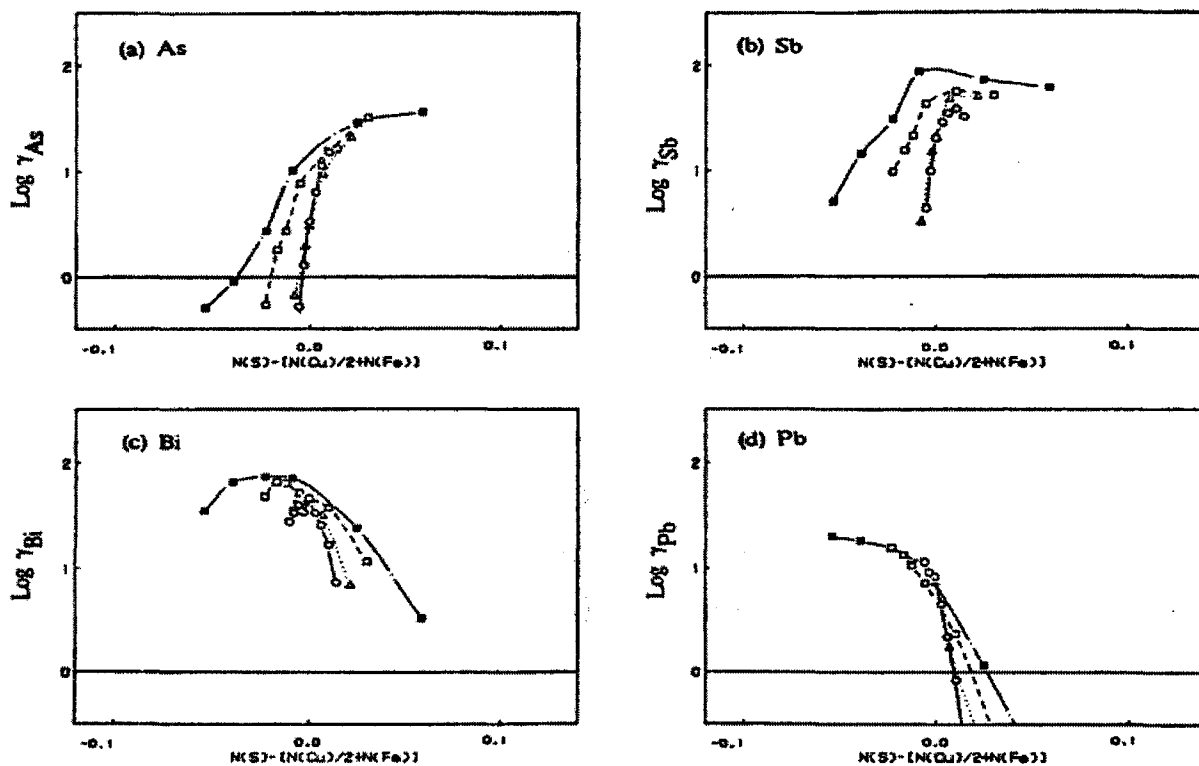


Figure 4.18. Relationship between γ_{M} and sulfur deficiency for As, Sb, Bi, and Pb reproduced from Akagi, 1988

4.2.6.2. Effect of Minor Constituents (other impurities)

Interactions with other species dissolved in the matte copper or slag can influence the behavior of minor elements. It can be expected that the minor constituents having the same ionic charge or occupying the same position as a specific minor element in the ionic matte melt will increase γ_M . On the other hand, an impurity with an opposite charge or a great affinity for an element will tend to bond in a metallic 'speiss' or other intermediate complexes lowering the γ_M . Again, this will affect both the $D_M^{\text{matte/slag}}$ and P_M^{gas} from Equations 4.12 and 4.5.

Roine, 1987, studied the effect of nickel and cobalt on γ_M of As, Sb, Bi, and Pb. He found that at stoichiometric and sulphur-deficient matte compositions, Ni and especially Co decreased γ_{As} and γ_{Sb} and had no effect on γ_{Bi} and γ_{Pb} . For matte with a stoichiometric or excess sulphur content, Ni and Co did not show any marked effect on the activity coefficients of As, Sb, Bi and Pb.

4.2.6.3. Effect of Temperature

Ignoring kinetic considerations, the smelting or converting temperature has an effect mainly on the oxidation reaction equilibrium constant, vapor pressure of volatile species and the activity coefficient of the element. The impact on the activity coefficient will affect both the department to slag and volatilization of the minor element from Equations 4.5. and 4.9. The change in the oxidation reaction equilibrium constant will affect the $D_M^{\text{matte,copper/slag}}$ and the change in vapor pressure has an effect on P_M^{gas} .

Table 4.5. presents the effect of temperature on the equilibrium constant of the oxidation reactions. It is observed that the equilibrium constant decreases with an increase in temperature. Therefore, an increase in $D_M^{\text{matte,copper/slag}}$ is expected at higher temperatures from Equation 4.12.

The change in vapor pressure of volatile elements with temperature is presented in Table 4.6. The vapor pressure increases with temperature. As a consequence, the volatilization should be increased at higher temperature from Equation 4.5.

Table 4.5. Effect of temperature on equilibrium constant of minor element oxidation reactions. ΔG° equations are from Takeda et al., 1983

		ΔG°	Log K (1150°C)	Log K (1200°C)	Log K (1250°C)
As	$\text{As}_{(l)} + \frac{3}{4} \text{O}_{2(g)} = \text{AsO}_{1.5(l)}$	$-330620 + 115.39T$	6.11	5.70	5.31
Sb	$\text{Sb}_{(l)} + \frac{3}{4} \text{O}_{2(g)} = \text{SbO}_{1.5(l)}$	$-334820 + 114.23T$	6.32	5.91	5.52
Bi	$\text{Bi}_{(l)} + \frac{3}{4} \text{O}_{2(g)} = \text{BiO}_{1.5(l)}$	$-284300 + 133.05T$	3.49	3.13	2.80
Pb	$\text{Pb}_{(l)} + \frac{1}{2} \text{O}_{2(g)} = \text{PbO}_{(l)}$	$-195100 + 77.70T$	3.10	2.86	2.63
Ni	$\text{Ni}_{(l)} + \frac{1}{2} \text{O}_{2(g)} = \text{NiO}_{(l)}$	$-249400 + 92.84T$	4.31	3.99	3.70

Table 4.6. Effect of temperature on vapor pressure of minor elements. $P^\circ = f(T)$ equations from Nagamori and Chaubal, 1982 and Allaire, 1986.

Cond'ed phase	Vapor pressure, P° atm	Temp. range (K)	P° (1150°C)	P° (1200°C)	P° (1250°C)
As	$\text{Log } P^\circ_{\text{As4}} = -6160/T + 6.94$	600-900	4.1×10^{-2}	5.7×10^{-2}	7.9×10^{-2}
	$\text{Log } P^\circ_{\text{As}} = -20540/T + 17.67^*$	-	34	5.3×10^3	1.5×10^4
Sb	$\text{Log } P^\circ_{\text{Sb2}} = -11170/T + 15.66 - 3.02 \log T$	900-1910	1.9×10^{-2}	3.2×10^{-2}	5.2×10^{-2}
Bi	$\text{Log } P^\circ_{\text{Bi}} = -10400/T + 9.47 - 1.26 \log T$	544-1953	1.5×10^{-2}	2.6×10^{-2}	4.3×10^{-2}
Pb	$\text{Log } P^\circ_{\text{Pb}} = -10130/T + 8.28 - 0.985 \log T$	597-2013	1.1×10^{-2}	1.9×10^{-2}	3.1×10^{-2}
	$\text{Log } P^\circ_{\text{PbO}} = -10598/T + 6.012$	1159-1745	3.6×10^{-2}	6.6×10^{-2}	1.1×10^{-1}
	$\text{Log } P^\circ_{\text{PbS}} = -11700/T + 7.50$	-	1.9×10^{-1}	3.6×10^{-1}	6.5×10^{-1}
Ni	$\text{Log } P^\circ_{\text{Ni}} = -22500/T + 10.72 - 0.96 \log T$	298-1718	7.6×10^{-9}	2.5×10^{-8}	7.8×10^{-8}
	$\text{Log } P^\circ_{\text{NiO}} = -24480/T + 8.3438$	1438-1566	1.7×10^{-9}	6.6×10^{-9}	2.3×10^{-8}
	$\text{Log } P^\circ_{\text{NiS}} = -9213/T + 2.96$	877-1077	3.1×10^{-4}	5.1×10^{-4}	8.1×10^{-4}

**from Allaire, 1986*

The impact of temperature on the activity coefficient of the elements in copper is given in Table 4.7. Generally, the activity coefficient tends to unity at high temperatures. The effect on elimination (slagging and volatilization) is specific to each element. As a general rule, if the activity coefficient is smaller than 1 around the smelting temperature, the elimination will increase (e.g., As and Sb in copper and As in matte). On the other hand, if γ_M° is greater than 1,

the elimination will decrease at higher temperatures (e.g. Bi, Pb, Ni in matte and copper and Sb in matte).

Table 4.7. Effect of temperature on γ_{Mo} in dilute Cu-M alloys. Equations from Nagamori and Chaubal, 1982

Temperature dependence		$\gamma_{\text{M}}^{\circ}$ (1150°C)	$\gamma_{\text{M}}^{\circ}$ (1200°C)	$\gamma_{\text{M}}^{\circ}$ (1250°C)
As	$\text{Log } \gamma_{\text{As}}^{\circ} = -4830/T$	0.0004	0.0005	0.0007
Sb	$\text{Log } \gamma_{\text{Sb}}^{\circ} = -4560/T + 1.24$	0.011	0.014	0.018
Bi	$\text{Log } \gamma_{\text{Bi}}^{\circ} = 1900/T - 0.885$	2.8	2.5	2.3
Pb	$\text{Log } \gamma_{\text{Pb}}^{\circ} = 2670/T - 1.064$	6.5	5.6	4.9
Ni	$\text{Log } \gamma_{\text{Ni}}^{\circ} = 1430/T - 0.546$	2.9	2.7	2.5

However, temperature in copper smelting furnaces is controlled over only a small range. The degree of freedom to maximize minor element elimination with variation in temperature of industrial furnace is small as furnace operating temperature is usually set by other considerations such as slag viscosity, refractory protection, off-gas temperature and fuel consumption.

4.3. EFFECT OF TYPE OF MATTE SMELTING FURNACE ON MINOR ELEMENTS

It was found that the impact of the type of matte smelting furnace on minor element behavior was much lower than is the typical belief of the industry. In fact, the impact on minor element distribution of operating parameters discussed earlier is much greater than the design of the furnace itself.

In comparing two processes, one should first look at things such as oxygen enrichment, matte grade, and all other parameters discussed in Section 4.2. prior to concluding that the type of smelting furnace is at the origin of the change in minor element distribution. Most modern smelting processes are given the flexibility to operate at various matte grades and levels of oxygen enrichment. As an example, the Noranda Process Reactor has operated from low oxygen enrichment (close to $\sim 21\% \text{O}_2$) up to $45\% \text{O}_2$ and at matte grade from $55\% \text{Cu}$ to $70\text{--}75\% \text{Cu}$ for test purposes [Persson et al., 1986]. The same is true for Outokumpu flash smelting furnaces which can operate at low matte grades ($56\% \text{Cu}$ at Kosaka) and low oxygen enrichment (e.g. $21\% \text{O}_2$ during start-up at Guixi) to levels up to $70\% \text{Cu}$ and $75\% \text{O}_2$ (Kennecott). The reverberatory furnace does not have this flexibility.

However, the type of furnace does influence the rate and amounts of dust generation which have an impact on the cost of hydrometallurgical dust treatment (c.f. Section 6.3 for more details). In addition, the type of furnace influences the following parameters, all of which have some effect on minor element deportment:

- 1- Partial roasting of the solid feed
- 2- Vapor saturation
- 3- Metal entrapment
- 4- Reducing agent

As discussed earlier in this chapter, partial roasting (or heating of the concentrate temporarily suspended in a low oxygen environment) happens when the solid feed does not instantaneously react with the oxygen from the blast. This happens in the Noranda Reactor (when slinger is used) and the Isasmelt and Mitsubishi processes as they are all fed by solid addition over the melt. Given that other parameters are constant, $P_{\text{M}}^{\text{gas}}$ should be greater for these furnaces. The effect would be perceivable mainly for volatile elements such as arsenic and bismuth. For a

furnace using concentrate injection (e.g., Teniente Converter) or flash processes, the reaction is almost instantaneous and partial roasting of the feed is not believed to happen.

Vapor saturation describes the efficiency of the gas/melt contact [Itagaki, 1986]. When low vapor saturation is observed, the partition to gas would be lower. For all modern processes (flash, bath and lance smelting), excellent contact exists diminishing the impact of this factor. In reverberatory furnaces, this contact is not as efficient resulting in lower P_M^{gas} for the volatile elements. However, the negative impact of vapor saturation in the reverberatory furnace is partly compensated by the low matte grade which enhances volatilization of all elements except lead.

The level of matte entrapment in slag is set by turbulence in the vessel and slag fluidity which is, in turn, affected by operating temperature and magnetite content. The effect would be perceivable in the industrial distribution for a given furnace. However, after pyrometallurgical slag cleaning or flotation of slag (Section 4.5.), the impact should be negated as entrained matte would be settled or floated and returned to the process. Bath and lance smelting processes are characterized as highly turbulent. In flash processes, turbulence is medium given the longer settling zone. Low turbulence is observed in reverberatory furnaces.

The use of a reducing agent (fuel or coke) to close the heat balance of the smelting furnace will be deleterious to the elimination in the slag as the equilibrium partial pressure of oxygen would be reduced. For volatilization, this decrease of oxygen partial pressure should be balanced by the increased amount of 'flush' gas, or lower vapor saturation.

4.4. MINOR ELEMENT DISTRIBUTION IN COPPER CONVERTING

Due to the difficulty to get accurate distribution and partition coefficients for batch converting the discussion in this part has to be qualitative. The observed elimination was seen to depend on initial matte grade and oxygen enrichment from general discussions with smelter personnel and references [Mendoza et al., 1995]. In general, the lower the initial matte grade and oxygen enrichment, the greater the deportment to the gas. During the 'slag blow', the thermodynamics at any given moment will be similar to the figures presented in this chapter for matte smelting at the given matte grade and oxygen enrichment. As soon as Cu_2S composition is reached, copper will start to form in the melt. At that moment, the elimination of As, Sb, Bi, Ni will be decreased because of their greater stability in copper than in matte as represented by a decrease in the activity coefficient (Table 4.2.). For lead, the elimination is anticipated to be greater in the 'copper blow' than the 'matte blow' as the activity coefficient increases.

For continuous converting, the conditions are steady and thermodynamics are fixed for a given system. Figure 4.19. presents the partition coefficients in two batch and three continuous converting furnaces. The batch converting furnaces chosen for comparison had an initial matte grade around 70% Cu to compare with continuous converters. The Noranda Continuous Converter (NCV) and Peirce-Smith converters can be directly compared as they use fayalite slag. It can be seen that the elimination by volatilization and deportment to slag in batch converting is much greater than for the continuous process. This is from the lower activity coefficient in copper than matte for most elements. The lower oxygen partial pressure at the beginning of 'slag blow' in comparison with a constant value for continuous converting is another reason for this difference.

For the Kennecott-Outokumpu Flash converting furnace (K-O FCF), Mitsubishi C-furnace and Noranda Continuous Converter (NCV), the differences can be explained mainly by the different type of slag used and the higher oxygen partial pressure prevailing. This was already discussed in Section 4.2.5. Again, a direct comparison between NCV and K-O FCF and Mitsubishi C-furnace is not appropriate because the NCV is used with a desulfurization vessel [Prévost et al., 1999] in which significant elimination both by volatilization and deportment to slag occurs. However, no published figures for the partitions in the desulfurization vessel were found.

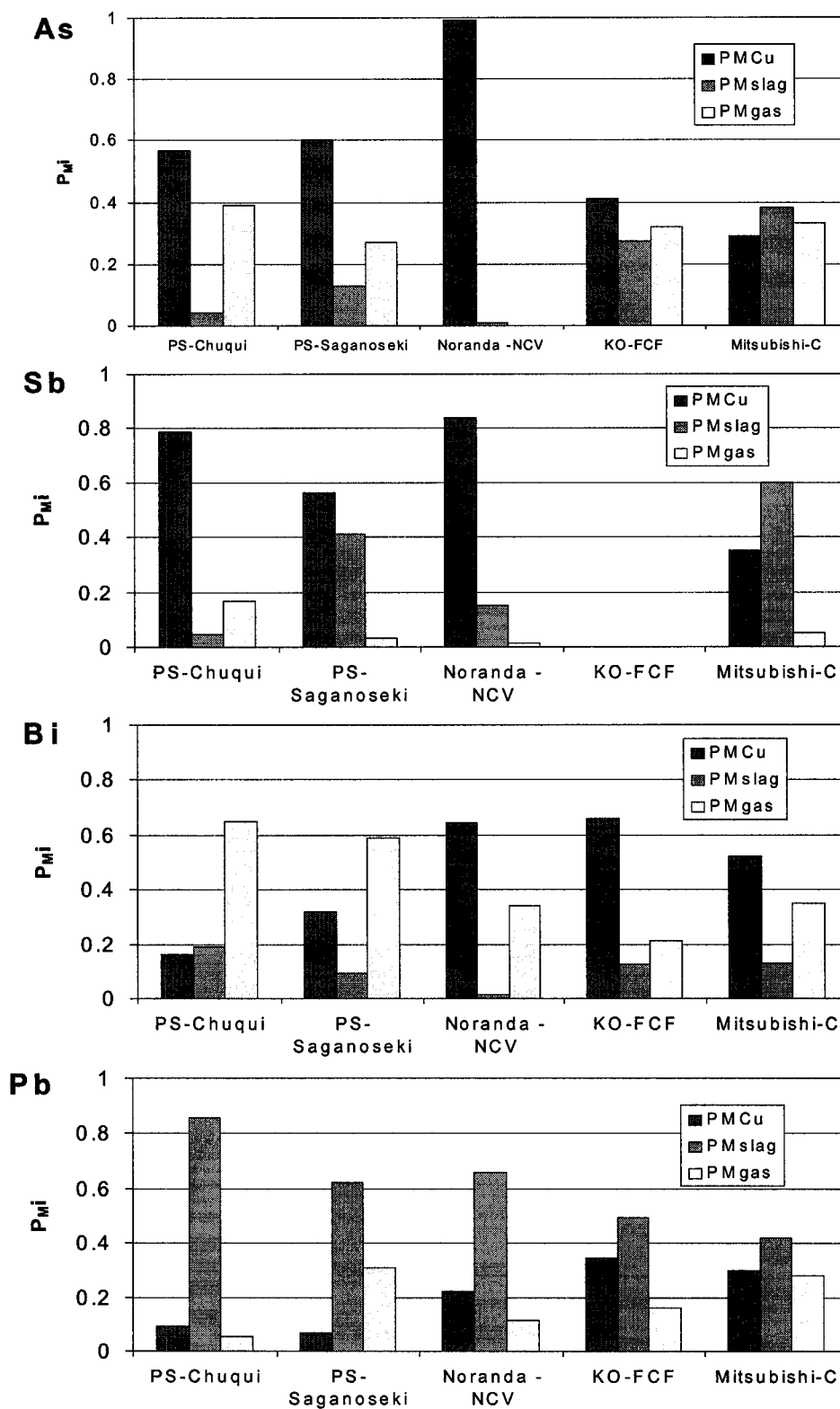


Figure 4.19. Partition coefficients for various converting furnaces. Source of info: PS Chuquicamata - Mendoza et al. 1995; PS Saganoseki – Visit 1999; Kennecott-Outokumpu Flash Converting Furnace – Visit 1999; Mitsubishi C-Furnace – Chenier et al. 1992; Noranda Continuous Converter – Levac et al. 1995

4.5. EFFECT OF SLAG CLEANING ON MINOR ELEMENT RECOVERY

The copper content of slag produced in matte smelting and converting furnaces justifies its treatment for recovery copper. This is especially true for modern smelting processes for which higher matte or copper entrapment occur due to large turbulence and high magnetite content of the slag as compared to the traditional reverberatory furnaces. Industrially, two types of treatment exist: mineral processing (flotation of finely ground slag in a mill) and molten slag cleaning in a quiescent furnace.

The technology selected has an impact on overall smelter's recovery of minor elements. A pyrometallurgical slag cleaning furnace acts primarily as a settling vessel but often a reducing agent is added to lower the magnetite content and favor separation. Given the lower pO_2 , a portion of the minor elements present in the slag as oxides should be reduced. For two pyrometallurgical slag cleaning furnaces visited (electric furnace and CODELCO-type slag cleaning furnace) the $D_{As}^{matte/slag}$, $D_{Sb}^{matte/slag}$ and $D_{Bi}^{matte/slag}$ ranged from 3.5 to 14, 2.1 to 5.1, and 2.1 to 4.3, respectively. It was not possible to calculate the partition coefficients as the volatilization in those furnaces was unknown. Moreover, the author did not find literature on minor element recovery in slag cleaning furnaces except for Kim and Sohn, 1997. This publication was for Cu_2O reduction which is thermodynamically different from cleaning of the matte smelting furnace as the recovered phase would be copper instead of high grade matte. As a general trend, it can be expected that an increase in the reducing agent would yield a greater recovery to matte recirculated to the process.

Slag milling is designed and operated to recover most of the copper present in the sulfide and metallic forms. Because some minor elements are generally associated with those phases, a partial recovery is expected. However, the part which is in slag (mainly oxides) will not be recovered. As an example, Mackey et al., 1975, gave the following recoveries for As, Sb, Bi, Pb and Ni to slag concentrate in flotation process: As=32%, Sb=29%, Bi=23%, Pb=16%, Ni=11% from Noranda Process on copper. It should be noted that the recovery in the milling process largely depends on the phases to which the minor elements are associated.

Minor element elimination for milling is expected to be greater than for pyrometallurgical slag cleaning furnaces. The effect on overall smelter's recovery should be mainly perceptible for Sb and Pb as they largely deport to slag in the matte smelting furnace.

CHAPTER 5

BEHAVIOR IN ELECTROREFINING

As discussed in Chapter 4, a significant portion of the deleterious minor elements contained in the copper-bearing materials feed is eliminated in the smelting operations. However, the impurity content of the anode copper is generally too high to respect typical quality market standards such as ASTM, LME, COMEX (Section 2.6.). The last purification stage in the copper-making flowsheet is electrorefining. In this chapter of the thesis, the behavior of As, Sb, Bi, Pb and Ni in electrorefining is discussed.

It should be noted that the focus of this M.Eng. work is on copper smelting and removal technologies. However, several electrorefineries were visited (Table 3.2.) when located at the same site as the smelter. In these industrial visits the behavior of minor elements in electrorefining was discussed though the information obtained did not permit a complete analysis as for smelting. Therefore, the key related literature is the main source of information. Appendix B lists the complete list of references used.

5.1. MINOR ELEMENTS IN ANODE COPPER

The composition and chemical form of the minor elements in the solid anodes have a direct influence on cathode contamination as they affect parameters such as electrolyte equilibrium composition, anode passivation, slime formation and settling rate, formation of floating or suspended slimes and physical quality of the cathode deposit.

The quality of the copper anode that is electrorefined varies widely due to variations in the initial content in the smelter feed and the smelters' efficiency to remove impurities. Typical anode compositions received at the refinery are given in Table 5.1.

Table 5.1. Typical anode composition from industrial visits. A complete set of results is given in Appendix A.

	Range (ppm)
Cu	98.5-99.8 %
As	240-4000
Sb	50-1100
Bi	10-600
Pb	30-4,000
Ni	70-6,500

Morphology of the copper anode

Most minor elements occur predominantly as a solid solution in the copper anode metal matrix or as discrete inclusions of copper oxides concentrated along the copper grain boundaries formed during anode solidification. The major mineralogical forms of the minor elements in anode copper were studied by Chen and Dutrizac, 1990, and Noguchi et al., 1992. A summary of their results is presented in Table 5.2.

Table 5.2. Microstructure of copper anode based on Chen & Dutrizac, 1990 and Noguchi et al., 1992

Element	Dominant phases	Minor phases
Cu	Metallic matrix	Cu_2O , $\text{Cu}_2(\text{Se,Te})$, complex oxides
As	Cu-solid solution, complex oxides	
Sb	Complex oxides	Cu-solid solution
Bi	Complex oxides	Cu-solid solution
Pb	Cu-solid solution, complex oxides	
Ni	Cu-solid solution	NiO , kupferglimmer ($\text{Cu}_3\text{Ni}_{2-x}\text{SbO}_{6-x}$), complex oxides

5.2. MINOR ELEMENT PARTITIONS

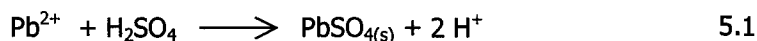
5.2.1. ELECTROMETALLURGICAL PROPERTIES

Standard electrochemical potential (E°_{red}) is a useful tool to interpret the behavior of an element in electrorefining. This parameter is given in Table 5.3. for selected compounds and ions found in the refining electrolyte.

Table 5.3. Standard electrochemical potentials of selected elements [Demopoulos, 1989]

Element	Electrochemical reaction	$E^{\circ}_{\text{red}}(\text{V})$
Cu	$\text{Cu}^{2+} + 2 \text{e}^{-} = \text{Cu}^{\circ}$	0.345
As	$\text{HAsO}_2 + 3 \text{H}^{+} + 3 \text{e}^{-} = \text{As}^{\circ} + \text{H}_2\text{O}$	0.25
Sb	$\text{SbO}^{+} + 2 \text{H}^{+} + 3 \text{e}^{-} = \text{Sb}^{\circ} + \text{H}_2\text{O}$	0.21
Bi	$\text{BiO}^{+} + 2 \text{H}^{+} + 3 \text{e}^{-} = \text{Bi}^{\circ} + \text{H}_2\text{O}$	0.32
Pb	$\text{Pb}^{2+} + 2 \text{e}^{-} = \text{Pb}^{\circ}$	-0.13
Ni	$\text{Ni}^{2+} + 2 \text{e}^{-} = \text{Ni}^{\circ}$	-0.26
Au	$\text{Au}^{3+} + 3 \text{e}^{-} = \text{Au}^{\circ}$	1.42
Ag	$\text{Ag}^{+} + \text{e}^{-} = \text{Ag}^{\circ}$	0.8

Impurities are often divided into three groups according to their behavior during copper electrolysis. The first group is formed of metals more electronegative than Cu (e.g., Ni, Fe, Zn, Co, and Pb). These elements are dissolved at the anode and are not deposited at the cathode, with the result that they accumulate in the solution unless removed by electrolyte purification. An exception is Pb since it reports principally to the slimes as PbSO_4 . This behavior is the result of a rapid reaction of the dissolving Pb with H_2SO_4 in the electrolyte to form an insoluble lead sulfate that precipitates as shown by the following expression:



The second group includes metals that are more noble than Cu (e.g., Au, Ag, Se, Te, Pd, Pt). These elements are largely not dissolved at the anode and pass into the anode slimes.

The third group is formed of the metal impurities with similar electrochemical potentials to copper (i.e., As, Sb, Bi). These elements have a mixed behavior i.e., a part is dissolved in the electrolyte and a part reports to the slimes mainly by the formation of complex insoluble compounds.

This classification is general and can only be used as a guideline to assess trends. The mechanism of electrorefining is much more complicated as complex compounds are formed both in the slimes and in the electrolyte upon dissolution. Major forms of the minor elements in the electrolyte and slimes found in related literature are summarized in Table 5.4.

Table 5.4. Major forms of minor elements in the electrolyte and slimes from the discussion in Chen & Dutrizac, 1990 and Noguchi et al., 1992

Element	Major forms in the electrolyte	Major forms in the slimes
As	HAsO_2 , AsO^+ , complex oxides	As_2O_3 , $(\text{Bi}, \text{Sb})\text{AsO}_4$, Cu_3As , $\text{xPbO} \cdot \text{As}_2\text{O}_5$,
Sb	SbO^+ , complex oxides	Sb_2O_3 , SbAsO_4 , $\text{xPbO} \cdot \text{Sb}_2\text{O}_5$
Bi	BiO^+ , complex oxides	Bi_2O_3 , BiAsO_4 , $\text{xPbO} \cdot \text{Bi}_2\text{O}_5$, $\text{Bi}_2(\text{SO}_4)_3$
Pb	Negligible [complex oxides]	PbSO_4 , $\text{xPbO} \cdot \text{As}_2\text{O}_5$, $\text{xPbO} \cdot \text{Sb}_2\text{O}_5$
Ni	Ni^{2+}	Negligible [NiO , $3\text{CuO} \cdot 4\text{NiO} \cdot \text{Sb}_2\text{O}_5$, $\text{NiSO}_4 \cdot 4 \text{H}_2\text{O}$]

5.2.2. INDUSTRIAL DISTRIBUTIONS

The industrial distributions generally follow the behaviors predicted by the analysis of electrochemical potentials. Figure 5.1. gives an example of a typical minor element partitions taken from the literature [Biswas and Davenport, 1994].

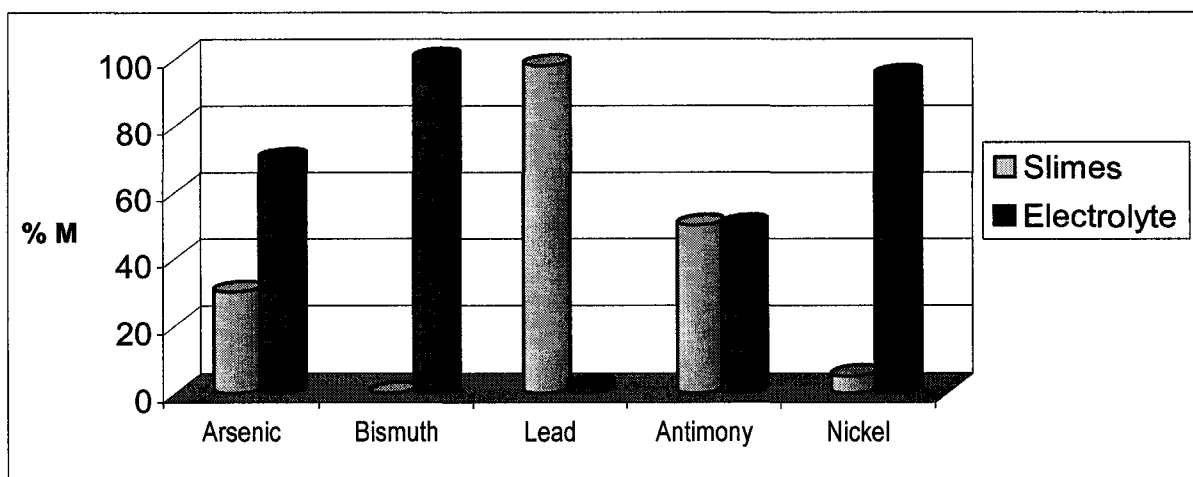


Figure 5.1. Typical industrial partitions of minor elements in copper electrorefining from Biswas and Davenport, 1994

The distribution presented confirms the trends discussed earlier: Pb reports mainly to slimes; Ni to the electrolyte; As and Sb have mixed behavior. An exception is Bi for which Figure 5.1. indicates complete dissolution into the electrolyte. From industrial visits and discussions with plant engineers, this is only valid at very low concentrations of both lead and bismuth in the anode. Although no indication was presented in the reference [Biswas and Davenport, 1994] for the provenance of this data, it is believed that the distribution presented is for a plant treating very low levels of both Pb and Bi. It was observed that up to 30% of the bismuth reports to anode slimes in most electrorefineries visited which confirms the mixed behavior of this element.

An industrial distribution should be taken with caution because the behavior of minor elements in electrorefining depends on the anode composition as well as several process parameters. As the operation of a given tankhouse can change with time and anode composition, the partition can vary significantly even for the same plant.

5.2.3. EFFECT OF INITIAL ANODE CONCENTRATION ON PARTITIONS

Most operating parameters (current density, cycle time, electrolyte circulation, etc.) are relatively constant for a given refinery as they are dictated by design and productivity considerations. However, a parameter that can vary considerably is anode composition. This is especially true for refineries treating anodes from various sources. Appendix A gives the average anode composition of the smelters visited. Several researches have proven minor element partitions in electrorefining to be affected significantly by anode composition. Their findings are summarized below for As, Sb, Bi. Because of their strong tendencies, Pb (to slimes) and Ni (to electrolyte) are not affected significantly by the anode composition.

Arsenic:

From experimental work on 24 anodes and industrial observations at the Canadian Copper Refinery (CCR), Claessens et al., 1983, revealed that the major factor influencing the distribution of As in electrorefining is its concentration in the anode. A non-linear relationship between the arsenic content of the anodes and the percentage of arsenic reporting to the slimes was found from their experimental results reproduced in Figure 5.2.

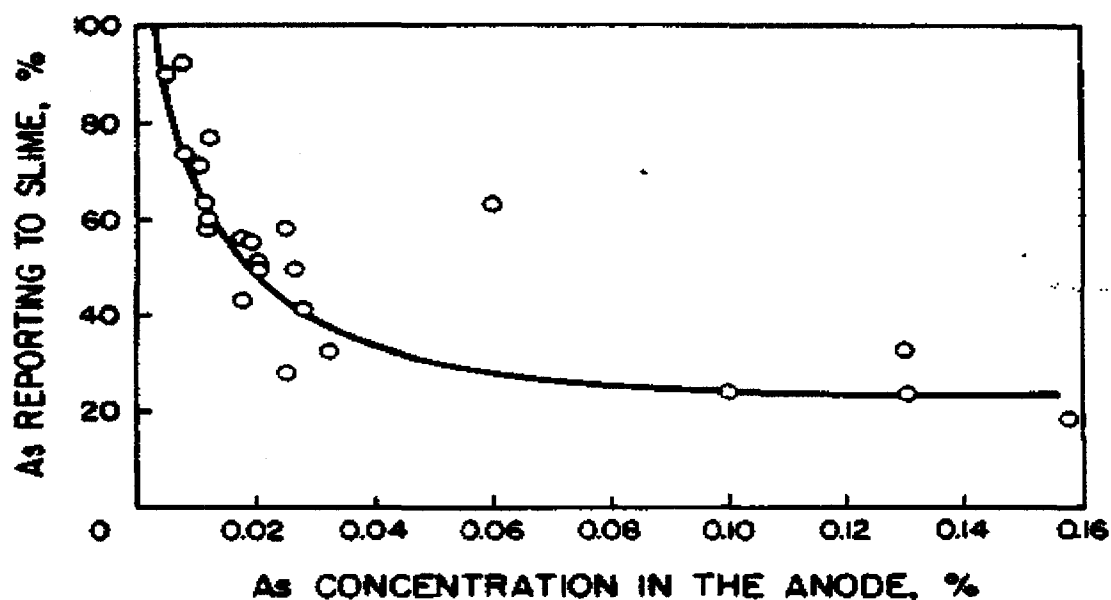


Figure 5.2. Effect of As concentration in the anode on distribution during electrorefining from Claessens et al., 1983

It was found that at low concentration, the fraction of As that reports to slime is strongly dependent on anode composition. For the electrorefining of an anode with more than 0.1 wt% As, approximately 25-30% reports to slime. These findings have been generally confirmed by Demaerel, 1987.

Based on the experimental work of Claessens et al., 1983, Baltazar et al., 1987 reported a mathematical correlation to quantify the distribution of As in electrorefining as a function of the anode composition:

$$\text{As (\% to electrolyte)} = 80 (1 - \exp [-45(\% \text{As})_{\text{anode}}]) \quad 5.2.$$

It can be noted that this relation is only useful to operators who need to anticipate the amount that is deported to the electrolyte to control its composition but it shows the dependence on anode concentration.

Antimony:

The behavior of Sb is not solely influenced by its concentration in the anode such as for As. Sb distribution depends primarily on the amount of slimes formed which is closely related to the Pb content and As/(Sb+Bi) ratio of the anode. Baltazar et al., 1987, correlated their observations on Sb distribution and derived the following expression:

$$\text{Sb(\% to electrolyte)} = 49.03 - 159.87 (\% \text{Pb})_{\text{anode}} + 10.46 [(\% \text{As})/(\% \text{Sb} + \% \text{Bi})]_{\text{anode}} \quad 5.3$$

This linear equation is valid only in a certain range of concentrations and for a given set of operating parameters. Nevertheless, it indicates that the Pb content of the anode is the dominant factor influencing the distribution of Sb.

Bismuth:

Similarly to Pb, Bi behavior is mainly affected by the Pb composition of the anodes. Claessens et al., 1983 derived a correlation for the distribution of Bi in electrorefining as a function of the anode composition. After simple mathematical transformations to respect the notation used before, their correlation can be modified to:

$$\text{Bi (\% to electrolyte)} = 73.0 - 336.6 (\% \text{Pb})_{\text{anode}} \quad 5.4$$

The observation that the relative amounts of Bi and Sb reporting to anode slimes increases rapidly with increasing Pb concentration in the anode is at the origin of the removal technique known as 'lead doping'. It consists essentially of doping the copper anode prior to its casting with Pb to eliminate more Sb and Bi to the anode slimes in the electrorefining. More details will be given in the next chapter.

5.2.4. CONTAMINATION MECHANISMS

Because As, Sb, Bi, Pb and Ni are more electronegative than copper (Table 5.3), they are anodically dissolved in the electrolyte but are not plated at the cathode. Except in rare cases with uneven current distributions and localized overpotentials, product contamination does not occur by electroplating [Abe & Takasawa, 1987].

Research and industrial observations have shown that during the electrorefining of copper, cathode contamination occurs either by electrolyte entrapment in porous, rough cathode deposits or by 'occlusion' of solid particles on the cathode surface.

ELECTROLYTE ENTRAPMENT

Electrolyte entrapment is a physical phenomenon by which the supporting electrolyte with all the impurities it contains is integrated into the cathode structure around open or coarse nodular deposits. The composition of the electrolyte and the quality of the cathodic deposit have a strong influence on the magnitude of contamination by electrolyte entrapment.

Electrolyte composition

Copper electrorefining is a dynamic process in which the minor elements are continuously dissolved at the anode and report either to the cathode, the electrolyte or the slimes. A portion of the electrolyte has to be taken out of the system for treatment to keep a steady-state composition. Electrowinning of the metals present in the bled electrolyte, also known as liberation, is the preferred purification method. Other means such as ion exchange and solvent extraction also exist to remove selectively some minor elements. More details on electrolyte purification methods are given in the next chapter.

Various parameters have an influence on the minor element content of the electrolyte in addition to anode composition (Section 5.1.). As an example, acid concentration [Baltazar et al., 1984] has a strong impact on minor element solubility, especially Bi. Noguchi et al., 1992; Abe et al.,

1987; and Demaerel, 1987 have also shown that the oxygen content of the anode and of the electrolyte have a strong influence on the deportment of minor elements.

Quality of the cathode deposit

The quality of the copper deposit is a major factor in the prevention of electrolyte entrapment. Additives (glue, thiourea, etc.) are used industrially to improve the physical structure of the deposit. The use of stainless steel starting sheets (ISA and Kidd processes) is also known to improve the physical quality of the deposit over the traditional process using copper as a starting material. It is noteworthy that surface properties of the copper cathode deposit deteriorate significantly at high current density [Baltazar et al., 1987] which characterize modern copper electrorefinery practice.

OCCLUSION OF SOLID PARTICLES

Two types of solid particles can contaminate the cathode deposit. Slime particles can be carried from the vicinity of the anode to the cathode surface by electrolyte convection. Also, particles can precipitate out of the electrolyte due to mutual interactions between the electrolyte constituents and then reach the cathode surface.

Slimes particles by convection

The extent of cathode contamination by slime occlusion depends on electrorefining parameters such as the composition of the anode, the morphology of the copper deposit, the electrolyte circulation rate and pattern, the anode passivation extent as well as characteristics of the slime particles such as specific gravity and particle size. Passivation is the inhibition of dissolution reaction caused by the formation of non-dissolving films, usually $\text{CuSO}_4 \cdot x\text{H}_2\text{O}$. Its occurrence depends on several electrorefining parameters as studied by Moats, 1999. The consequence of anode passivation on cathode purity is that the non-adherent slime layer causes an increase in the amount of suspended anode slime particles in the electrolyte. As a result, the probability of contamination of the cathode deposit is increased.

Precipitation of insoluble complexes

Chemical reactions within the electrolyte yield the formation of complexes with low solubility at the operating temperature. They are usually Cu-Pb-As-Sb-Bi-Ni oxides of varying stoichiometry. Precipitation can occur in the bulk of the electrolyte but is usually localized on a surface such as anode, cathode, cell walls and electrolyte circulation circuit internal surfaces. Precipitates of high minor element concentration are frequently observed in regions where the electrolyte temperature is locally lower than in the cell such as the circulation pipes.

FLOATING SLIMES

Among these complex precipitates, floating slimes are probably the most famous category of compounds leading to cathode contamination. They get their name because they usually separate as fine floating particles that can be entrained easily by the cathode. Floating slimes include various amorphous compounds containing high concentration of Sb^{5+} as well as As and Bi. The presence of variable quantities of carbon has also been observed in the industry. The structure of the floating slimes has not been defined with exactitude because of the several chemical compounds grouped in this category. Another type of floating slimes has been observed in industry in the form of a viscous and transparent film, which can cover the anode surface and results in anode passivation. This will affect the tankhouse productivity and cathode purity as discussed earlier in this section.

The presence of As has a major impact on the formation of floating slimes. As and Sb dissolve as trivalent species at the anode and can be oxidized further in the electrolyte in the presence of oxygen by the catalytic action of the cuprous ions. Because the oxidation of As^{3+} to As^{5+} is faster than the oxidation of Sb^{3+} to Sb^{5+} , As^{3+} oxidizes preferentially. Therefore, as long as As^{3+} is present in the system, most Sb stays in the trivalent state. When no more As^{3+} is available, Sb^{3+} oxidizes readily to Sb^{5+} , which further hydrolysis to $\text{Sb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, one of the major compounds of floating slimes. A similar situation can be expected for Bi, another important constituent of the floating slimes.

As a consequence, a control strategy to minimize the occurrence of floating slimes has been adopted by most electrorefineries. The philosophy is to ensure the presence of As^{3+} . Practically, it is controlled with a ratio, the simplest version of which is the ratio $(\text{wt}\% \text{ As})/(\text{wt}\% \text{ Sb})$. For refineries with relatively high level of Bi in the circuit, the ratio is modified to $\text{As}/(\text{Sb}+\text{Bi})$. Some plants use weight fraction in the anode whereas others calculate the ratio from the fraction of the deleterious elements passing to the electrolyte. The set point of these ratios varies from 0.5 to 8 according to the experience of the electrorefinery with floating slimes.

When the ratio is under the set point of the refinery, As can be added to the anode or the electrolyte to ensure enough As^{3+} is present to suppress the formation of floating slimes. This action is referred to as 'arsenic anode or electrolyte doping' in the jargon of the industry. More details on this control technique are given in Chapter 6.

CHAPTER 6

REMOVAL TECHNOLOGIES

The ability to remove minor elements in a conventional smelting/electrorefining flowsheet is sometimes not sufficient to treat a given feed and produce quality cathodes, i.e., optimization of operating parameters alone may not be sufficient. As a consequence, specific technologies were conceived and integrated into conventional copper production to permit an improved elimination of minor elements.

In this chapter, specially developed control and removal technologies encountered in the industry are described and a brief analysis is presented. The financial aspects (operating and capital cost) are only qualitatively estimated as it was not the main purpose of this work.

Removal technologies were arbitrarily classified into five categories: (i) feed pre-treatment; (ii) extraction from molten matte or copper; (iii) dust bleed and treatment; (iv) anode doping; and (v) electrolyte purification. It should be noted that a few ideas/concepts without current industrial application, such as vacuum refining and hydrometallurgical pre-treatment of concentrate, are also presented because they appear promising to the author.

It should be pointed out the description of each technology is brief. More details can be found in the references, specially organized in Appendix B to guide the reader to related articles on a specific technology. Moreover, the names of the companies operating the technique are usually given and direct contact or visit is certainly the best route to obtain updated information.

6.1. FEED PRE-TREATMENT

The objective of feed pre-treatment is to remove the minor elements prior to sending the concentrate (or other contaminated feed material) to the smelter. It can be carried out at the mine or smelter site. This approach would deal with the problem at the source instead of being forced to develop complicated treatment for their removal later in the flowsheet. Examples of pre-treatment are impurity removal by roasting, vacuum refining in the solid state and leaching, all of which are briefly described in this section. To the knowledge of the author, only one specialized industrial application exists namely, the roasting plant at El Indio in Chile. The main restriction of feed pre-treatment is the limited flexibility as removal efficiency depends to a large extent on the mineralogy of the concentrate/feed to be treated. In addition, stabilization of the effluents (gas or liquid effluent) can represent environmental challenges.

6.1.1. ROASTING

Target elements: As, Bi, Sb, Pb

During the pre 1980's, roasting was used in the copper smelting operations to partially oxidize the copper concentrate prior to melting in electric, blast or reverberatory furnaces. The need to capture the off-gases from the smelting furnace and high roaster operating cost eliminated the use of this technology in modern smelting processes. Nevertheless, roasting has found localized application in the pre-treatment of contaminated materials to preferentially remove the volatile forms of the minor elements at high temperature.

Principle:

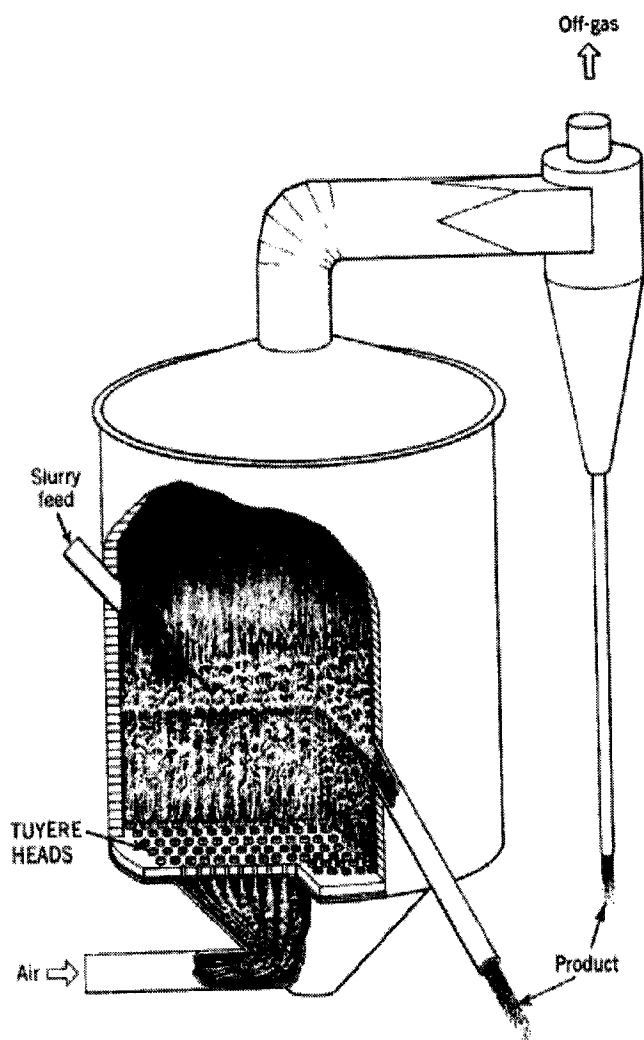
The theory behind the application of roasting for minor element elimination simply consists of heating the solid contaminated material (concentrate, flue dust, ore, etc.) to increase the sublimation of the impurities. Temperature, type of atmosphere and design of roaster (exposed area over volume) are critical parameters.

The roasting temperature should be as high as possible without melting or detrimental sintering of the solid product or calcine, i.e., the roasted material. Table 4.6., presented earlier, gives numerical correlations for the vapor pressure of selected minor element species as a function of temperature. It can be seen that the vapor pressure increases with temperature. The kinetics of volatilization reactions are also favored by an increase in temperature.

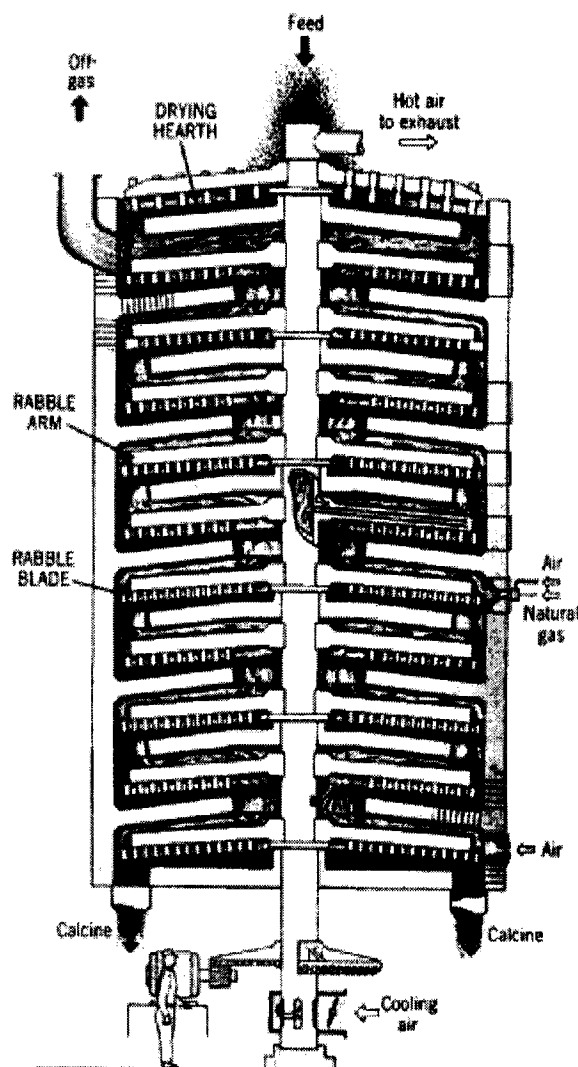
The composition of the atmosphere strongly affects the roasting rate. In theory, roasting pre-treatment can be performed under virtually any atmosphere to maximize vapor pressure of the element to be removed. For the treatment of copper concentrates, the main two choices of roasting atmospheres are oxidizing (high pO_2) or reducing conditions (high pS_2). Oxidizing atmospheres can be produced by having air or oxygen-enriched air surroundings the solids while a reducing atmosphere minimizes oxygen presence through the use of fossil-fuel burners at air/fuel ratio below stoichiometry. Oxide species volatilization is enhanced by oxidizing conditions whereas sulfide species volatilization is favored by reducing conditions. It is also noted that laboratory research has been performed with success for selective roasting of Sb, As and Bi in a chlorinated atmosphere due to the high vapor pressure of their chlorides [Holmstrom, 1989].

Increasing the surface area of the material exposed to roasting atmosphere to volume of material (A/V ratio) is of prime importance to increasing the kinetics of roasting. The size of the roaster required to achieve a desired level of elimination is determined primarily by this ratio. The higher the A/V ratio is the smaller the roaster would be. In order to maximize this ratio, two different designs of roasters are industrially used: fluid-bed and multiple-hearths roasters. The A/V ratio is higher in a fluid bed roaster because the particles are surrounded by the roasting atmosphere but a multiple-hearths roaster has the advantage for impurity removal that temperature and gas composition on each tray can be controlled. Figure 6.1 provides a schematic representation of each type of equipment.

Specific roasting applications have been patented around the general principles presented above. A complete description of all patented technology features such as NESA's selective roasting, Outokumpu's sulfidizing vaporization roasting, and fluid bed roasting of low grade bismuth containing sulfide ore is beyond the scope of this work. Appendix B contains references detailing each of these processes.



(A)



(B)

Figure 6.1. Schematic representation of industrial roasters: A- fluid-bed ; B- multiple-hearths reproduced from Biswas and Davenport, 1994

Industrial practice:

In the copper industry, pre-treatment of concentrate by roasting has found a niche mainly for arsenic removal. It is presently used by El Indio in Chile to treat high arsenic copper concentrate. In the past, it was applied at NMM-Saganoseki (Japan), Tsumeb (Namibia), Pasar (Philippines) and Boliden-Ronnskar (Sweden), Asarco-Tacoma (USA), and Refimet S.A. (Chile). Several gold mines have adopted this practice for arsenic removal prior to cyanide process. Other applications might also be ignored by the author.

Although arsenic removal can be achieved under oxidizing atmosphere via the volatilization of As_4O_6 , the $p\text{O}_2$ has to be strictly controlled to avoid formation of non-volatile compounds such as As_2O_5 and FeAsO_4 . Therefore, reducing conditions are generally selected for industrial roaster as control is easier and it is the As_4S_6 specie that volatilizes. More details on Saganoseki and El Indio's experiences with roasting are given below based on Yoshimura, 1962 and Smith, 1986, respectively.

SAGANOSEKI:

In the 1950's, the Saganoseki smelter had to treat an ore with about 2% As as enargite (Cu_3AsS_4) from the Kinkaseki mine. Saganoseki was among the first to evaluate the feasibility of roasting as a pre-treatment of enargite to enhance the volatilization of arsenic. Extensive testwork and pilot tests were performed to identify the optimum roasting conditions. A 40 tons per day fluid bed roaster was built in 1959. Dearsenizing of more than 80% was observed in an atmosphere rich in SO_2 (14-16%) and low in O_2 (<0.6%) and CO_2 at temperatures above 600°C . Volatilization occurred from the decomposition of enargite as follow:



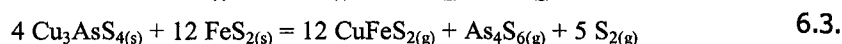
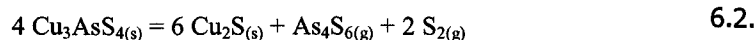
The volatilized As_4S_6 and part of the S_2 were oxidized to As_2O_3 and SO_2 in the presence of air in the off-gas and recovered as As_2O_3 and sulfuric acid, respectively. The roasted ore was sent to the matte smelting furnace. The roasting plant at Saganoseki is now closed most likely because of the exhaustion of the Kinkaseki ore and high cost of the operation.

EL INDIO MINE:

Concentrate with an average composition of 8.5% As is produced from an arsenic-rich ore body containing enargite (Cu_3AsS_4), scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$), and tennantite ($(\text{CuFe})_{12}\text{As}_4\text{S}_{13}$). It should be noted that roasting is done directly at the mine site as opposed to the smelter site at Saganoseki. Roasting is performed under reduced conditions in 3 multiple-hearth roasters to reduce the As content to less than 0.5% As which is acceptable for copper smelting. Arsenic trioxide is also produced as a by-product through subsequent oxidation.

About 8.5 tph of concentrate is treated at this facility and the residence time of 3 hrs is obtained with a rotation of the rates adjusted to 2 RPM. The upper part of the roaster is maintained at about 650°C with an oxygen concentration of 2% while the bottom is at 725°C and 1% O_2 .

Heating is by bunker-C oil-fired burners. Enargite decomposition is believed to happen as follows:



A post-combustion chamber at about 775°C and 4-8% O₂ ensures the conversion of As₄S₆ to As₂O₃. After cooling the gases to increase the efficiency of the gas collection device, As₂O₃ of a purity greater than 95% is packaged and can be sold.

Process Evaluation:

Industrial roasters at Saganoseki and El Indio have shown excellent removal efficiency for arsenic. Because roasting is performed under reduced atmosphere, low sulfur oxidation in the roasted material occurs and it can be sent to the smelter. If oxidizing or dead roasting (complete oxidation) is carried out, a significant part (or all) of sulfur associated with iron and copper is anticipated to be oxidized. Therefore, this feed would not be suitable for a modern smelting furnace as a large part of the heat supply comes from sulfur oxidation and it would probably have to be treated hydrometallurgically where a large part of the precious metals are lost.

Roasters (fluid bed or multiple-hearths) are mature technologies with well established operations. However, there are limited health and safety risks for workers around the unit if proper protection equipment is not worn as leakage of gas rich in harmful arsenic can occur.

The cost of construction of the roasting unit is not known but believed to be moderate. The operating costs are mainly labor and fossil fuel which largely depend on the location. They have to be compared to the benefits related with the high elimination of minor elements. If the roaster off-gas could be emitted directly to the atmosphere, roasting would certainly be a removal technique of choice. However, from environmental regulations in most countries, a costly off-gas treatment has to be constructed to fix arsenic and SO₂. Typical off-gas treatment includes a cooling system, a baghouse or ESP, a wet scrubber and sometimes an acid plant to fix SO₂. A scrubbing liquor treatment plant has to be built to ensure stabilization of arsenic in the effluent. The cost of all these units related to gas treatment is greater than the cost of the roaster itself and may represent a major obstacle. This is especially true if a costly acid plant has to be constructed for SO₂ fixation.

The demand for As_2O_3 by-product is gradually shrinking due to the high concerns regarding the potential toxicity of arsenic. As a consequence, it may be necessary to sell it at a loss or pay extra charges for proper disposal if no market is found.

Although antimony, bismuth and lead removal by roasting has not found industrial application it is theoretically possible [Cauwe et al., 1983; Imris et al., 1980; Imris and Komorava, 1993; Wadia and Olivares, 1975]. However, elimination should be slower resulting in a lower efficiency for a given size of roaster as corresponding compounds are less volatile than those of arsenic.

6.1.2. THERMAL DECOMPOSITION OF CONCENTRATE UNDER VACUUM

Target elements: As, Bi, Pb, Sb

Principle:

The principle is similar to roasting except a vacuum is created over the concentrate to increase volatilization kinetics by decreasing the partial pressure of volatilized species in the gas phase to increase the rates of phase mass transport. This enhances the thermal decomposition of the element. Again, the concentrate is heated to maximum temperature without melting or sintering.

Experimental work carried out by Villarroel, 1999, showed elimination greater than 99% for As, Bi, Sb and Pb for a one hour treatment in a vacuum of 10^{-2} mm Hg at 950°C . Three main variables affecting the extent of elimination were identified, namely, temperature, time of treatment and level of vacuum. Impurity elements and elemental sulfur separated in the condensation apparatus. Preliminary laboratory results from Jiang and Roumeliotis (to be published in 2002) are also promising.

Industrial practices:

None reported

Process evaluation:

The concept is simple and preliminary laboratory evaluations prove the technical feasibility of the process. However, the greatest challenge that faces thermal decomposition of impurity species under vacuum is the lack of technology to transfer the concept to the industry. In the laboratory, the volatilization rates were high resulting in good removal efficiencies. However, in those experiments, the area/volume ratio of the particles is high and quantities of concentrate that were used were small. The existing large-scale equipment used to maximize A/V (rotary kiln,

multiple-hearths and fluid-bed roasters) is not currently compatible with the vacuum. In addition to complex condensation equipment required, gas treatment (probably baghouse) under vacuum will be needed to avoid damage to the vacuum pump that is also a technological challenge.

The energy cost to heat up concentrate (fuel or electricity) from room temperature to about 900°C also has to be considered especially because of poor concentrate thermal conductivity. Villarroel, 2000, proposed a new design of industrial furnace for the concept. He suggested to heat up the concentrate in an indirect way using the thermal energy from the hot gases produced in smelting and converting. The concentrate is submitted to a vacuum in an hermetically sealed vacuum tunnel where it flows by gravity. The species in the off-gas can be separated by stepwise condensation. To the opinion of the author, Villarroel's proposal is a good start but many uncertainties have to be addressed by piloting prior to industrial application of refining copper concentrate with the use of vacuum.

On the positive side, the advantages of the concept exist and if proper technology is developed, it might represent a breakthrough in the copper industry. Moreover, experimental work by Villarroel, 1999, performed on various concentrates suggests that the dependence of the origin or mineralogy of copper concentrate on process efficiency is small. However, the removal efficiency was so high that it is very hard to compare for the various concentrates tested. More tests should be performed to confirm this observation.

The gas treatment from decomposition of concentrate under vacuum is also uncertain. If condensers can be used as suggested by Villarroel, it might eliminate the need for a costly acid plant associated with conventional roasters. Elemental sulfur and minor element sulfides would be condensed in this way. However, more work needs to be done to confirm off-gas treatment as environmental performance might represent a major limitation.

6.1.3. HYDROMETALLURGICAL PRE-TREATMENT OF CONCENTRATE

Target elements: As, Sb, Bi

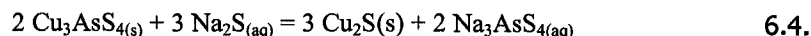
Hydrometallurgical treatment of copper sulfide ores and concentrates, as an alternative to smelting, has been the subject of several research efforts in the last few decades. Precious metal recovery, dependence on mineralogy, stabilization of residues and cost are still obstacles to large-scale production. However, the application of hydrometallurgical pre-treatment of concentrate for minor element removal represents a promising option.

Principle:

Selective leaching and removal of deleterious minor elements from the copper concentrate is the general objective of hydrometallurgical pre-treatment. The leach residue containing copper sulfide and precious metals is sent to the smelter.

The element targeted and mineralogy of the concentrate would be the main factors determining the process. Examples from laboratory research are the leaching of tenantite in acid medium of FeCl_3 [Dutrizac and Morrison, 1994], ammonia leaching of enargite at small overpressure of oxygen [Gajam and Raghavan, 1998], leaching of enargite in sodium sulfide [Achimovicova et al., 1998], leaching of tetrahedrite calcine (from roasting) by alkaline solution (NaOH , Na_2S) [Anderson, 2000 ; Komorava and Imris, 1993] and bismuth extraction by sulfuric and hydrochloric solutions [Wadia and Olivares, 1975]. Bio-oxidation was also claimed to be capable of removing selectively bismuth from copper concentrate [Tuovinen and Setälä, 1982].

An example of selective leaching of enargite to remove arsenic by sodium sulfide, is given in the following equation [Achimovicova et al., 1998]:



The copper sulfide can be sent to the smelter with the precious metals in the leach residue and Na_3AsS_4 can be discarded by proper stabilization treatment.

Industrial practices:

None reported in the copper industry presently. However, a similar application for antimony removal was used at Equity Silver Mines Ltd. in Canada [Anderson et al., 1992; Edwards, C.R., 1985; Edwards, C.R., 1991].

Process evaluation:

Capital costs are believed to be moderate for a hydrometallurgical pre-treatment. On the other hand, high operating cost from reagent consumption is the main barrier to industrial use. Excess reagent would probably be necessary due to side reactions. Costs could be reduced by treating only the part which is contaminated with high levels of minor elements as compared with the overall smelter's feed.

Impurities might be recovered from leach solution by selective precipitation. If a market exists for them, additional revenues may be generated. On the other hand, if disposed in the environment, a stabilization process is required for the effluent. In both cases, extra costs are involved. Cost of drying also has to be considered if this process is carried out at the smelter site whereas at the mine the concentrate has to be dried anyway. In addition, expensive fine grinding might also be necessary to maximize the surface area exposed to the leach solution.

For most hydrometallurgical processes, the lack of flexibility caused by the influence of mineralogy on leaching thermodynamics and kinetics is a weakness. This is especially true for a custom smelter where this process would be used on various feeds.

6.2. EXTRACTION FROM MOLTEN MATTE OR COPPER MELT

6.2.1. COPPER BLOW WITH CALCIUM OXIDE TYPE SLAG IN PEIRCE-SMITH CONVERTERS

Target elements: As, Sb

Some continuous converting processes (Mitsubishi C-Furnace, Kenecott-Outokumpu Flash Converting Furnace) use calcium-ferrite slag because, at the high oxygen partial pressure encountered, this type of slag remains fluid from its greater solubility for magnetite. Another property of this Ca-Fe slag system is to favor deportment of acidic arsenic and antimony oxides to slag. Some smelters with high loads of these elements have adapted their traditional Peirce-Smith vessel operation to take advantage of this property.

Principle:

The objective is to use a CaO based slag during the final 'copper blow' in the Peirce-Smith converters to increase deportment of arsenic and antimony to slag as described in Section 4.2.5. Calcium oxide bearing material (CaO or CaCO₃) is added to the converter to this extent. It reacts with Fe_xO_y and SiO₂ present in the converter from added cooling materials and carried over from the 'slag blow' and Cu₂O formed during the blow. Acuna and Zuniga, 1995, have measured the pseudoternary Cu₂O-Fe₃O₄-CaO system (1473 K) at 9% SiO₂ as reproduced in Figure 6.2. This diagram indicates that depending on Cu₂O and Fe₃O₄ slag content, fluid slag can be obtained up to about 28% CaO at 1200°C and up to 35% CaO at 1300°C.

Industrial practices:

CODELCO - Chuquicamata [Acuna et al., 1999] and Mexicana de Cobre - La Caridad [Fernandez, 1993] smelters tested the use of Ca-Fe slag to enhance deportment of arsenic to slag during copper blow. Since 1996, Chuquicamata has been using this process industrially in conjunction with alkaline fire refining (Section 6.2.3). La Caridad tested the process successfully for 6 months in 1992-1993 and now uses it only when high arsenic matte has to be converted. At the Dow - Kosaka smelter, a similar process (same type of slag) is used in conjunction with high overblowing (formation of Cu₂O and Me_xO_y of major minor elements) in the final copper blow to improve elimination of As and Sb. Discussions indicated that some European smelters use a similar process for Sb removal but this has yet to be confirmed.

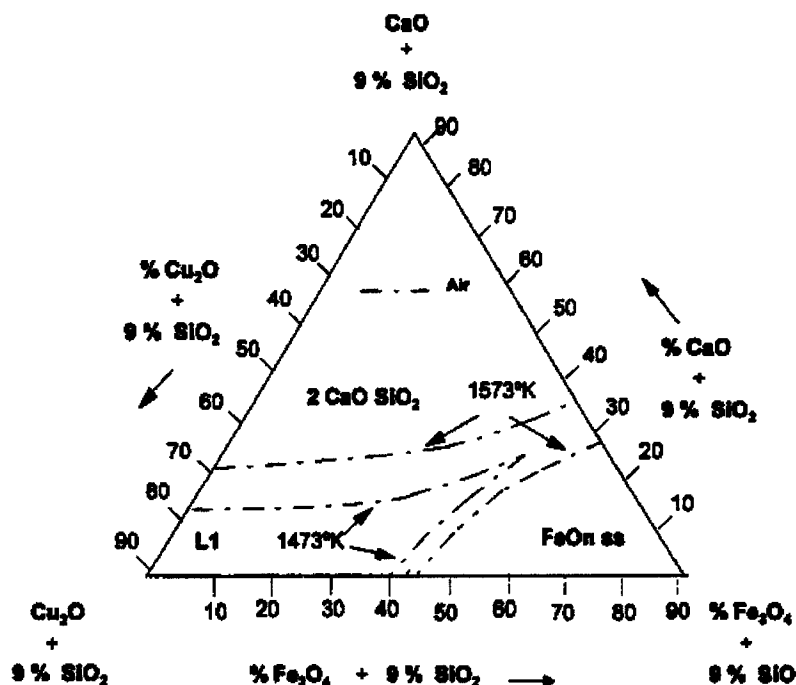


Figure 6.2. Pseudoternary Cu_2O - Fe_3O_4 - CaO system at 9% SiO_2 for smelting tests under air atmosphere. Reproduced from Acuna and Zuniga, 1995.

Limestone is the reagent of chosen for industrial applications because it is less expensive than lime. It is added to the Peirce-Smith converter during the copper blow. At La Caridad, the amount added is fixed at around 2.5 tonnes limestone per charge while at Chuquicamata, the tonnage added is controlled to obtain between 18-24% CaO in slag depending on converters' temperature.

Results at La Caridad indicated a reduction of average arsenic content in anodes from 1250 to 950 ppm (~25%) with this practice with the same feed to the smelter. At Chuquicamata, an optimum distribution coefficient $L_{\text{As}}^{\text{slag/matte}}$ having a value of around 5 was observed in industrial operations. It was noted by Acuna et al., 1999, that oxygen content in copper with an optimum around 7000 ppm $[\text{O}]$, arsenic composition in white metal and basicity index $[\% \text{CaO} / (\% \text{FeO} + \% \text{Fe}_2\text{O}_3 + \% \text{SiO}_2 + \% \text{Cu}_2\text{O})]$ are the main variables affecting removal efficiency.

Process evaluation:

This process is simple and requires negligible capital investment. The cost of reagent is the main operating cost. Limestone is decomposed to CaO and CO_{2(g)} at the converting temperatures. Acuna et al., 1999, noted that the decrease in fluxing efficiency was less than 10% with limestone as compared with pure lime. On the other hand, the use of limestone has an impact the temperature of the vessel as its decomposition is endothermic. Some health and safety related issues from the thermal decomposition of limestone at the surface of the bath that might be violent also exist.

To obtain a significant improvement in arsenic and antimony elimination, this Ca-Fe minor element fluxing in Peirce-Smith converters has to be fully understood and major operating parameters controlled. Just adding calcium oxide during copper blow might help but a strict control of dissolved oxygen in copper and slag chemistry affect dramatically the elimination as highlighted by Acuna et al., 1999. Fluidity of the slag will also be set by the chemistry and temperature of operation.

The benefits of improved As and Sb deportment to slag might be offset by the lower Pb (and potentially Bi) removal with this type of slag in comparison with fayalite-based slag. This requires a case-to-case evaluation as it depends on the relative input of these elements to the smelter and refinery limits for anode copper.

The use of calcium ferrite slag is reputed to accelerate refractory wear. Industrial experience at Chuquicamata and La Caridad was contradictory. At La Caridad, a significant reduction in converter life was observed during the tests performed (24,000 vs. 35,000 tonnes blister/converter cycle = 30% reduction). At Chuquicamata, no significant/visible refractory wear was observed.

The slag produced contained high levels of Cu₂O and/or entrained copper and had to be recycled to the smelting or converting vessels for economic reasons. Recycling to the smelting vessel would permit a better overall elimination than to the converting furnace. This slag is highly oxidized and might react violently with sulfides present in other vessels upon recycling which may lead to fugitive SO₂ that is difficult to capture by process ventilation. In the extreme case, recycling of the molten slag might generate foaming in the vessel. Also, the impact of recycled CaO on smelting or converting slag has to be considered (fluidity, minor element removal, etc.).

6.2.2 CONCENTRATE INJECTION IN PEIRCE-SMITH CONVERTERS

Target elements: Bi, As, Sb and Pb

Concentrate injection in Peirce-Smith converters is generally used by smelters to improve productivity and to give more flexibility to the converting aisle. In addition to these primary objectives, concentrate injection is an excellent way to increase the elimination of the most volatile minor elements (Bi, As, Pb) when clean concentrate is injected.

Principle:

Concentrate injection permits the prolongation of the 'slag blow' in the converter and so enhances volatilization which is especially important for volatile elements such as As and Bi. The greater the amount of slag produced also serves to eliminate more Sb and Pb in slag. This is only valid if a clean concentrate (free of minor elements) is injected. Otherwise, the effect of concentrate injection is diluted by the impurities added during the blow.

Copper concentrates to be injected need to be dried. An injection system (usually pneumatic) is required to add the concentrate by blowing through the tuyeres during the 'slag blow'. It should be noted that oxygen enrichment (or fuel) is needed to close the heat balance of the converter because of the cold concentrate added. The slag produced during concentrate injection is skimmed after the blow and the converter charge moves to its 'going high' (remaining Fe removal) or another injection blow is done. A matte grade between 60 and 70% Cu is generally targeted for injection. In reality, concentrate injection reproduces matte smelting conditions in a Peirce-Smith converting vessel.

Industrial practices:

All Noranda smelters (Horne, Gaspé, Altonorte) have used concentrate injection in Peirce-Smith converters. It is still in use at Gaspé and Altonorte, whereas, it was stopped at the Horne in 1996. Concentrate injection in Peirce-Smith converters is also used at Onahama smelter. They all follow the same operating philosophy described above. Presently, concentrate injection is mainly used to increase productivity. However, its use for minor element control (Sb and Bi) was particularly developed at the Horne smelter where it was sometimes done as a polishing tool for converter charges with impurity levels higher than anode requirements [Godbehere et al., 1993].

Process evaluation:

The capital cost of the bins, dryer, injection system is from moderate to high depending on the size of the system. To this, the cost of an oxygen production plant has to be added. The process can be fully automated and operating costs are low. This is certainly an attractive alternative to any smelter for productivity improvement at minimum capital cost (versus changing the whole smelting process). However, this process is too capital extensive for minor element control only. If concentrate injection is in place, it can be used to the advantage of the smelter to improve the elimination of minor elements.

Nowadays, a challenge might be to find a clean concentrate (low impurity levels) to inject for minor element elimination. This is especially true for a custom smelter as the clean concentrates on the market are scarce and treatment charges are much lower than for the dirty ones.

The operation of concentrate injection is relatively simple. The metallurgical challenges, except for chemistry (constant matte grade during injection) and heat balance control (O_2 vs. tonnage injected), are minimum. However, a level of complexity is introduced to the operation of the converter aisle scheduling when concentrate injection is first implemented. Experience shows that such difficulties are short lived.

6.2.3. FLUXING IN ANODE FURNACE

Target elements: As, Sb and Pb

Extraction of arsenic and antimony from copper by alkaline fluxing has been used for several decades by the copper industry [e.g., Eddy, 1931]. Silica fluxing to remove lead from copper is also used industrially. In this section, the general principle of fluxing to remove impurities from copper is explained. Alkaline and silica fluxing will be treated separately for a discussion on industrial applications and process evaluation. It should be noted that no fluxing system for Bi elimination has been transferred industrially yet.

Principle:

Fluxing in anode furnace entails oxidation of the minor elements contained in the copper and their transfer to the slag phase. Oxidation reactions were discussed earlier in Chapter 4. It was found that deportment to slag can be expressed by the distribution coefficient for which the following expression was derived:

$$D_M^{\text{matte,copper/slag}} = \frac{1}{(K_T)(pO_2)^{y/2}} \left(\frac{\gamma_{MO}}{\gamma_M} \right) \left(\frac{MW_{slag}}{MW_{matte,copper}} \right) \quad 4.12.$$

Here, K_T is the equilibrium constant of the slagging reaction (Equation 4.8) at a given temperature, p_{O_2} is oxygen partial pressure at the reaction slag/copper interface, γ_{MO} and γ_M are the activity coefficients of the oxide and the element in slag and copper respectively.

The discussion below is similar to that in Section 4.2.5. except that the anode furnace is being considered instead of in the smelting and converting vessels. As discussed earlier, the type of slag mainly affects the activity coefficient of the oxide in slag. The addition of flux to copper forms a molten slag system with the objective of obtaining the lowest γ_{MO} possible. The effect of the type of slag on the activity coefficient can mainly be explained by the acidity/basicity theory discussed earlier in Section 4.2.5. The activity coefficients of $AsO_{1.5}$ and $SbO_{1.5}$ are lower with a basic flux. On the other hand, the activity coefficient of PbO is lower in acidic flux.

As opposed to smelting or continuous converting for which the oxygen partial pressure is fixed for a given matte grade or copper production, it is an extra variable in pyrorefining. Fundamental research has highlighted the significant influence of oxygen potential on the distribution coefficient between copper and slag as it can be anticipated by Equation 4.12. Figure 6.3. reproduced from Mangwiro and Jeffes, 1997, illustrates this phenomena for arsenic and antimony in the sodium carbonate slag system. It should be noted that 'P' is the inverse of

$D_M^{\text{Cu/slag}}$ in this text. Deportment to slag increases significantly with an increase of the oxygen partial pressure. The same trend is expected for the elimination of any element by oxidation from copper. Although the absolute value of $D_M^{\text{Cu/slag}}$ (or P) will be different for a different slag system, a decrease is expected with pO_2 . For maximum elimination by oxidation, the oxygen content of the melt needs to be close to, at, or slightly above copper saturation (maximum pO_2 at which blowing of air is stopped). This limit is set to avoid the excessive formation of Cu_2O in slag.

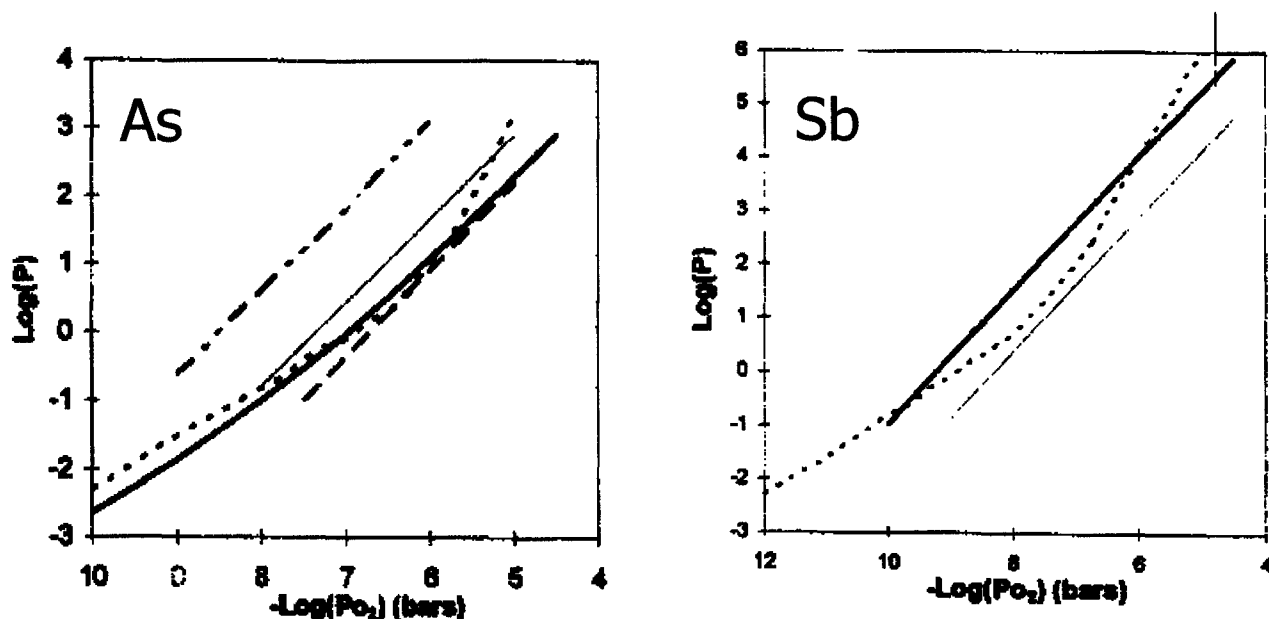


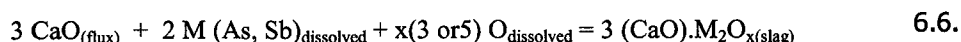
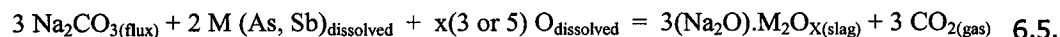
Figure 6.3. Effect of pO_2 on distribution coefficient ($P = 1/D_M^{\text{Cu/slag}}$) reproduced from Mangwiro and Jeffes, 1997

A- Alkaline Fluxes

Target elements: As, Sb

Alkaline fluxes (Na_2CO_3 , $CaCO_3$, CaO , Li_2CO_3 , K_2CO_3) could be used to lower the activity coefficient of the arsenic and antimony oxides in the slag. Na_2CO_3 - CaO system is certainly the most popular and well documented. From various thermodynamic studies, it can be observed that the equilibrium $D_M^{\text{copper/slag}}$ for As and Sb are very small (large deportment to slag) for pO_2 greater than 10^{-6} atmospheres in this slag system. $D_{As}^{\text{copper/slag}}$ and $D_{Sb}^{\text{copper/slag}}$ in the order of 0.0001-0.001 for As and 0.01-0.1 for Sb are observed for this system. In general, if the basicity of the slag decreases (e.g., by adding SiO_2 from entrained slag or reverts), deportment of arsenic and antimony to slag decreases.

The reaction with sodium carbonate and calcium oxide fluxes can be described as :



It was noted by Peacey et al., 1980 and confirmed by Kozłowski and Irons, 1990 that a miscibility gap in the Cu_2O -(Na_2CO_3 - Na_2O) system exists. This results in a two-phase slag: a Na_2O - CaO rich phase (high As and Sb) and a Cu_2O rich phase (low As and Sb).

Other alkaline fluxing systems for As and Sb removal are known but have not been used in industry due to various reasons. Examples are CaO - CaF_2 - SiO_2 , CaF_2 - CaO - MgO - SiO_2 [Gortais et al., 1994], FeO - Fe_2O_3 - CaO , Na_2CO_3 - CaO - Fe_2O_3 , Na_2CO_3 - CaO - Al_2O_3 - CaCl_2 , Na_2CO_3 - Cu_2O - CaO - Al_2O_3 , Cu_2O - CaO [Fujisawa et al., 1995]

Industrial practices:

Alkaline refining is usually integrated to the anode furnace cycle in the following matter:

- Charging of blister copper to anode furnace
- Oxidation (sulfur oxidation + increasing the oxygen level approximately to oxygen saturation)
- Alkaline flux injection
- Slag skimming (As + Sb removal)
- Reduction stage (O removal)

Hibi smelter in Japan [Monden, 1983] used alkaline fluxing. A CaCO_3 - Na_2CO_3 flux was injected through a submerged tuyere. The flux injection was divided into two steps. The slag was skimmed after each step. Operating conditions and results are presented in Table 6.1. The old smelter (blast furnace) has since been replaced by the Mitsui-Tamano smelter where soda fluxing is not used anymore because of higher removal efficiency of the newer technology coupled with lower input of As and Sb.

Alkaline refining is used at two CODELCO divisions in Chile: Chuquicamata and Caltones. At Caltones, alkaline fluxing (Na_2CO_3 + CaCO_3) is used to produce As and Sb content around 30 ppm for each element for fire-refined-copper to be sent to the market (ASTM standard No. B216 or BS1038). At Chuquicamata, the mine is located in a zone rich in arsenic (up to 1% As in concentrate) which forces the utilization of alkaline fluxing to produce anode with an acceptable As content for electrorefining. The operation in these two plants is similar. A mixture of Na_2CO_3 -

CaCO_3 (Chuqui. 1:1 and Caletones 1:1.5) is added using pneumatic injection in submerged tuyere. An example of the injection system used by CODELCO is illustrated in Figure 6.3. The slag bearing high levels of As is recycled to the Teniente Converters for maximum As volatilization.

Noranda Inc.- Horne smelter introduced alkaline fluxing to remove antimony and arsenic from complex custom feeds [Baboudjian et al., 1995]. Alkaline flux ($\text{Na}_2\text{CO}_3\text{-CaO}$) is introduced by pneumatic tuyere injection. The slag produced is recycled to the Noranda Reactor. Guixi smelter in China also reported to use soda fluxing [Zeping, 1998] Table 6.1. summarizes published results for Hibi, CODELCO and Noranda.

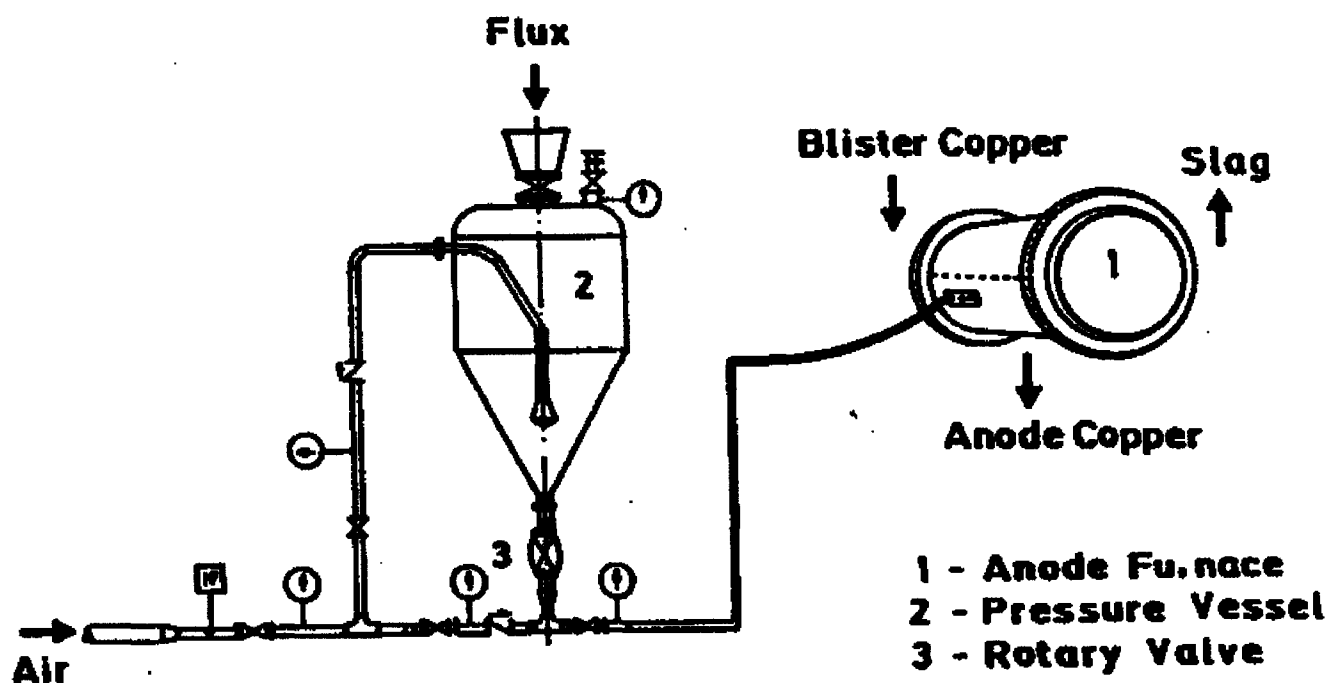


Figure 6.4. Schematic of apparatus used by CODELCO for alkaline injection reproduced from Riveros et al., 1993

Table 6.1. Published industrial results for alkaline refining

Location	Source	Mass of Cu (tonnes)	Temperature (°C)	Mode of addition	[O] _{Cu}	Flux	Flux flowrate (kg/min)	Flux (kg/tonne Cu)	%As removal efficiency	%Sb removal efficiency	Copper losses
Hibi	Industrial test* [Monden 1983]	63	1150	Injection tuyere	0.6%	100% CaCO ₃	25-27	6.34	93	86	
Hibi	Industrial test* [Monden 1983]	65	1150	Injection tuyere	0.6%	70% CaCO ₃ – 30% Na ₂ CO ₃	25-27	6.15	92	77	
Hibi	Industrial test* [Monden 1983]	59	1150	Injection tuyere	0.6%	50% CaCO ₃ – 50% Na ₂ CO ₃	25-27	6.78	91	59	
CODELCO	Industrial test #1 [Riveros et al. 1993]	200	1180	Lance injection	0.73%	37% Na ₂ CO ₃ – 63% CaO	140	13	98	57	Slag 35.8% Cu
CODELCO	Industrial test #4 [Riveros et al. 1993]	271	1180	Injection tuyere	0.70%	30 % Na ₂ CO ₃ – 70 % CaO	47.4	6.7	96	53	Slag 31.5% Cu
CODELCO	Industrial test #16 [Riveros et al. 1993]	270	1200	Injection tuyere	0.71%	50% Na ₂ CO ₃ – 50 % CaO	80	6.5	91	61	Slag 27.0% Cu
CODELCO	Industrial test #19 [Riveros et al. 1993]	260	1200	Injection tuyere	0.75%	50% Na ₂ CO ₃ – 50 % CaO	44	6.9	96	62	Slag 38.2% Cu
Noranda	Industrial test [Peacey et al. 1980]	290	1200	Lance injection + mouth	-	80% Na ₂ CO ₃ – 20% CaCO ₃	-	21	95	83	9.2% of total
Noranda	Industrial test [Peacey et al. 1980]	310	1160	Lance injection	-	40% Na ₂ CO ₃ – 60% CaCO ₃	-	12	93	62	8.2% of total

*Only a few plant trials have been chosen for this table. The complete list is available in Monden, 1983

Process evaluation:

Table 6.1. shows that removal efficiency of arsenic (91-98%) and antimony (53-86%) is high with the use of alkaline fluxing. The removal of arsenic is always better than antimony. This can be explained by the greater stability (lower activity coefficient) of As as compared to Sb in the Na₂CO₃-CaO slag system.

- **Cost**

The capital cost necessary for the construction of a pneumatic injection system is believed to be moderate. Flux consumption depends mainly on reagent utilization efficiency (type of addition),

amount of remaining slag in the furnace and initial and target As and Sb levels in blister. The composition of the flux injected has a great impact on its cost. On the other hand, indirect costs can be considered to be additional refractory brick replacement, due to accelerated refractory wear, gas treatment and the effect of slag recycling on other parts of the process.

- Choice of flux

Na_2CO_3 (~US\$200/tonne) is more expensive than CaO (~US\$100/tonne) or CaCO_3 (~US\$10/tonne). However, price is not the only criteria for flux selection. Slag fluidity which is important for smooth operation and to minimize entrained copper losses is mainly set by bath temperature and slag composition. The decomposition of CaCO_3 to CaO and CO_2 is endothermic and necessitates excessive heating of the bath that is usually done by fossil fuel burners. Liquidus of the slag generally increases at higher concentration of CaO .

Slag composition also has a large impact on refractory wear which is a significant problem of using alkaline flux. Na_2CO_3 and Cu_2O are highly corrosive compounds for the refractory bricks. The aggressiveness of the slag decreases at higher CaO levels. The use of high alumina refractories has been suggested by Nakamura et al., 1984, to improve resistance to sodium carbonate slag but no industrial application is known to the author.

To add to the dilemma in the selection of the injection flux composition, the literature is contradictory with respect to the comparative efficiency of CaO and Na_2CO_3 for As and Sb removal. It is the author's opinion that the presence of CaO will improve the elimination of As and Sb because of the great stability of $\text{Ca}_3\text{As}_2\text{O}_8$ and $\text{Ca}_3\text{Sb}_2\text{O}_8$ which is in agreement with most of the literature. On the other hand, an increase of efficiency with Na_2CO_3 content in slag was also mentioned by Devia and Luraschi, 1984.

In summary, the choice of fluxing composition is a balance between several criteria such as efficiency of removal, refractory wear, operating cost (reagent + heating), slag fluidity (ease to skim and copper losses) and impact on the metallurgy of other parts of the plant (e.g., Ca and Na in smelting furnace slag from recycling). It is site specific.

- Mass transfer:

Thermodynamics predict that large quantities of As and Sb could be removed with small flux volumes from the low $D_{\text{As}}^{\text{copper/slag}}$ and $D_{\text{Sb}}^{\text{copper/slag}}$. However, in industrial practice, stoichiometric excess of reagent is necessary as fluxing reactions are not limited by thermodynamics but by mass transfer. A theoretical kinetic analysis of the process by Kozłowski and Irons, 1990,

demonstrated that minor element diffusion in the copper (Sb in that case) is the rate-limiting step of the reaction while rate of diffusion of oxygen in copper and diffusion of the product in slag and gas are relatively rapid. These results were confirmed for As and Sb by Zhao and Themelis, 1990.

- Reversion caused by improper slag skimming:

Efficient slag skimming in large cylindrical vessels such as anode furnaces is difficult due to design geometry. With alkaline fluxing, good skimming practice is essential to avoid reversion of the fluxing reaction when reduction is carried out (removal of O) in the subsequent process step. Industrially, as a consequence of poor anode furnace skimming, reversion is observed to increase the arsenic and antimony levels by up to 25%. Skimming efficiency may be improved by yet unused techniques as discussed by Ng, 2001 whereby fluid slags are transported out of the furnace by gentle gas blowing.

- Slag recycling:

The alkaline flux has high levels of Cu_2O and entrained copper and precious metals necessitating its treatment by recycling for metal recovery. Independent hydrometallurgical treatments to eliminate arsenic and sodium from this slag prior to its recycling have been proposed by Peacey et al., 1980, and Nakamura et al., 1984. However, they are not used industrially for economic considerations and potential problems with the stabilization of the residue prior to disposal.

Because of the high arsenic and antimony levels, pyrorefining slag is usually recycled to the smelting vessel for maximum elimination. This operation can have negative safety consequences in the workplace because oxidized slag can react violently with matte with high sulfur content. The reaction generates SO_2 gas which is difficult to capture due to suddenness and volume released and in extreme cases, may lead to foaming of the smelting vessel. Also, recycling has various effects on the smelting process such as a change in the chemistry of the smelting furnace slag (Na and Ca), accelerated refractory wear, change in morphology of the dust, stability of the slag for disposal or treatment, etc.

- Arsenic volatilization:

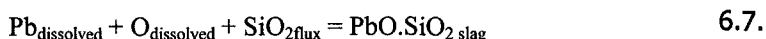
It was reported by Peacey et al., 1980, that up to 31% of As present initially in the copper was volatilized in a plant test using lance injection. Mangwiro and Jeffes, 1997, also discussed the problem on a theoretical basis predicting the emissions are probably in the form of NaAsO_3 . It is the opinion of the author that the partition to gas reported by Peacey is too high due to the relatively high stability of arsenic in molten copper represented by its low activity coefficient.

However, volatilization certainly occurs to a certain extent in the form suggested by Mangwiro and Jeffes or as other complex oxides. At the moment, the Horne smelter treats the off-gas from alkaline fluxing with electrostatic precipitators but no gas treatment was reported in other industrial applications. A dedicated gas treatment system (scrubber, ESP or baghouse) may be required for all applications in the future to eliminate or reduce arsenic emissions from alkaline refining.

B- Acidic Fluxes:

Target element: Pb

The use of Na_2CO_3 or any other basic slag is not suitable for promoting the transfer of Pb to slag as PbO is also a basic oxide. On the other hand, a flux producing an acid slag as SiO_2 , P_2O_5 or B_2O_3 will promote its deportment its slagging by lowering γ_{PbO} . In industry, the silica system is the major system used for removal of lead by fluxing in the anode furnace. The general fluxing reaction for lead in the silica system can be represented as follows:



Considerably less fundamental studies on this system have been carried out than for alkaline fluxing. This can be partly explained because silica is a natural flux for copper smelting for more than a century and by its relatively low cost in comparison with basic fluxes. Also, Pb has not presented a significant challenge at the levels usually encountered in more concentrates since it is removed efficiently in copper electrorefining.

Industrial practices:

Industrially, to reduce the cost of reagent and heating (melting cold flux), liquid smelting slag (fayalite) can be co-added with silica sand if not already saturated with Pb. Known industrial applications of lead removal by silica fluxing in the anode furnaces are Falconbridge – Kidd Creek [Chenier et al., 1992], Kennecott Utah Copper and Codelco-Caletones [Riveros et al, 1985 and 1993, Rojas et al., 1996]. The main difference between these processes is the ratio of silica flux/smelting furnace slag added. Flux can be dumped or injected to the anode furnace. Kidd Creek uses dumping and mass ratio of silica/S-furnace slag around 1. Kennecott also uses dumping and proportions of SiO_2 to smelting furnace slag are adjusted from lead levels in blister. Caletones uses this process only for fire-refined copper-grade and the mass of SiO_2 to reverberatory furnace slag added is around 0.5.

A small variation exists at the Dowa - Kosaka smelter [Tenmaya, 1993] where the first stage of 'overblowing' is carried out in the Peirce-Smith converter with silica-based flux for Pb removal (dumping). Although it is carried out in the Peirce-Smith converters, the thermodynamics of the system are very similar to fluxing in the anode as it is done at the end of the converting cycle during 'overblowing'.

Process evaluation:

The capital costs of this operation are low if the flux is dumped prior to copper in the vessel as no extra equipment is required. If injection is preferred, the costs would be higher from the injection system. The cost of silica sand raw material has to be considered. If it is dumped, it is believed to be cheap but the cost may be higher if fine sand is required for injection.

The major drawback of this process to remove Pb is the impact on smelter productivity and the potential need for extra anode furnace capacity. Process time, sometimes greater than two hours (flux addition, oxidation, reaction, skimming, slag transfer to smelting furnace) can be required. This increases the energy costs to maintain furnace temperature during the operation.

Slag recycling, usually to smelting vessel for maximum elimination of Pb, is required to recover the entrained copper and precious metals. Because the slag is silica based, recycling is much less problematic than for alkaline slag. The fugitive SO₂ emissions and foaming while recycling in the molten state are again potential safety risks. At Kennecott, the off-gas from the anode furnace is treated with a scrubber/baghouse tandem for minimum lead and other heavy metal emissions.

Similarly to alkaline flux a portion of the slag remains in the vessel and a pick-up (reversion) occurs during the reduction stage due to poor skimming efficiency in the anode furnace [Chenier et al., 1992].

6.2.4. HALIDE REFINING

Target elements: As, Sb, Bi, Pb

Principle:

Experimental studies have shown the possibility to refine molten copper with chlorides or fluorides introduced in the solid or gaseous forms. The principle is to form halide compounds of the minor element that can be vaporized easily from the melt due to their high vapor pressure.

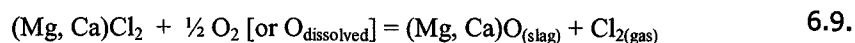
It was suggested to inject SF₆ [Zhao et al., 1995; Seanson and Shaw, 1993] beneath the bath surface in an anode furnace to remove preferentially the minor elements from the copper melt. Submerged injection maximizes the contact between the gas and molten phase. In this case, the elimination reaction would be:



It can be noted that oxygen is necessary. If no oxygen (or air) is added to the copper melt, the sulfur content might rise up to copper saturation (about 1.2% S from Biswas and Davenport, 1994) which might require additional desulfurization. In addition, co-injection of air helps mass transfer by increasing the turbulence.

It is found from laboratory experiments that the process removes the minor element in this order: Sb > As > Bi. Therefore, bismuth is found to be the limiting species for the refining process. Various factors were found to be important for the bismuth removal rate such as impurity inter-effects, initial oxygen content in metal and injection rate of SF₆.

Chloride addition was also suggested by Swanson and Shaw, 1993. The advantage is that chlorine can be added in the solid form (MgCl₂, CaCl₂, etc.). Again the minor element chlorides are volatilized preferentially out of the copper melt. The following two reactions for decomposition of the solid and volatilization were suggested:



where M is As, Sb, Bi, Pb. It should be noted that the blister is also partly deoxidized. The reactions were found at the laboratory scale to be very rapid and independent of temperature.

Industrial practices:

No industrial application is reported.

Process evaluation:

Although thermodynamics predict high elimination, low SF₆ and chloride efficiency (between 30-50%) were found in laboratory experiments. However, this is believed to be increased with improved process design (e.g., sufficient mixing and greater injection dept) if industrial application was developed.

Several uncertainties exist with respect to this process and have to be addressed prior to an industrial application. Halide compounds are potentially toxic and have deleterious effects on global warming and their emissions are usually restricted to very low levels. Direct exhaust into the atmosphere would not be possible. A complex gas treatment involving a wet scrubbing and effluent stabilization would certainly be necessary. Another concern is the corrosiveness of fluoride and chloride compounds with respect to off-gas ducting. An anode furnace vessel is never perfectly sealed with the off-gas hood and fugitive emissions would occur. The environment and health and hygiene issues in the workplace may require a new type of anode furnace. The above uncertainties require answers prior to estimating capital and operating cost for the industrial application of halide refining for minor element removal.

6.2.5. VACUUM REFINING OR COPPER MELT OR MOLTEN MATTE

Vacuum has the advantage of increasing rate of mass transport in the gas phase by increasing the gas phase diffusivity. Vacuum distillation, in which physical separation of one species from another, is possible if they have different partial pressure over the melt. Vacuum refining has been used for steel purification and alloying since 1932 [Humbert and Blossey, 1990]. In copper pyrometallurgy, the use of vacuum is still being evaluated for minor element removal and desulfurisation but no industrial application has been reported. Mt. Isa performed the largest trial at 2 tonnes per batch scale [Player, 1980]. With increasing levels of minor elements in concentrate and progress towards continuous processes or direct-to-copper furnaces, it is the opinion of the author that vacuum metallurgy will be part of the future copper smelting flowsheet. This is especially true because it is one of the few treatments (with dust bleed and treatment and concentrate pre-treatment) that can be applied for efficient bismuth removal.

Principle:

Refining of a melt occurs by the transfer of an impure element to the gas phase from the bulk solution. The role of the vacuum is to increase the gas phase diffusivity.

Refining occurs when the ratio of the species evaporating and leaving the liquid exceeds the ratio of their concentration in the bath [Li and Harris, 1991]:

$$\frac{n_i}{n_b} \geq \frac{N_i}{N_b} \quad 6.11.$$

where ' n_i ' can be expressed as:

$$n_i = kA\Delta C_i \quad 6.12.$$

where ' i ' and ' b ' are elements of the melt, ' n ' is the molar flux (kgmol/m²*s), ' N ' is the mole fraction, ' A ' is the surface area exposed to volatilization and ' C ' is concentration. The partial pressure of a substance can be defined by Equation 4.3. presented earlier:

$$p_i = \gamma_i x_i P_i^o \quad 4.3.$$

Olette's criterion for volatilization was presented earlier in Chapter 4 which states that for refining to happen, the volatility coefficient (ϕ_i) given by Equation 4.4. has to be greater than 1.

$$\phi_i = \frac{\gamma_i P_i^o}{P_B^o} \left[\frac{MW_B}{MW_i} \right]^{1/2} \geq 1 \quad 4.4.$$

The larger the volatility coefficient, the greater the rate of separation would be if the mass transfer rates are controlled by evaporation alone and not transfer in the liquid and/or gas phases. For a system that meets the thermodynamic requirements for vacuum refining (Olette's criterion), the kinetics of removal determine the practicality of industrial application. The mechanism of vacuum refining has three steps [Harris and Davenport, 1982]:

- A- transport of the element into the melt to the liquid/gas interface;
- B- evaporation of the atoms;
- C- transport of the element into the gas phase away from the liquid/gas surface.

All these steps have their own resistance affecting the overall mass transfer coefficient ' k ' in Equation 6.12.

VACUUM REFINING FROM COPPER MELTS:

Target elements: Bi, Pb

Li and Harris, 1988, have calculated the volatility coefficient for various impurities in different solvents based on available thermodynamical data. Volatility coefficients for vacuum refining of selected minor elements from molten copper at 1183°C are reproduced in Table 6.2.

It can be observed that the volatility coefficient of Bi and Pb are significantly greater than those of As, Sb and Ni. This is mainly attributable to the extremely low activity coefficients (Table 4.2.) of arsenic and antimony in copper as the vapor pressure above pure substance at this temperature is significant (Table 4.6). On the other hand, the low volatility coefficient of nickel is mainly due to its low vapor pressure.

Table 6.2. Volatility coefficients of selected minor elements from Li and Harris, 1991

Element	Volatility coefficient (ϕ_i) @ 1183 °C
As ₄	5.3×10^{-2}
Sb ₂	3.25
Bi	9.33×10^3
Pb	1.65×10^4
Ni	1.68×10^{-2}

This predicts that removal of Bi and Pb from copper by vacuum refining is more favorable than As, Sb, and Ni which was confirmed experimentally [Harris et al., 1983; Bryan et al., 1980; Ozberk and Guthrie, 1980]. As an example, for an exposed area/volume ratio (A/V) of 7, 120 minutes, pressure of 13.3 Pa, temperature of 1250°C, the following removal efficiencies were obtained in experimental work by Ozberk and Guthrie, 1986: Bi = 53-79%, Pb = 73-95%, As = 0-22%, Sb = 0-26%. Harris et al., 1983, found negligible As and Sb elimination and typically 70% of bismuth removal in 1 hour for A/V around 7.0 and temperature around 1227 °C. Bryan et al., 1980, averaged 99.2% bismuth elimination from copper at 1170°C, pressure of 0.08 torr, 60 minutes in a small crucible (large A/V).

The experimental work also analyzed the kinetics of the process for potential scale-up. It was generally found that elimination of bismuth and lead by vacuum refining follows first order kinetics. The effect of pressure and temperature on mass transfer coefficients is also highlighted in the literature [Harris et al., 1983].

There is an agreement that elimination rates are largely controlled by mass transport of impurities in the gas phase at the levels of vacuum (~130 Pa or ~0.1mm Hg) expected for industrial vacuum equipment handling molten phases. When melt vapor pressure exceed chamber pressure by more than a factor two, Harris et al., 1983, found that a mixed kinetic control exists from gas and liquid phase diffusion for Bi and Pb. The influence of oxygen and sulfur content in the melt were not found to have any effect by Bryan et al. 1980, while Ozberk and Guthrie, 1980, noted an increase of the removal rate of Bi and Pb with increasing S or O content of the melt.

FROM MOLTEN COPPER MATTE:

Target elements: Bi, As, Sb, Pb

Experimental studies have been carried out for vacuum refining of copper matte [Allaire, 1986 and 1991; Allaire and Harris, 1985; Allaire and Harris, 1989; Allaire et al., 1986] mainly to increase the removal rate of As and Sb as compared to that for copper melts. The higher activity coefficients (Table 4.2.) in copper matte as compared to those in copper for As, Sb, Bi should increase their elimination. Volatility coefficients could not be calculated due to the lack of data for equilibrium vapor pressure of the bulk liquid species such as Cu_2S and FeS [Allaire, 1986 and 1991]. In addition, this coefficient for minor element species would be affected by matte grade (Section 4.2.2.)

Experimental results showed that removal of As, Sb, Bi and Pb was possible from copper matte. Allaire and Harris, 1989, have reported removal of these elements respectively of 80-98%, 40-90%, 90-98%, 70-95% in 40 minutes at 1450 K, from 50-130 Pa and matte grade between 34% and 73% Cu. Kinetics were found to be controlled by liquid phase mass transport for most elements [Allaire and Harris, 1989]. Rates of refining were seen to be influenced by the sulfur and oxygen partial pressure in the melt. Moreover, the effect of sulfur deficiency was not explored and, following the arguments presented in Section 4.2.6.1. may be significant in affecting the rates of refining..

Industrial practices:

There are presently no vacuum refining units used in the copper industry although several patents [e.g. Harris and Davenport, 1984 and Outokumpu Oy, 1985] have been issued and some large scale pilot tests trials performed [Player, 1980]. Vacuum purification technology is widely used in the steel industry. A brief description of the technologies used in steelmaking will be given to provide the reader an idea of how vacuum refining can be carried out industrially.

Vacuum treatment is used in steelmaking works producing ultra-low carbon grades of steel or stainless steels. In the flowsheet, it is located after the metal has been transferred into ladles from the steelmaking furnaces and prior to casting, i.e. a ladle treatment. It was first developed in the early 1950's for hydrogen removal but several new applications have been found since. In 1981, more than 300 vacuum degassing installation existed the steel industry [Holappa, 1981]. Besides degassing (H_2 , N_2), the process is used for decarburization and alloying but can also serve to deoxidize or desulfurize the steel. The vacuum pump used industrially is steam ejector type since it must be suited to the large-capacity degassing vessel. In the steel industry two

major types of vacuum technology are used: ladle vacuum purification and the vacuum circulating process (also known as the RH-vacuum unit). A schematic representation is given in Figure 6.5.

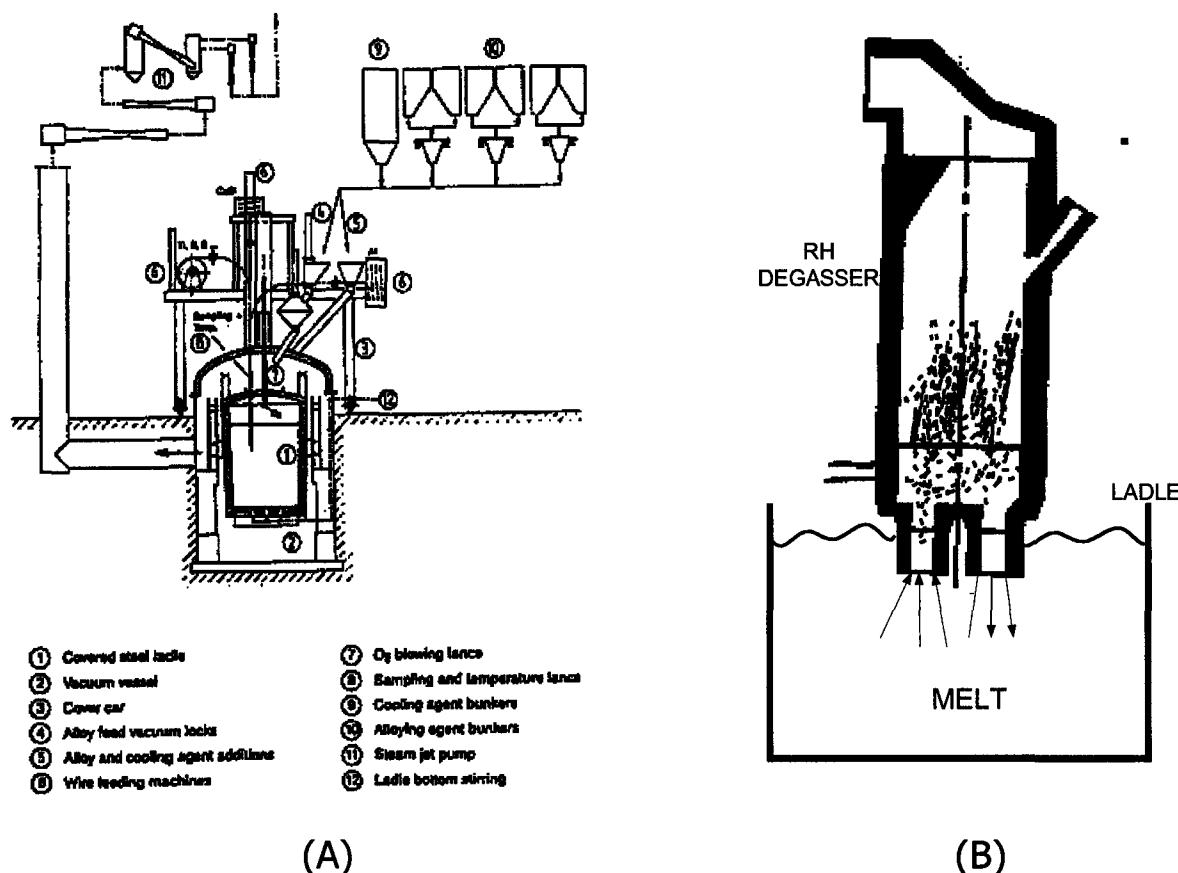


Figure 6.5. Schematic of ladle vacuum purification (A) and RH vacuum technology (B) reproduced Humbert and Blossey, 1990.

In ladle vacuum purification, a vacuum tight lid is placed on the ladle or the whole ladle is inserted into a vacuum vessel. Efficiency of this system has been enhanced with the development of porous plugs for mixing and maximizing the gas/liquid surface area .

In the vacuum circulating process a portion of the steel from the ladle is continuously circulated through the vacuum vessel. The siphon is introduced in the steel ladle (mechanical displacement of the vacuum vessel or raising the ladle). The vacuum is started. The principle is simple and consists of creating a flow of steel by injecting an inert gas (Ar) to change the density of the steel in one leg of a siphon. This results in a continuous flow through the vacuum chamber. One of the major advantages of RH degassing (circulation) is that it permits addition of alloying element in the same unit since it provides enough mixing to quickly homogenize the melt. Heat losses

are about 30-40 degrees celsius in 30 minutes [Holappa, 1981]. This system is widely used because of rapid treatment time, ability to treat many heats in a row, higher operating availability, and the ability to treat almost any steel grade. A variance of the system consists of oxygen blowing in the vacuum system via a tuyere to increase the decarburization rate. This is also known as RH-OB (oxygen blowing). It is also possible to inject flux in the system for slagging other elements (e.g. sulfur, phosphorus, etc.).

For the vacuum refining of copper matte, 'Lift-Spray' apparatus developed at McGill University was suggested by Allaire and Harris, 1991. A schematic of the proposed technology is presented in Figure 6.6. The process aims to increase the exposed area of melt. Lifting gas (inert or reactive) is injected into a riser only partially submerged into the melt. Bubbles formed create a pumping action. At the top of the riser, the bubbles collapse. The overpressure in the bubbles developed from the hydrodynamics of the flow in the riser creates large turbulence when the bubbles are broken and produces a spray of liquid maximizing the area of liquid exposed to vacuum.

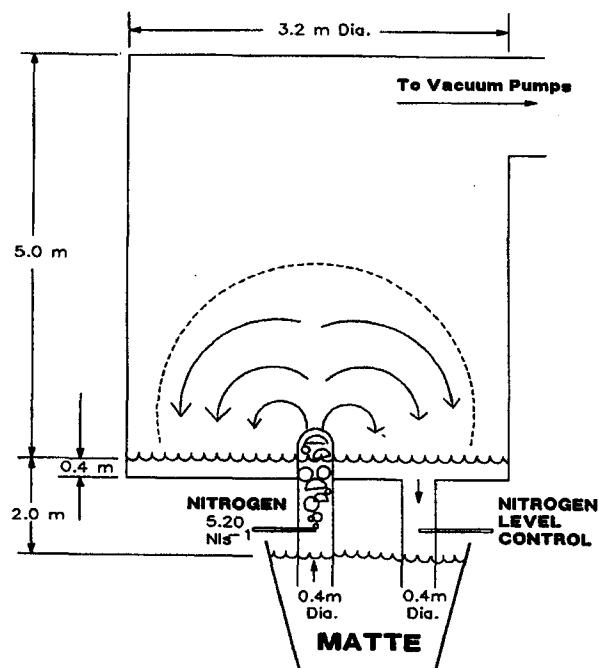


Figure 6.6. Schematic of Lift-Spray Vacuum Refining Process reproduced from Allaire and Harris, 1991

Process evaluation:

Vacuum refining is a relatively mature technology in the steel industry and transfer to the copper industry of similar units should not be a problem apart from issues of capital cost, higher volume

of off-gas produced and smelter' operating practices. Also, the non-selectivity of the process, i.e. to achieve high Sb elimination all As, Bi and Pb are eliminated whereas certain levels of As and Pb are desirable for electrorefining as mentioned in Chapter 5.

As part of the activities of this project, an RH-OB vacuum unit in operation at Stelco-Lake Erie Works was visited. The capital cost was around US\$60 M. It should be noted that the smaller size is expected for application in the copper industry could significantly reduce this cost. In his PhD. thesis, Allaire, 1991, examined the feasibility of using the lift spray vacuum process to refine copper matte. General scale-up equation is derived by first order kinetics observed:

$$\ln (C_{i \text{ final}}/C_{i \text{ initial}}) = -k_o t A / V \quad 6.13.$$

where C_i is the concentration of the melt, k_o is the overall mass transfer coefficient (m/s), A is the surface area for evaporation (m^2), V is the melt volume (m^3) and t is the time (s). The same values of k_o as determined experimentally (for matte, k_o : As= 1.5×10^{-4} , Sb= 0.6×10^{-4} , Bi= 3.6×10^{-4} , Pb= 1.5×10^{-4} m/s) were used. Calculations for vacuum refining using an LSV apparatus to increase the surface area of the matte gave dimensions and circulation well in the limits of current know-how. Nitrogen could be used as lifting gas instead of air because the injector blocked after a few minutes. Calculated dimensions compared well to R.H. degassing units used in the steel industry. As an example, it was found that a refining time of 30 minutes would be sufficient. Energy necessary to run the unit, maintenance, longer process time and decrease in the temperature of matte or copper would represent the operating costs associated with the use of vacuum for minor element removal.

Gas treatment represents a significant uncertainty. Selective condensation of the minor elements, if practiced, would generate additional revenues from by-products. However, extra cleaning equipment would be required to protect the vacuum pump from damage by dust particles. Baghouse or ESP under vacuum represents a technical challenge. In addition, SO_2 evolution from the melt was observed in laboratory and pilot scale treatment of matte [Allaire and Harris, 1986; Player, 1980]. This might have to be treated to comply with environmental regulations.

A change in mentality for production personnel would come about by the use of vacuum treatment of matte or copper. Presently, most smelters think in terms of large copper charges (>150 tonnes). With vacuum refining, the operation would have to consider a smaller volume at the time so the operation would be more continuous than batch.

6.2. DUST BLEED AND TREATMENT

Target element : Bi, Pb, As and to a smaller extent Sb

Principle:

Most minor elements are volatile as compared to copper bearing phases in the smelting flowsheet. Consequently, dust captured from primary off-gas in smelting and converting represents an ideal stream to remove minor elements from the system because of its high concentration of impurities and low volume. Generally, the mass of dust produced in the matte smelting furnace represents around 5% of the total input. It varies mainly from the type of smelting furnace and mode of concentrate addition to the furnace. As an example, dust generation in a Outokumpu flash smelting furnace varies from 4 to 10% of mass of initial input whereas it is around 1.5-4.0% for a Noranda Reactor (slinger) and between 0.5-3.0% in a Teniente Converter (submerged injection).

Typical concentration of electrostatic precipitator dust produced in matte smelting and converting furnaces is given in Table 6.3. It depends mainly on the total input and partition of volatile elements to gas. As a general trend it can be observed that converting furnace dust is generally richer in minor elements than the matte smelting furnace. However, its volume is much lower so a bleed of this dust from the system might not be sufficient to greatly effect a smelter's overall minor element treatment capacity.

In most copper smelters, treating relatively clean concentrate, the dust is completely recycled, generally, to the smelting furnace to improve elimination. This is done because of its relatively high content in valuable metals (Cu, Ag, Au) which are recovered at low cost by reprocessing. If the dust bleed or treatment is carried out there would be a loss of value metal recovery.

For smelters with high loads of minor elements, part of the dust is generally bled. Table 6.4. presents the total smelter recoveries for arsenic, antimony, bismuth and lead of different smelters visited in this study as a function of dust bleed. From the discussion in Chapter 4, it was observed that recovery is also influenced by factors other than dust bleed (matte grade, oxygen enrichment, levels in concentrate, type of slag, etc.). From Table 6.4., it appears that elimination of volatile minor elements such as lead and bismuth generally increases with dust bleed. For arsenic, a similar situation is to be expected but as most smelters having dust bleed also do alkaline (soda) fluxing that Table 6.4. gives little insight. Also, arsenic capture by electrostatic precipitators is lower than for other elements ending in a large part inside the

scrubbing liquor (prior to acid plant) so recovery is less dependent on dust bleed than for Pb and Bi. For Sb and Ni, volatilization is low and although dust bleed will improve elimination, other factors influencing deportment to slag would have more influence on their overall recoveries than dust bleed.

Table 6.3. Typical electrostatic precipitator dust composition.

Furnace	Data source	% Cu	% As	% Sb	% Bi	% Pb
Smelting –Outokumpu	Kennecott – Gabb et al., 1995	15-30	0.9-4.2	0.03-0.09	0.11-0.6	0.5-2.0
Smelting – Noranda	Horne – Godbehere et al., 1995	4	2-5	0.4	2	30
Smelting – Teniente	La Caridad – Robles et al., 1999	-	1.8	0.25	0.32	-
Smelting – Outokumpu	SM A – visit '99	15	2.2	0.2	0.5	4
Smelting – Outokumpu	SM B – visit '99	-	2	0.2	0.6	1.4
Smelting – Outokumpu	SM C – visit '99	10.9	3.3	0.9	1.5	20.6
Smelting – S-furnace	SM D – visit '99	17	1.0	0.06	0.4	10
Smelting – Reverb	SM E – visit '99	8.31	1.37	0.13	0.10	3.27
Smelting – Teniente	SM F – visit '99	4.7	2.6	0.16	0.16	18.2
Smelting – Teniente	SM G – visit '99	9.14	6.38	0.38	-	22.45
Converting – PSCv	Saganoseki – Hino et al., 1995	5.5	6.5	0.2	3.2	21
Converting – PSCv	Krompachy – Vircikova and Havlik, 1999	5.27	2.83	3.08	2.79	28
Converting – C-furnace	SM H – visit '99	35	0.7	0.01	0.06	5
Converting – PSCv	SM I – visit '99	5	6.5	-	3	22.5
Converting – PSCv	SM J – visit '99	3.92	4.8	0.12	1.16	26.90

Table 6.4. Effect of dust bleed on overall smelter recovery for As, Sb, Bi, Pb from industrial visits 1999. Note that designation of smelter (e.g. smelter A) does not correspond to those in Table 6.2 to protect proprietary information.

Smelter name	Smelting furnace Dust bleed	Converting furnace dust bleed	Arsenic recovery (% of input)	Antimony recovery (% of input)	Bismuth recovery (% of input)	Lead recovery (% of input)
A	No	no	31	-	-	-
B	No	no	23	-	-	-
C	No	no	38	25	22.2	Doping
D	No	no	62	-	31.2	13.4
E	No	No	soda fluxing	Soda fluxing	-	5.0
F	No	No	Doping	17	-	Doping
G	No	No	22	43	18	1.6
H	No	Part	Doping	7	8.5	Doping
I	No	Part	-	-	-	-
J	No	Part	6	12	-	-
K	No	Full	25	7	7.4	1.6
L	No	Full	12	52	18.5	2.4
M	No	Full	43	5	25.5	Doping
N	Part	-	33	-	-	-
O	Part	No	38	25	22.2	Doping
P	Part	No	-	-	15	1.6
Q	Part	Part	soda fluxing	Soda fluxing	-	0.5
R	Part	Part	soda fluxing	Soda fluxing	-	0.5
S	Part	Part	soda fluxing	Soda fluxing	-	1.0
T	Full	Full	5	4	7.5	1.3

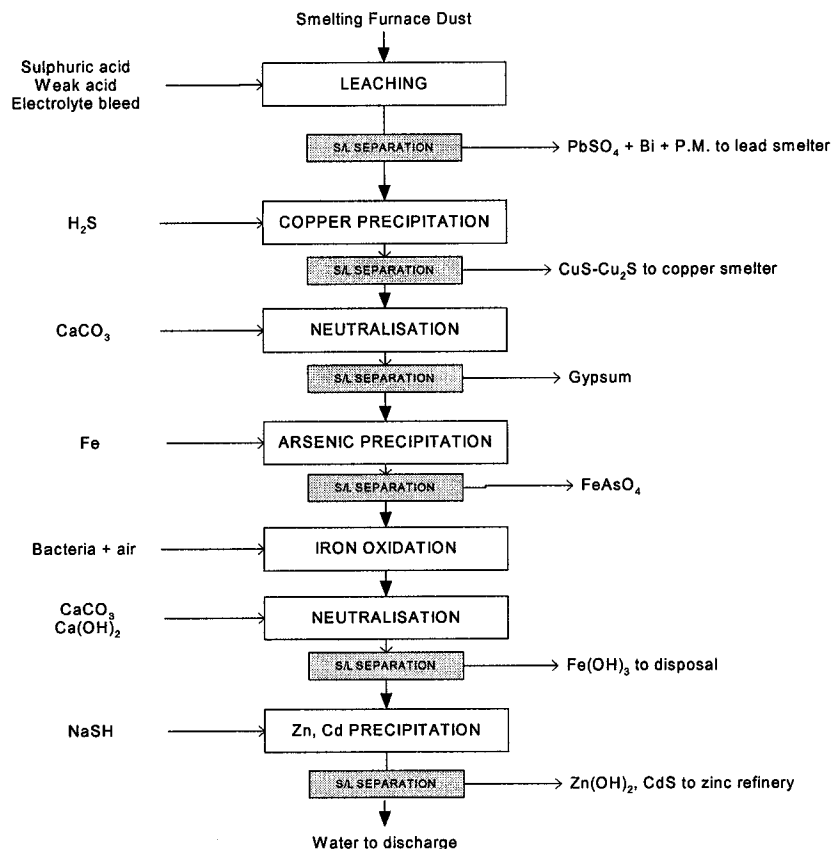
Industrial practice:

Dust bled from the system cannot be discarded directly because of high copper and P.M. values. Two different approaches are taken to manage this dust. The first is to sell it for part of its metal values on the market (for a treatment charge) or affiliated smelters. Converting furnace dust is especially attractive to lead smelters because of high Pb and Bi content and low copper content. All or a part of the converting dust is sent to associated smelters in the following industrial cases: Noranda Inc. - Gaspé smelter (to Noranda – BM&S Pb smelter); ASARCO – Hayden (to ASARCO - East Helena Pb smelter); Onahama (to external Pb smelter); Dowa – Kosaka (to external Pb smelter); Mitsui – Tamano (to external Zn smelter).

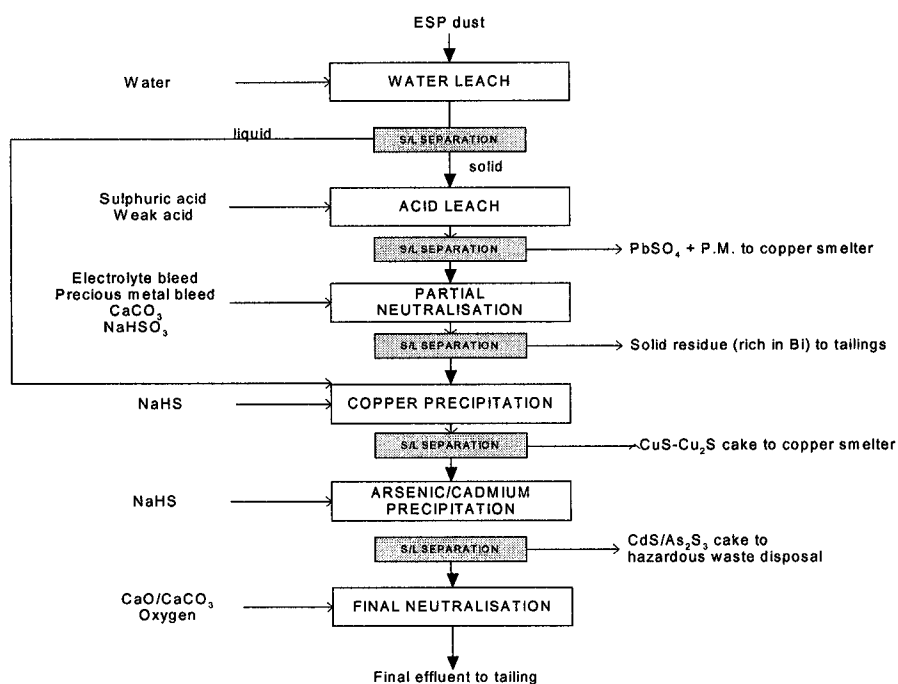
The other option is to treat the dust on-site to partly recover the copper and the precious metals values. This is especially important if matte smelting dust has to be treated because of higher copper levels. Pyrometallurgical dust treatments have been studied but are not industrially used to the knowledge of the author (e.g., Ausmelt in Swayn et al., 1993; sulfidising smelting in Hanks et al., 1979; roasting in Wadia et Olivares, 1975). On the other hand, various types of hydrometallurgical dust treatment plants exist. A general description of some hydrometallurgical dust treatment is presented in this section.

1. LEACHING PLUS RECOVERY OF COPPER AS COPPER SULPHIDE

To lower minor element recovery to anode, the philosophy used at Dowa – Kosaka [Minoura and Maeda, 1984; Mohri and Yamada, 1976] and Kennecott copper smelter [Gabbs et al., 1995] includes a treatment of matte smelting dust. The flowsheets of these processes are shown in Figure 6.7. Although differences exist, the general principle is to leach copper from the dust with sulfuric acid and to recover it as copper sulfide by precipitation. It should be pointed out that these two processes also treat electrolyte bleed and weak acid (from gas cleaning) from both refinery and the smelter.



(A)



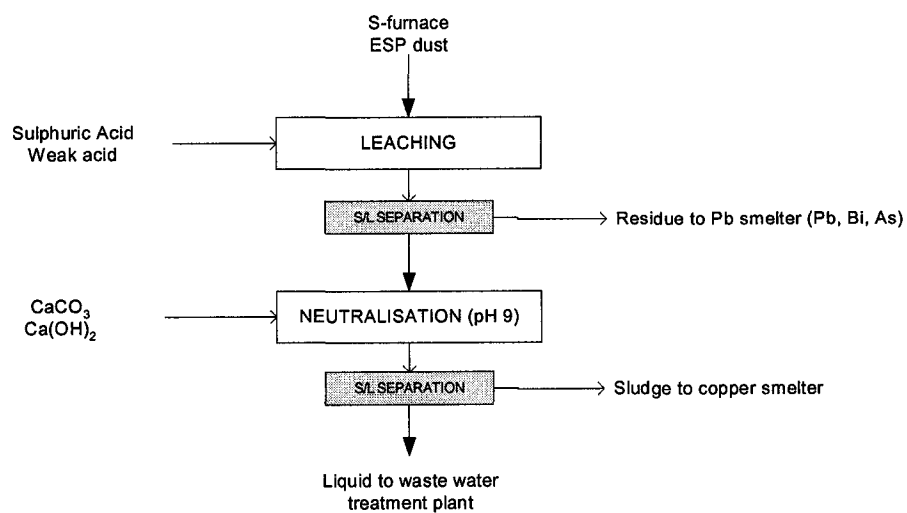
(B)

Figure 6.7. Hydrometallurgical dust treatment flowsheet at (A) Kosaka smelter [visit 1999] and (B) Kennecott smelter [visit 1999 + Gabbs et al., 1995].

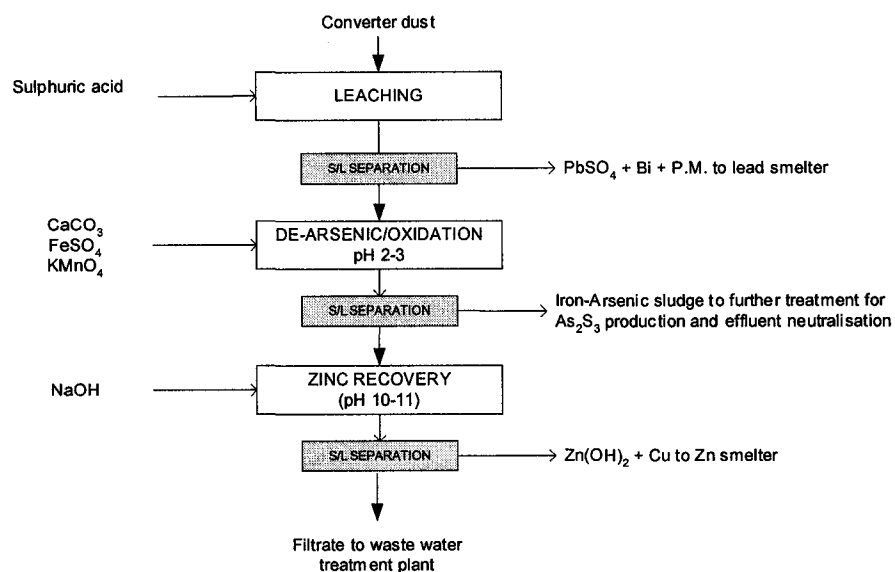
2. LEACHING + RECOVERY OF COPPER BY NEUTRALISATION:

Hydrometallurgical treatment of S-furnace dust at Mitsubishi – Naoshima [Ajima et al., 1995; Oshima et al., 1998; Suzuki et al., 1977] is simple and efficient. It consists of concentrated sulfuric acid leaching of copper from the dust. The residue rich in Pb, Bi and precious metals is sent to a Pb smelter. Complete neutralization of the leach solution (rise in pH) causes the precipitation of copper in a sludge to be recycled to the smelter. Flowsheet is presented in Figure 6.8A.

The process used to treat Peirce-Smith converter dust at NMM – Saganoseki [Hino et al., 1995; Tomita et al., 1991] is somewhat similar to Naoshima. Partial leaching of the dust solubilizes arsenic and a part of the copper. Because the leaching conditions are not as extreme as at Naoshima, a part of copper also stays in the leach residue with lead, bismuth and precious metals which is sent to a Pb smelter. Selective precipitation of copper and iron-arsenic residue is carried out with pH control. Treatment of this sludge to produce As_2S_3 was simplified in the flowsheet of the process shown in Figure 6.8B. but can be found in the references [Hino et al., 1995]. Zinc hydroxide recovery and final polishing of the leach solution is also carried out by neutralization.



(A)



(B)

Figure 6.8. Hydrometallurgical dust treatment flowsheet at (A) Naoshima smelter [visit 1999 + Ajima et al., 1995] and (B) Saganoseki smelter [visit 1999 + Hino et al., 1995].

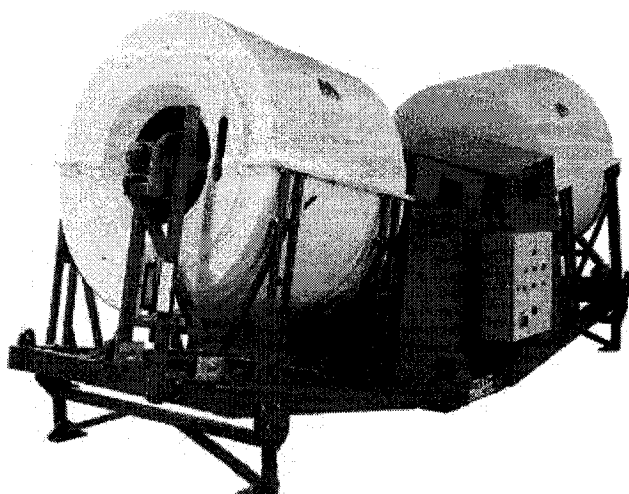


Figure 6.10. Picture of Multi-Gravity Separator from AXIA MOZLEY homepage <http://www.mozley.co.uk/mg.htm>. It is similar to the equipment used in box 7 of Figure 6.9.

4. ACID LEACH / SOLVENT EXTRACTION AND ELECTROWINNING

When the copper smelter is located on the same site as a leach/SX/EW facility for recovering the copper oxide part of the ore body, it might be advantageous to use the infrastructure to treat the smelter dust to recover the copper fraction as electrowon cathode and to discard most of the impurities with the selective solvent extraction process. Offsetting the capital cost advantage of using an existing facility, the drawbacks are the lower copper recovery, high precious metal losses and difficulty to stabilize the high content of heavy metals (usually rich in As) prior to discharge into the environment. CODELCO – El Teniente and Chuquicamata are using this route for dust treatment. Their flowsheets are presented in Figure 6.11. Moreover, BHP – Magma used a similar dust treatment process prior to its closure in 1999 [Young and Um, 1992].

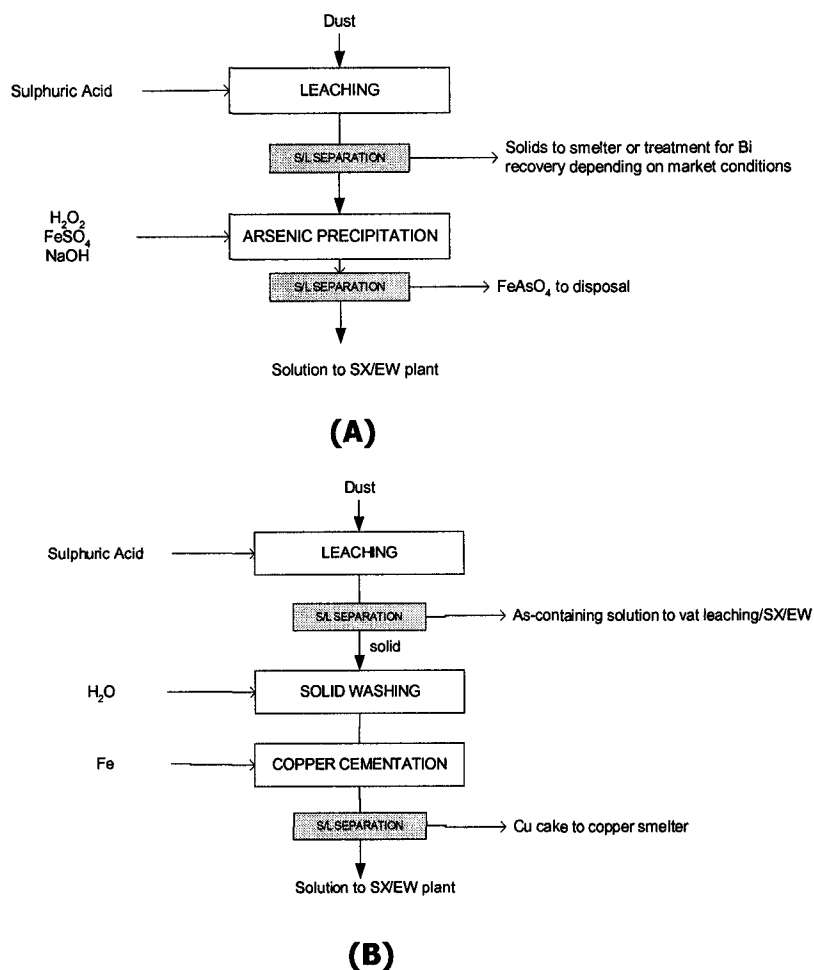


Figure 6.11. Hydrometallurgical dust treatment flowsheet at (A) El Teniente smelter and (B) Chuquicamata smelter [Valenzuela, 2000]

5. LEACH/CEMENTATION FROM A ZINC PLANT

Falconbridge - Kidd Creek metallurgical complex [Chenier et al., 1992] comprises a copper smelter and zinc hydrometallurgical plant. A part of the electrostatic precipitator (ESP) dust is leached with spent zinc electrolyte and jarosite water from the zinc plant. Copper in the solution is cemented with zinc dust. The Cu cement residue is recycled back to the smelter and the filtrate is sent to the zinc effluent treatment tank. The solid residue from the first leach is treated to recover Pb/Ag and to dispose of the effluent in an environmentally stable form. The simplified flowsheet is shown in Figure 6.12. (the lead/silver recovery is not shown)

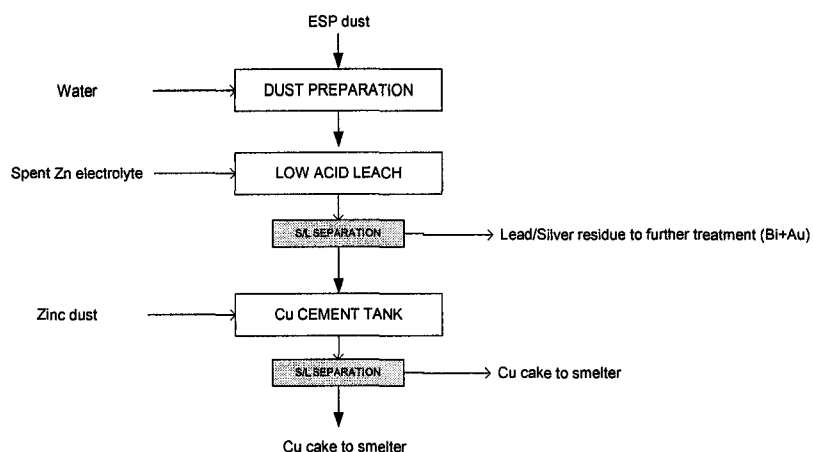


Figure 6.12. Hydrometallurgical dust treatment flowsheet at Kidd Creek smelter [visit 1999]

6. OTHERS

Several other hydrometallurgical concepts have been developed to treat smelter dusts. As presented in this section, only few have been applied at the large scale for various reasons. In the opinion of the author, the alkaline leaching of dust is the most promising among those that have not found industrial applications yet. Alkaline leaching is selective for arsenic and antimony. On the other hand, it is probably not a process of choice for a smelter with high loads of Bi and Pb.

A proposed flowsheet from the analysis of the various publications on the subject [Robles et al., 1999; Robles et al., 1998; Vircikova and Havlik, 1999; Vircikova and Imris, 1995] is presented in Figure 6.13. Other hydrometallurgical routes using chloride ions for Bi removal and recovery from smelter dusts have been suggested and piloted. More details can be found in Asahina et al., 1976; Reid, 1977; Hanks et al., 1979; Wadia and Olivares, 1975; Piret, 1994, Kunte and Bedal, 1993.

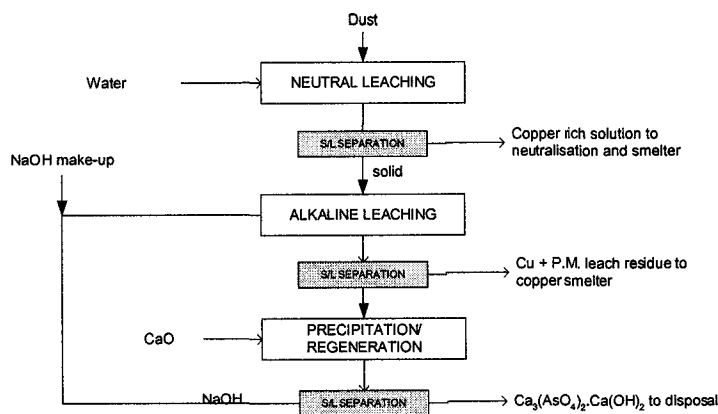


Figure 6.13. Suggested flowsheet for alkaline treatment of dust to remove arsenic and antimony.

Process evaluation:

Dust bleed followed by dust treatment is certainly the philosophy of choice for bismuth and lead control. A dust treatment process is not a black box that can be used to treat any kind of dust with the same efficiency. It is conceived according to a specific dust for a given smelter. As for most hydrometallurgical processes, they are largely dependent on the mineralogy and composition of the feed. Therefore, a comparison of the efficiency between each dust treatment is uninformative.

Capital cost of dust treatment varies based on the type of treatment used. It is believed to be fairly high for a treatment such as Kennecott and Kosaka. For the others, it should be lower because of less equipment and tanks. Operating cost (reagent) and metal losses (Cu and precious metals) are the main factors influencing the economics of the operation. Modern dust treatment plants are usually fully automated minimizing labor cost. Stabilization of the effluent for environmental disposal needed with any dust treatment usually involves extra operating and capital costs.

6.4. ANODE DOPING (ARSENIC AND LEAD)

Target elements: Sb, Bi

Doping can be defined in copper smelting as the deliberate addition of an impurity element to the system to improve the elimination of others. Arsenic and lead are the more frequent elements added for this purpose in the conventional copper production flowsheet. Doping can be carried out at the smelter (usually at the end of the converting cycle or into the anode furnace) or to the electrolyte in electrorefining.

Principle:

ARSENIC DOPING

The addition of arsenic to the anode or the electrolyte is carried out to modify the behavior of other impurities during electrorefining. Arsenic oxidation (As^{3+} to As^{5+}) is known to be more favorable and faster than antimony oxidation (Sb^{3+} to Sb^{5+}). Arsenic doping results in more arsenic in the electrolyte that can be oxidized preferentially than antimony helping to maintain Sb in the lower Sb^{3+} valence state. This would help to minimize floating slimes apparitions because a major constituent of the floating slimes is Sb^{5+} (c.f. Section 5.2.4.).

Baltazar et al., 1987, found in laboratory experiments that when the ratio As/Sb entering the electrolyte was greater than 2, the anode showed no sign of passivation related to floating slimes even at high current density. A relation between antimony and a minimum of arsenic necessary in the anode to avoid formation of floating slimes has been established. As an example, Baltazar determined the relation presented in Figure 6.14. It should be noted that this relation will be site specific as it depends on several other parameters. Recently, the bismuth has been added to the relationship as it is also a major constituent of floating slimes. Often, when doping is performed in the smelter, the ratio $\text{As}/(\text{Sb}+\text{Bi})$ of anode composition is used for control purposes.

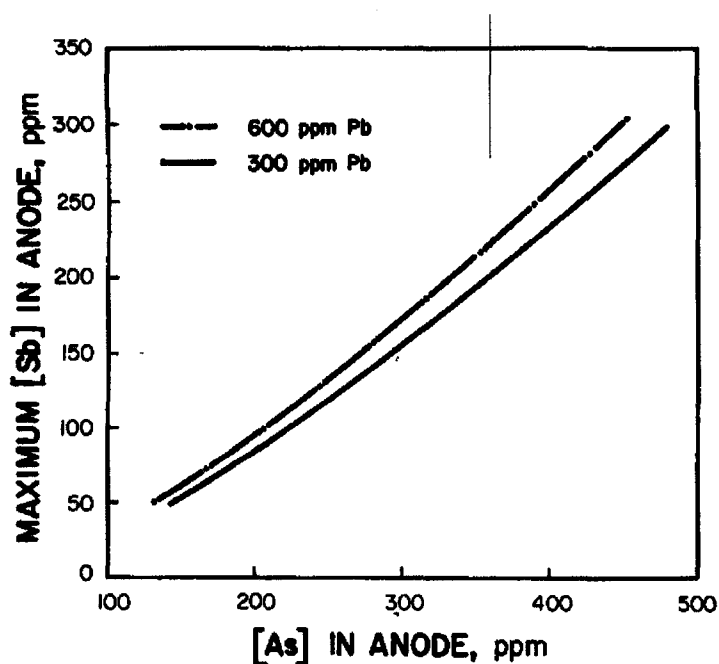


Figure 6.14. Maximum acceptable Sb in anode as a function of As in anode reproduced from Baltazar et al., 1987

LEAD DOPING

Similarly to arsenic doping, the addition of lead to the anode changes the electrochemistry of anode refining. The influence of lead on department of Sb and Bi to slimes was presented earlier in Section 5.2.3. In general, an increase in lead concentration in the anode will favor scavenging of Sb and Bi from the electrolyte by the slimes. Cifuentes et al., 1999, have identified the compound bindheimite ($\text{Sb}_2\text{Pb}_2\text{O}_7$) to be responsible for this phenomenon for antimony.

Industrial practices:

Although not many smelters directly dope the anode, arsenic is often adjusted in the smelter feed by blending to provide adequate proportion versus antimony and sometimes bismuth in the anode. The ratios As/(Sb+Bi) in the anodes of some smelters visited are presented in Table 6.5.

Table 6.5. As/(Sb+Bi) in anode from industrial visits (c.f. Appendix A)

Smelter name	As/Sb+Bi (anode)
Horne*	0.6
Kosaka	0.7
Hayden*	0.8
Toyo	1.6
Las Ventanas	1.8
Gaspé*	3.0
La Caridad	3.0
Altonorte	3.1
Onahama	3.3
Saganoseki	3.6
Naoshima	4.0
Kennecott	4.9
Tamano	5.0
Miami*	5.3
Chuquicamata – FSF	5.9
Kidd Creek*	6.7
Average	3.3

*arsenic doping

Industrially, arsenic doping at the smelter was made by adding arsenic bearing material at the end of converting or in the anode furnace if gas treatment permits. Pure arsenic and speiss (Cu-As-Sb-Pb) which is a by-product of lead smelting have been used for arsenic doping. As doping is being used as per a request of the refinery for impurity control measure at ASARCO-Hayden (speiss), Cyprus-Miami (pure arsenic), Falconbridge – Kidd Creek (speiss) [Chenier et al., 1992], Noranda Inc. – Horne smelter (pure arsenic), and Noranda Inc. – Gaspé smelter (speiss).

Mexicana de Cobre – La Caridad and Kennecott performed arsenic doping in the electrolyte as H_3AsO_3 or As_2O_3 . It should be noted that this is not carried out on a continuous basis and may be used only when arsenic level in the electrolyte drops below certain values.

Lead doping is far less common. It was observed industrially at Mexicana de Cobre-La Caridad (target around 800 ppm Pb in anode) by adding lead ingots in the anode furnace. Significant increase in lead content between the converters and anode at Mitsui - Tamano Smelter (from

370 to 950ppm Pb in anode) although not observed at the visit. Laboratory and pilot research in Chile on Pb doping have been successful [Cifuentes et al., 1999] and application is not far from reality in that part of the world. It should be noted that smelters doping arsenic from speiss are doping with lead at the same time as Pb concentration is usually high in this material.

Process evaluation:

Cost of pure arsenic, speiss, lead ingots or other forms of arsenic or lead has to be balanced against potential benefits of this operation. It is the main criterion provided that the refinery purification system can handle the additional amounts of arsenic and mass of slime per anode.

Generally, doping in the smelter has only minor effects on process time as it can be integrated with little disturbance at the end of the smelting flowsheet. Other issues such as the impact on environmental emissions and hygiene conditions in the building (smelter and refinery) also have to be considered. Doping of lead and arsenic should always be carried out in a furnace with a hood to capture off-gas. In certain circumstances, a gas treatment might also be required for environmental regulations. It is the opinion of the author that research should be intensified to dope the refinery electrolyte directly instead of forcing the doping to be realized at the smelter where arsenic volatilization occurs causing potential hygiene issues.

For lead doping, passivation should be considered. At lead concentrations greater than 0.15% in anode and ratio $As/(Sb+Bi) < 0.5$, Claessens et al, 1983 found that anodes tend to passivate. The effect of lead concentration on passivation was confirmed by Moats, 1999. There is no unique level at which Pb doping has to be stopped to prevent this drawback as it depends on several other factors (e.g. current density, As concentration, etc.). However it should be kept in mind, that Pb cannot be doped to very high levels because of passivation. Also, impact of high lead anode on refinery's hygiene has to be considered.

6.5. ELECTROLYTE PURIFICATION

It was seen in Chapter 5 that impurities with similar oxidation potential to Cu (e.g. As, Sb, Bi) readily pass into solution from the anode in electrefining. If electrolyte is not removed from the circuit and purified, impurity concentration would gradually increase until it reaches solubility limit and precipitation may contaminate the cathode. Moreover, as mentioned in Section 5.2.3., cathode contamination by electrolyte entrapment/occlusion at the surface of the cathode increases especially for a electrolyte with high impurity levels. Therefore, a part of the electrolyte has to be continuously removed (bled) and purified to keep the levels of impurities constant.

In addition to removing impurities from the electrolyte, the amount bled (generally between 0.2-0.6 m³ electrolyte/tonne of cathode from Toyabe et al., 1987) is usually set to maintain constant copper composition in the electrolyte. This is necessary to offset for the copper which is chemically dissolved at the anode, from soluble Cu₂O.

Some purification techniques used in industry are described in this section, namely: liberation, evaporative crystallization, ion exchange, and solvent extraction. Other practices exist but are minor in comparison. As an example, when a leach/SX/EW plant for copper oxide exists near-by the refinery, it is a potential treatment facility without large additional capital and operating cost, for example at Cyprus-Miami and CODELCO-Chuquicamata. Another example of treatment not discussed in this section is to use the electrolyte bleed stream in the hydrometallurgical dust treatment, for example at Kosaka and Kennecott [Gabb et al., 1995] discussed in Section 6.3.

Other possible electrolyte treatment practices have been proposed in the literature but their description is beyond the scope of this thesis. However, they should not be neglected as they might be part of the future of electrolyte treatment. Related literature (Appendix B) should be consulted for more details. Examples are a reduction of Sb⁵⁺ from electrolyte with SO₂ [Abe et al., 1986], selective adsorption of As, Sb, Bi from the electrolyte by stannic acid, selective removal of Bi and Sb from the electrolyte by adding carbonate of barium, strontium or lead [Toyabe, 1987], use of electrodialysis for the separation of various impurities from copper electrolyte [Cifuentes et al., 1999].

6.5.1. LIBERATION

Target elements: As, Sb, Bi

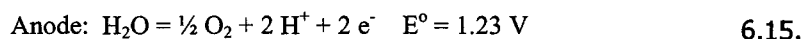
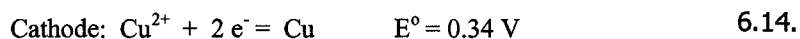
Liberation is the standard and most common practice to treat the electrolyte bleed stream for the purpose of controlling tankhouse electrolyte's composition (copper and minor elements). In liberation, Sb, Bi, As are successfully removed from the electrolyte by co-deposition with copper. Evaporative crystallization generally follows liberation in conventional electrolyte purification to remove Ni (Section 6.5.2.).

Principle:

The general objective of liberation is to treat electrolyte bleed to recover most of its copper content and isolate the impurities. Usually, it is done in a sequence comprising two to three steps.

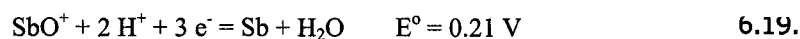
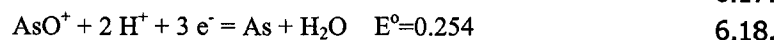
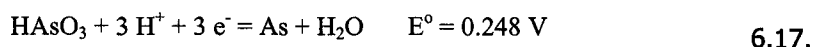
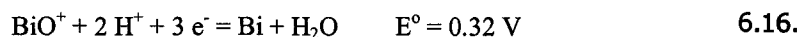
1- COPPER REMOVAL:

Treatment by liberation starts by electrowinning most part of copper. The following anode/cathode reactions occur:



2- IMPURITY REMOVAL:

Following the liberation of copper, the impurities (As, Sb, Bi) are electrowon from the partially decopperized electrolyte. Because these impurities are less noble than copper, their plating also removes the remaining copper from the bleed stream. As a consequence, the deposition potential at the cathode gradually increases in this second stage of liberation. Electrowinning of these impurities will occur according to the following cathodic reactions:



The anodic reaction will be the same as for copper electrowinning.

Industrial practices:

Most refineries around the world use liberation for decopperization of the electrolyte and to remove impurities. It should be noted that other technologies exist such as copper sulfate precipitation to replace first stage liberation but it is not discussed in more detail as it is not directly related to minor element behavior and application is limited.

For liberation, anodes are insoluble Pb based alloys (Pb-Sn-Ca or Pb-Sb) and starting sheets are usually made of copper or stainless steel. It is generally carried out in two or three stages. In this first stage, the copper concentration in the electrolyte is lowered from about 40-45 gpl (tankhouse electrolyte) to levels around 10-15 gpl [Toyabe, 1987 and Hoffmann, 1997]. decopperization is stopped as the surface of the cathode becomes progressively rougher at lower levels of copper increasing the risk of contamination. In general, little impurities are deposited with copper, producing marketable cathodes.

Impurity removal can be performed in one stage but it is generally divided into two stages. After the first liberation, the partly decopperized electrolyte (~10 gpl Cu) is lowered to moderate levels of copper (around 5 gpl). The final (3rd stage) liberation is to remove the remaining copper (< 1gpl Cu) and specifically aims to plate arsenic. It is usually performed under ventilated hoods as purification experience has shown elemental or arsine generation which has resulted in isolated case in the death of refinery personnel. Several techniques have been developed and used to minimize the risk of arsine generation such as periodic reverse current, maintaining a concentration around 5 gpl Cu during electrowinning of arsenic in the form of Cu_3As , or use of solvent extraction to remove As (Section 6.5.4). The cathodes (or residues falling not adhering to the surface) from the second and third stages contain high levels of impurities. They are generally recycled to the smelter to maximize impurity removal. The liberated electrolyte is sent to nickel recovery or is treated prior to its discharge into the environment.

Bleed of surface electrolyte (Shibata et al., 1987):

At Mitsui-Tamano only the surface electrolyte is bled. This is because the copper concentration level in the top 10 mm from the surface was found to be, in general, about 10 gpl smaller than the bulk electrolyte (35 gpl vs. 45 gpl). On the other hand, the impurity levels are very similar to bulk composition. By doing this practice, Tamano estimates to 20% the increase of impurities removed in the liberation.

Process evaluation:

For a company dealing with low to moderate levels of impurities, it is an ideal technique to control simultaneously copper content of the electrolyte and to remove most of the impurities introduced from new anodes. In fact, in several instances, 2nd and 3rd stage liberation are the only units in the whole smelter/electrorefinery flowsheet designed for impurity control. However, at higher impurity loads, this technique alone is usually not sufficient as larger volumes of electrolyte would need to be treated with the result that copper depletion in the electrolyte may occur which has to be avoided.

Cost of liberation is generally offset by copper recovery even if current efficiency is extremely low, especially for final purification. In looking at liberation only from the refinery point of view, a significant elimination of minor elements is observed. However, for the smelter/refinery complex, the use of liberation does not really represent an efficient method to remove minor elements. This is because the liberated cathode from 2nd and 3rd stage liberation are recycled to the smelter. As the copper content is high (no sulfur or iron), these cathodes are generally added at the end of the smelting cycle (usually in converting or anode furnaces). Recovery of minor elements to anode is extremely high when this is done. Therefore, most of the impurities sent by the refinery to the smelter are coming back with the new anodes. To recirculate the contaminated cathodes earlier in the process (e.g., smelting furnace) is a potential solution but it is seldom used as these cathodes are almost pure copper and their recycling to the smelting furnace would be highly inefficient from the copper production point of view. In addition, metallic copper charge to the smelting furnace is not suitable as it can attack refractories in the melting region.

Hygiene around the 2nd and 3rd stage liberation is of prime importance and requires that arsine and metallic arsenic levels have to be monitored because they are highly toxic. Proper hooding over the 3rd stage liberation electrowinning cells is a protection measure which was observed worldwide.

6.5.2. EVAPORATIVE CRYSTALLIZATION

Target element: Ni

After being depleted of copper and impurities less noble than copper (As, Sb, Bi) by liberation, the bleed stream is usually treated for nickel recovery. The most common way to remove and recover nickel from electrolyte bleed is by evaporation and crystallization [Toyabe, 1987].

Concentration of nickel in the bled electrolyte by evaporation saturates the stream in nickel sulfate and causes its precipitation as $\text{NiSO}_4 \cdot x\text{H}_2\text{O}$. Evaporation is usually done under reduced pressure. Several options can be used for water evaporation such as steam heating with tantalum clad bayonet heaters, graphite heat exchangers, submerged combustion evaporation, submerged electrode heating or steam jacketed glass-lined reactor [Hoffmann 1997].

Evaporation continues until the sulfuric acid concentration is high enough to ensure precipitation of most nickel originally present in the bled electrolyte. Cooling is then carried out and filtration, or more frequently centrifugation is used to separate the solids. After washing, this crude nickel sulfate can be sold on the market as a valuable by-product.

The final solution remaining is often referred to as black acid because of its dark color (from organics) and high sulfuric acid concentration (1000-1500 gpl, Hoffmann 1997). Several methods exist for its disposal but recycling is the most attractive option when possible.

6.5.3. ION EXCHANGE

Target elements: Sb & Bi

Ion exchange has recently found application for Sb and Bi removal by selective purification of copper electrorefining tankhouse solutions. A part of the electrolyte is sent to one or several packed ion exchange columns loaded with a chelating resin that specifically adsorb Sb and Bi from the electrolyte. When the resin is loaded, it is eluted and ready to be reused.

Principle:

The ion exchange principle to purify copper electrolyte follows conventional ion exchange theory [Demopoulos, 1989]. The resin is first loaded. For Sb/Bi removal from Cu electrolyte, the resin has aminophosphonic acid functional groups that are highly selective for SbO^+ and BiO^+ [Abe and Takasawa, 1987].

Elution is performed with concentrated hydrochloric acid (4-8M) or other Cl^- sources such as $\text{H}_2\text{SO}_4\text{-NaCl}$ [Abe and Takasawa, 1987] and aqueous HCl solution with CaCl_2 , NaCl or MgCl_2 [Cunningham et al., 1997]. The metals are eluted as chlorocomplexes (SbCl_4^- and BiCl_4^-).

Industrial practices:

Ion exchange is used at Mitsui-Tamano, NMM-Hitachi and Saganoseki, Sumitomo-Niihama, ASARCO-Amarillo, and Noranda Inc. - CCR. Several resin suppliers exist commercializing them under various trademarks (Miyoshi MX-2, Duolite C-467, MESCO-Unitika Co. UR-3300, etc.).

At Tamano, it was said to almost double refinery capacity for antimony treatment [Shibata et al., 1987] using a 3 m³ resin volume plant constructed in 1984. Performance was 50 kg Sb and 7 kg Bi per day. Since, the ion exchange plant at Tamano has been upgraded to a 5m³ resin giving a capacity of 83 kg Sb and 11 kg Bi per day [Oda et al., 1995].

The ion exchange plant at Saganoseki [Ishikawa, 1994] has 5m³ of MX-2 resin with a design capacity of 2.2 tonnes of Sb per month. Elution is carried out with 6N HCl. The residue is neutralized with Ca(OH)_2 to form a Sb_2O_3 residue. The raffinate is treated in the waste water plant.

The ASARCO-Amarillo ion exchange plant started in 1993. The flowsheet of the process is presented in Figure 6.15. Zeneca resin (mixture of mono-isooctadecyl ester and phosphoric acid), is used in 2 skids of 4 columns operated in parallel with a special stripping system that permits the recycling of the eluant. This reduces the cost associated with new elution reagents.

At the Sumitomo-Niihama refinery [Toyabe, 1987] activated carbon is used in a similar fashion as ion exchange for antimony removal (believed to be adsorbed as SbAsO_4). The loaded activated carbon is used as reducing agent in the silver plant providing an efficient way to dispose of the residue instead of being eluted like other conventional resins. Ion exchange was also piloted recently in Chile for Sb removal [Roman et al., 1999].

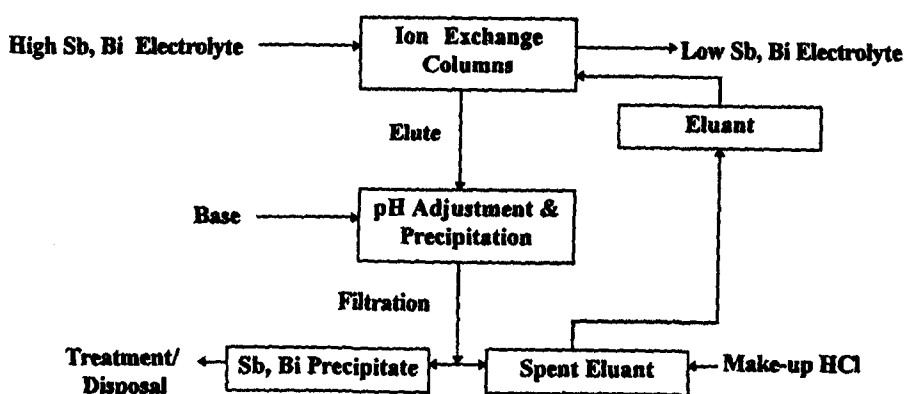


Figure 6.15. Flowsheet of ion exchange plant at the ASARCO-Amarillo refinery reproduced from Cunningham et al., 1997

Process evaluation:

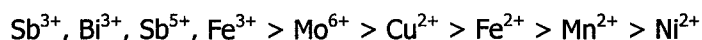
A clear advantage of ion exchange of other purification technologies is that it is independent of the bleed for copper control in the electrolyte (usually by liberation). Therefore, it can be turned on or adjusted as a response to Sb and Bi contents in the electrolyte without affecting the copper balance.

Capital cost of an ion exchange unit is believed to be moderate. Spare columns, eluant purification system, pumps, control equipment, residue stabilization process are associated equipment which also have to be considered. The operating cost depends mainly on the resin

longevity, electric power cost and cost of reagents (eluant, steam and neutralization) as the process is generally fully automated. Several ways are used to regenerate as much as possible the eluant. The most frequent is evaporation/distillation of HCl.

The safe disposal of Sb and Bi chlorides is a problematic issue for most refineries using ion exchange. Highly concentrated chlorides solutions are recovered by means of evaporation such as Tamano [Shibata et al., 1987]. Neutralization with slaked lime is used at Saganoseki [Ishikawa, 1994]. Pyrohydrolysis or precipitation with H₂S [Ando and Tsuchida, 1997] are other potential treatments. Sumitomo has developed a process to recover Sb and Bi from the residue by electrowinning using a mixture of H₂SO₄ and NaCl as an eluant for desorption as noted by Ando and Tsuchida, 1997.

Unit's performance is set by design and type of resin used. Selectively for antimony and bismuth is generally high with all commercial resins. As an example, the selectivity of UR-3300 follows this tendency [Shibata et al., 1987]:



Ferric iron was found to depress adsorption rate by Ando and Tsuchida, 1997. When it accumulates in the chelating resin, the resin gradually becomes poisoned which decreases its efficiency.

Other:

The Falconbridge - Kidd Creek refinery complex also uses a technology based on ion exchange to treat refinery bleed. The process uses ECO-TEC resin to remove and recover sulfuric acid from electrolyte bleed. The acid-free solution is neutralized to precipitate all impurities including Cu and Ni. The cake is sent to Falconbridge's nickel smelter in Sudbury. No directly related literature to its use at Kidd Creek was found but Sweedy and Swaine, 1997, and Cole and Feather, 1995, discuss the general properties of ECO-TEC, 'recoflo' ion exchange for other applications.

6.5.4. SOLVENT EXTRACTION

Target element: As

Purification of copper tankhouse's electrolyte by solvent extraction is carried out industrially only for arsenic removal. However, research is ongoing to develop similar applications for Sb and Bi removal.

Principle:

In strongly acidic solutions such as copper electrolytes, arsenic is believed to exist as undissociated acid (HAsO_2 , Section 5.2.1). The stability of this complex is probably due to formation of strong bonds with water molecules [Baradel et al., 1986]. In order to extract As from the solution, a solvent insoluble and immiscible with the electrolyte must be able to substitute for these water molecules in a compound of a greater stability. The reagents that form such complexes are characterized by the presence of an oxygen atom (or sulfur) which is able to donate an electron pair. After extraction, the solvent is stripped to isolate arsenic and regenerate the extractant.

Industrial practices:

Only the Mount Isa – Townsville refinery [Scholten and Davenport, 1995] and Union Minière – Olen refinery [Rondas et al., 1995] have reported applications of solvent extraction for arsenic removal. Tri-Butyl-Phosphate (TBP) is the solvent used.

The Olen refinery built their solvent extraction plant in 1974 and it has been running smoothly for more than 25 years. Pure TBP is the solvent used. The unit operation is described to be environmentally friendly and to produce As_2O_3 or H_3AsO_4 as saleable by-products. Otherwise, disposable residues of FeAsO_4 or $\text{Ca}_3(\text{AsO}_4)_2$ can be disposed in the environment [Rondas et al., 1995]. The flowsheet of solvent extraction at Olen is presented in Figure 6.16.

With the use of solvent extraction, the electrolyte purification system at Olen is:

- 1- Decopperizing by EW (conventional 1st stage liberation);
- 2- Concentration to reduce bleed volume and increase H_2SO_4 concentration to the level required for SX;
- 3- Solvent extraction with pure TBP; and
- 4- Evaporative precipitation of nickel sulfate.

Step 1 is carried out to recover copper. Step 2 has to be performed to lower the volume of the stream in order to reduce TBP consumption. The use of less TBP permits higher loading and also reduces solvent losses as there is a lower solubility of TBP in more acidic raffinate. Extraction yield for arsenic is industrially found to be 96.7% after 6 extraction steps in series. A disadvantage is co-extraction of H_2SO_4 in the solvent. Partial scrubbing of H_2SO_4 (about 60%) is carried out with water. Arsenic is finally stripped with water. This solution is sent for As_2O_3 precipitation

At the Townsville refinery, diluted TBP (50%) is used to extract As after primary Cu liberation while stripping is carried out with $(\text{NH}_4)_2\text{SO}_4$. Arsenic is further precipitated by adding CuSO_4 and neutralization using NH_3 [Moldoveanu, 1999].

Other possible phosphate-based solvents such as Di-butyl-butyl-phosphate (DBBP), di-pentyl-pentyl-phosphate (DPPP) [Moldoveanu, 1999] have not been used industrially with success yet. Research has also evaluated solvent extraction of arsenic with alcohols, which are more stable than TBP, is less expensive and toxic. Results showed that solvent extraction of arsenic is low but possible with aliphatic long-chain alcohol. Phenols were not effective [Baradel et al., 1986].

Process evaluation:

Efficiency of this technique is relatively high but complete arsenic removal is not possible as TBP does not extract As^{3+} . Thus, the effluent must be treated to produce an environmentally stable residue.

Because it is done after decopperization, the volume of electrolyte treated by solvent extraction is determined by the copper level in the electrolyte and not necessarily the arsenic content. This lack of flexibility represents the major disadvantage of the technology. As a consequence, it should only be viewed as an alternative to the 2nd and 3rd stage of liberation described earlier in this chapter by which arsenic, antimony and bismuth are usually removed.

A clear advantage of solvent extraction over typical liberation is that the arsenic removed in this way can directly be taken out of the circuit versus the recycling of liberation cathodes to the smelter. It also presents the advantage of eliminating health and environmental hazards of liberation (arsine emissions).

A risk of fire exists with organic solvents if the temperature reaches levels close to flash point. For TBC, the high flash point ($>150\text{ }^{\circ}\text{C}$) versus bleed temperature ($50\text{--}60\text{ }^{\circ}\text{C}$) reduces this risk in comparison with other solvents with lower flash points closer to bleed temperature.

Others:

Indications exist that recent developments in the use of solvent extraction for removal of antimony and bismuth are almost ready for industrial application. The nature of solvent is unknown to the author. Navarro et al., 1999, also proved in laboratory scale experiments that diluted LIX-1104 (hidroxamic acid) solvent can be successfully used for extraction of Sb^{3+} from highly concentrated sulfuric acid solutions. High selectivity for Sb^{3+} was found in comparison with Cu^{2+} , As^{5+} and Fe^{3+} . Stripping was achieved with high concentration HCl.

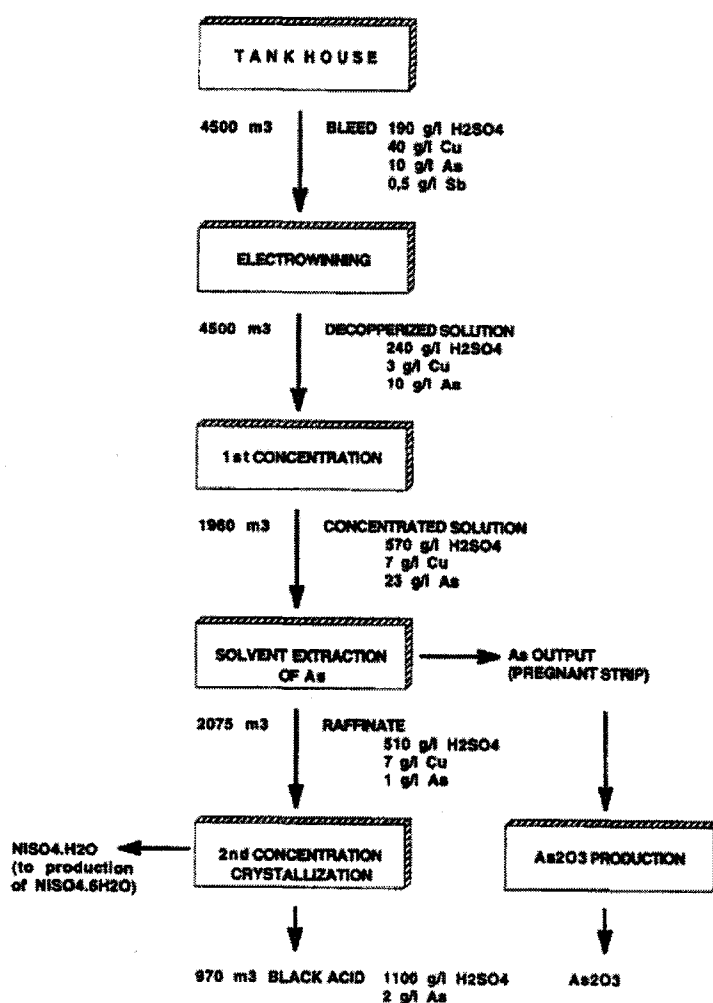


Figure 6.16. The electrolyte bleed treatment at Union Minière (Olen Plant) reproduced from Rondas et al., 1995

CHAPTER 7

CONCLUSIONS

Minor element (As, Sb, Bi, Pb, Ni) behavior and removal techniques in the conventional copper smelting/electrorefining process was studied. To this end, an extensive literature review, industrial visits and consultations with experts in the field were carried out. A total of 23 smelters and 14 copper electrorefineries were visited for data collection and to learn the industrial issues related to minor element treatment and control techniques used. Consultations at 9 universities, 4 industrial research institutes and 2 engineering offices were also realized.

When available, industrial data related to minor element distribution in matte smelting were collected. With those, the effect of various operating parameters and concepts on the behavior of minor elements were investigated. The effect of matte grade, oxygen enrichment, minor element concentration in feed on the distribution coefficient ($D_M^{\text{matte/slag}}$) and partition to gas (P_M^{gas}) was discussed both from industrial data and on the theoretical point of view. Effects of other parameters such as sulphur content of the matte, other minor constituents and temperature were discussed conceptually as not enough information was available for a comparison with industrial data.

The discussion on converting was not as exhaustive because less data was available both in the industry and literature. This can partly be explained as most smelters use Peirce-Smith converting where distributions change with progression of the batch cycle. Minor element partitions between Peirce-Smith overall values and new continuous converting processes were compared from the data available. In addition, deportment to slag in continuous converting vessels was compared with the slag systems used in each vessel.

Minor element behavior in electrorefining was briefly addressed. Most of the discussions were based on the literature as the focus of this project was on smelting and removal techniques.

A descriptive analysis of major techniques for control and removal of minor elements in copper smelting and electrorefining was performed. Dominant technologies used in the smelting process are alkaline and acidic fluxing in the anode furnace, dust bleed and hydrometallurgical treatment, roasting of concentrate, arsenic and lead doping, copper blow with calcium oxide slag, and concentrate injection in Peirce-Smith converters. In electrorefining, electrolyte purification methods discussed include liberation, evaporative crystallization, ion exchange, and solvent extraction. Promising concepts without present industrial

application were also described. These include vacuum refining of copper melt and matte, hydrometallurgical pre-treatment of concentrate, thermal decomposition of concentrate under vacuum, and halide refining.

The following can be underlined from this thesis:

- The growing importance accorded to minor element control and removal in the industry as a result of:
 - Gradual exhaustion of clean concentrate sources;
 - Pressure from customers to get higher quality copper;
 - Additional revenues from penalty charges for custom copper smelters;
 - Lower elimination in modern smelting and converting as compared with traditional practices.
- Marked effect of operating parameters and strategy on industrial minor element distributions for matte smelting furnaces;
- Furnace design is of little significance to minor element distribution in comparison with operating parameters (matte grade, oxygen enrichment, etc.);
- Elimination of most minor elements were favored in smelting over converting;
- Elimination of Bi and Pb were higher for traditional batch converting than in new continuous processes;
- Elimination of As and Sb were improved with the use of calcium ferrite slag and higher oxygen partial pressure in the new continuous converting processes;
- Overall elimination of elements that report largely to slag (e.g., Sb and Pb) was potentially influenced by the type of slag cleaning (pyrometallurgical or mineral processing);
- In electrowinning, Pb reports predominantly to slimes and Ni to electrolyte. The behaviors of As, Sb and Bi depend primarily on anode composition for a given process;
- Nickel volatilization was found to be low and elimination occurs mainly by deportment to slag. Ni was not a problematic element in the smelters/refineries visited;
- Control techniques for the removal of minor elements are widely used in industry. Alkaline refining for As and Sb and dust bleed/treatment for Bi and Pb have found the most industrial applications;
- Arsenic and lead removal practices have to consider hygiene and environmental issues as they involve potentially toxic emissions for which standards and/or regulations exist;
- Vacuum treatment of matte or concentrate and hydrometallurgical pre-treatment of concentrate are the two most promising concepts that have not yet found industrial applications.

A summary of the behaviors and removal techniques for As, Sb, Bi, Pb, Ni follows. It should be noted that average values are given for partitions in the matte smelting furnace as an indication. For converting and electrowinning, only a qualitative indication of the behavior is given because very large variations exist industrially. The Table of Results in Appendix A should be consulted for more data.

ARSENIC

MATTE SMELTING FURNACE:

- Volatilization : HIGH (P_{As}^{gas} avg. = 0.66)
enhanced by: -low oxygen enrichment
-high concentration in feed
- Deportment to slag: LOW TO MODERATE (P_{As}^{slag} avg. = 0.17)
enhanced by: -high matte grade
-high oxygen enrichment

CONVERTING FURNACE:

- Volatilization : LOW TO MODERATE
enhanced by: -batch converting (+ effect of initial matte grade)
-high oxygen partial pressure for continuous converting
- Deportment to slag: LOW TO MODERATE
enhanced by: -use of calcium ferrite slag
-batch converting (+ effect of initial matte grade)

ELECTROREFINING:

- Deportment to slimes: LOW TO MODERATE
enhanced by: -low As concentration in anode

REMOVAL AND CONTROL TECHNIQUES:

- Industrial applications (in order of importance):
-alkaline fluxing in anode furnace;
-electrolyte liberation;
-solvent extraction of electrolyte;
-dust bleed and treatment;
-copper blow with calcium oxide slag;
-roasting pre-treatment;
-concentrate injection in Peirce-Smith converters.
- Proposed methods and strategies:
-hydrometallurgical pre-treatment of concentrate;
-vacuum refining of matte;
-thermal decomposition of concentrate under vacuum;
-halide refining.

ANTIMONY

MATTE SMELTING FURNACE:

- Volatilization: LOW TO MODERATE (P_{Sb}^{gas} avg. = 0.22)
- Deportment to slag: HIGH (P_{Sb}^{slag} avg. = 0.49)
enhanced by: -high oxygen enrichment

CONVERTING FURNACE:

- Volatilization : LOW
enhanced by: -batch converting (+ effect of initial matte grade)
- Deportment to slag: MODERATE TO HIGH
enhanced by: -use of calcium ferrite slag
-batch converting (+ effect of initial matte grade)

ELECTROREFINING:

- Deportment to slimes: MODERATE
enhanced by: -high lead concentration in anode
-high As/(Sb+Bi) in anode

REMOVAL AND CONTROL TECHNIQUES:

- Industrial applications (in order of importance):
 - alkaline fluxing in anode furnace;
 - electrolyte liberation;
 - ion exchange on electrolyte;
 - arsenic and lead doping;
 - concentrate injection in Peirce-Smith converters;
 - dust bleed and treatment.
- Proposed methods and strategies:
 - copper blow with calcium oxide slag;
 - roasting pre-treatment;
 - hydrometallurgical pre-treatment of concentrate;
 - vacuum refining of matte;
 - thermal decomposition of concentrate under vacuum;
 - halide refining.

BISMUTH

MATTE SMELTING FURNACE:

- Volatilization: HIGH ($P_{\text{Bi}}^{\text{gas}}$ avg. = 0.46)
enhanced by: -low oxygen enrichment
-low matte grade
- Deportment to slag: LOW ($P_{\text{Bi}}^{\text{slag}}$ avg. = 0.11)
enhanced by: -high matte grade
-high oxygen enrichment

CONVERTING FURNACE:

- Volatilization: MODERATE TO HIGH
enhanced by: -batch converting (+ effect of initial matte grade)
-low oxygen partial pressure for continuous converting
- Deportment to slag: LOW
enhanced by: -high oxygen partial pressure for continuous converting
-batch converting (+ effect of initial matte grade)

ELECTROREFINING:

- Deportment to slimes: LOW TO MODERATE
enhanced by: -high lead concentration in anode

REMOVAL AND CONTROL TECHNIQUES:

- Industrial applications (in order of importance):
 - dust bleed and treatment;
 - electrolyte liberation;
 - ion exchange on electrolyte;
 - lead doping;
 - arsenic doping;
 - concentrate injection in Peirce-Smith converters.
- Proposed methods and strategies:
 - vacuum refining of copper or matte;
 - roasting pre-treatment;
 - hydrometallurgical pre-treatment of concentrate;
 - thermal decomposition of concentrate under vacuum;
 - halide refining.

LEAD

MATTE SMELTING FURNACE:

- Volatilization : MODERATE (P_{Pb}^{gas} avg. = 0.22)
enhanced by: -high matte grade
- Deportment to slag: MODERATE TO HIGH (P_{Pb}^{slag} avg. = 0.36)
enhanced by: -high matte grade
-high oxygen enrichment

CONVERTING FURNACE:

- Volatilization: LOW TO MODERATE
enhanced by: -high oxygen partial pressure for continuous converting
-batch converting (+ effect of initial matte grade)
- Deportment to slag: MODERATE TO HIGH
enhanced by: -use of silicate slag
-batch converting (+ effect of initial matte grade)

ELECTROREFINING:

- Deportment to slimes: HIGH

REMOVAL AND CONTROL TECHNIQUES:

- Industrial applications:
 - dust bleed and treatment;
 - acidic fluxing in anode furnace;
 - concentrate injection in Peirce-Smith converters;
- Proposed methods and strategies (in order of importance):
 - vacuum refining of copper or matte;
 - roasting pre-treatment;
 - thermal decomposition of concentrate under vacuum;

NICKEL

MATTE SMELTING FURNACE:

- Volatilization: LOW ($P_{\text{Ni}}^{\text{gas}}$ avg. = 0.02)
- Deportment to slag: MODERATE ($P_{\text{Ni}}^{\text{slag}}$ avg. = 0.27)
enhanced by: -high matte grade
-high oxygen enrichment

ELECTROREFINING:

- Deportment to slimes: LOW

REMOVAL TECHNIQUES:

- Industrial applications:
-evaporative crystallization.

CHAPTER 8

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APPENDIX A

TABLE OF RESULTS **(INDUSTRIAL + LITERATURE)**

NOTE:

'Data from industrial visits' were collected directly at the smelter site. As discussed in Section 4.2., the ratios (P_M^i and $D_M^{\text{matte/slag}}$) were generally calculated from raw assays and tonnages of matte and slag given at the smelter. In most cases, the assays given were monthly or yearly averages but some exceptions (selected samples) exist. P_M^{gas} was usually calculated by difference from the total input to the furnace. As per the request of the smelters visited, no chemical assays of internal streams (feed, matte, blister, slag) used for the calculations are published. The exception is the anode composition.

In the section 'data from literature', the same information is presented from related literature with reference to the source article.

LEGEND:

$D_M^{\text{matte/slag}}$: Distribution coefficient between matte and slag $[\text{wt}\% \text{ M}]_{\text{matte}}/(\text{wt}\% \text{ M})_{\text{slag}}$

P_M^i : Fraction of element 'M' to phase 'i'

Anode: Average (or number given) composition of anode copper produced (in ppm)

Smelting:

- O. FSF: Outokumpu Flash Smelting Furnace
- I. FSF: Inco Flash Smelting Furnace
- T.C.: Teniente Converter (smelting furnace)
- Nor. R.: Noranda Process Reactor
- M-S: Mitsubishi S-furnace
- ISA: Isasmelt
- Rev: Reverberatory furnace

Converting:

- P-S: Peirce-Smith converters
- K-O. FCF: Kennecott-Outokumpu Flash Converting Furnace
- NCV: Noranda Continuous Converter
- M-C: Mitsubishi C-furnace
- H: Hoboken converters
- Inj.: Concentrate injection in Peirce-Smith Converters

Type of slag:

- F: Fayalite
- Ca-Fe: Calcium Ferrite
- Ca: Calcium oxide (CaO or CaCO_3) at the end of converting

ARSENIC

	Smelter name	Data source	Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
			Furnace type	Matte grade (%Cu)	%O ₂	Dust Bleed	Type	Type of slag	Dust bleed		D ^{matte/slag}	p ^{gas}	p ^{matte}	p ^{slag}	Anode (ppm)
D A T A F R O M I N D U S T R I A L V I S I T S	Chagres	Visit 1999	O. FSF	62	71	no	P-S	F	no						968
	Chuquicamata - FSF	Visit 1999	O. FSF	60	50	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting	2.0	0.42	0.36	0.22	1720
	Hidalgo	Visit 1999	O. FSF	62.5	40	no	P-S	F	no		1.4	0.591	0.02	0.39	320
	Kennecott	Visit 1999	O. FSF	70	75	part - hydro	K-O. FCF	Ca-Fe	part - hydro	SiO ₂ fluxing	1.2	0.583	0.183	0.235	1000-4000
	Kosaka	Visit 1999	O. FSF	56	45	full - hydro	P-S	F + Ca	full - hydro	overblowing with SiO ₂ & CaCO ₃	0.7	0.803	0.117	0.079	1100
	La Caridad	Visit 1999	O. FSF	63	50	no	P-S	F	no	CaCO ₃ at the end of converting	1				2490
	Saganoseki	Visit 1999	O. FSF	65	71	no	P-S	F	full - hydro		1.5	0.439	0.35	0.211	1080
	Tamano	Visit 1999	O. FSF	63	47.5	no	P-S	F	full				0.467		1000
	Toyo	Visit 1999	O. FSF	61	44	no	P-S	F	no		0.4				800
	Caletones	Visit 1999	T.C.	75	33	part	P-S	F	part - hydro	soda fluxing	1.9	0.765	0.112	0.123	1500
	Chuquicamata	Visit 1999	T.C.	74	36	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting	1.0	0.84	0.07	0.09	1720
	La Caridad	Visit 1999	T.C.	73	31	part	P-S	F	no	CaCO ₃ at the end of converting	0.9	0.642	0.121	0.237	2490
	Las Ventanas	Visit 1999	T.C.	75	33	part - hydro	P-S	F	-						900
	Hernan Videla Lira	Visit 1999	T.C.	72.9	35	no	P-S	F	no		1	0.65	0.15	0.2	240
	Potrerrillos	Visit 1999	T.C.	72.2	29	part - hydro	P-S	F	part	soda fluxing	2	0.888	0.058	0.054	890
	Horne	2000	Nor. R.	70	40	part - hydro	NCV	F	no	soda fluxing	2.5	0.85	0.075	0.075	500
	Naoshima	Visit 1999	M-S	67	57	part - hydro	M-C	Ca-Fe	full - hydro		1.5				1000
	Kidd Creek	Visit 1999	M-S	69	48	full - hydro	M-C	Ca-Fe	part - hydro	SiO ₂ fluxing					600
	Miami	Visit 1999	ISA	56.9	45	no	P-S + H	F	no		0.4	0.887	0.054	0.059	770
	Hayden	Visit 1999	I.FSF	60	96	no	P-S	F	full		0.7	0.126	0.531	0.343	390
	Altonorte	Visit 1999	Rev.	50	21	no	P.S. + Inj.	F	no	concentrate injection	0.8	0.597	0.207	0.196	894
	Caletones	Visit 1999	Rev.	52	21	no	P-S	F	part - hydro	soda fluxing	3.6	0.78	0.166	0.054	1500
	Gaspé	2000	Rev.	41	21	no	P.S. + Inj.	F	part	concentrate injection	0.6	0.57	0.18	0.25	885
	Onahama	Visit 1999	Rev.	42	21	no	P.S. + Inj.	F	part	concentrate injection	1				460
	Potrerrillos	Visit 1999	Rev.	47.2	21	no	P-S	F	part	soda fluxing	0.4	0.769	0.172	0.059	890

INDUSTRIAL AVERAGE*

1.3 0.66 0.19 0.17 1100

STDEVATION

0.8 0.20 0.15 0.11 657

*The industrial average should be used with great care as minor element distributions change to a great extent with operating conditions (Chapter 4)

ARSENIC

			Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
	Smelter name	Data source	Furnace type	Matte grade (%Cu)	%O ₂	Dust Bleed	Type	Type of slag	Dust bleed		D _{matte/slag}	p _{gas}	p _{matte}	p _{slag}	Anode (ppm)
D A T A F R O M L I T E R A T U R E	Kosaka	Tenmaya et al., 1993	O.FSF	52.5	42	full - hydro	P-S	F	full - hydro	overblowing with SiO ₂ & CaCO ₃	0.7	0.577	0.153	0.27	1000
	Chuquicamata-Out FSF	Mendoza et al., 1995	O.FSF	60	50	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting		0.48	0.305	0.215	
	Saganoseki	Hino et al., 1995	O.FSF	60	81.3	part - hydro	P-S	F	full - hydro			0.258	0.495	0.247	
	Outokumpu #1	Weisenberg et al., 1979	O.FSF	45			P-S	F				0.76	0.07	0.17	
	Chuquicamata-CT	Mendoza et al., 1995	T.C.	71.1	30	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting		0.87	0.058	0.072	
	Teniente global	Harris, 1999	T.C.	75.7	32	n/a						0.88	0.06	0.06	
	Las Ventanas	Diaz, et al., 1997	T.C.	75	33	part	P-S	F				0.59	0.25	0.16	
	Noranda - Home	Harris, 1999	Nor. R.	70	42	n/a						0.8	0.08	0.12	
	Kidd Creek	Chenier et al., 1992	M.S.	69	48	full - hydro	M-C	Ca-Fe	part - hydro	SiO ₂ fluxing		0.44	0.14	0.42	
	Naoshima	Ajima et al., 1995	M.S.	67	47.5	part - hydro	M-C	Ca-Fe	full - hydro		1.37	0.75			
	Reverb Slovakia	Virckova and Imris, 1995	Rev.				P-S	F		soda fluxing		0.118	0.34	0.542	
	Naoshima	Suzuki et al., 1977	Rev.	45	21	no	P-S	F	full - hydro		0.6	0.67	0.03	0.3	
	Onahama	Saitoh et al., 1994	Rev.	39.2	21		P.S. + Inj.	F		concentrate injection	1.2				
	Reverb #1	Weisenberg et al., 1979	Rev.	40	21		P-S	F				0.55	0.2	0.25	
	Reverb #2	Weisenberg et al., 1979	Rev.	40	21		P-S	F				0.73	0.17	0.097	
	Reverb #3	Weisenberg et al., 1979	Rev.				P-S	F				0.29	0.45	0.26	
	Reverb #4	Weisenberg et al., 1979	Rev.				P-S	F				0.8	0.1	0.1	

ANTIMONY

	Smelter name	Data source	Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
			Furnace type	Matte grade (%Cu)	%O ₂	Dust Bleed	Type	Type of slag	Dust bleed		D ^{matte/slag}	p ^{gas}	p ^{matte}	p ^{slag}	Anode (ppm)
D A T A F R O M I N D U S T R I A L V I S I T S	Chuquicamata - FSF	Visit 1999	O. FSF	60	50	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting					183
	Kennecott	Visit 1999	O. FSF	70	75	part - hydro	K-O FCF	Ca-Fe	part - hydro	SiO ₂ fluxing					100-125
	Kosaka	Visit 1999	O. FSF	56	45	full - hydro	P-S	F + Ca	full - hydro	overblowing with SiO ₂ & CaCO ₃	0.6	0.115	0.235	0.65	1100
	La Caridad	Visit 1999	O. FSF	63	50	no	P-S	F	no	CaCO ₃ at the end of converting	0.7				628
	Saganoseki	Visit 1999	O. FSF	65	71	no	P-S	F	full - hydro		1.1				200
	Tamano	Visit 1999	O. FSF	63	47.5	no	P-S	F	full						140
	Toyo	Visit 1999	O. FSF	61	44	no	P-S	F	no		1.3				200
	Caletones	Visit 1999	T.C.	75	33	part	P-S	F	part - hydro	soda fluxing	0.4		0.18		170
	Chuquicamata	Visit 1999	T.C.	74	36	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting					183
	La Caridad	Visit 1999	T.C.	73	31	part	P-S	F	no	CaCO ₃ at the end of converting	0.4				628
	Las Ventanas	Visit 1999	T.C.	75	33	part - hydro	P-S	F							360
	Hernan Videla Lira	Visit 1999	T.C.	72.9	35	no	P-S	F	no						51
	Potrerrillos	Visit 1999	T.C.	72.2	29	part	P-S	F	part	soda fluxing					133
	Horne	2000	Nor. R.	70	40	part - hydro	NCV	F	no	soda fluxing	0.4	0.13	0.12	0.75	375
	Naoshima	Visit 1999	M-S	67	57	part - hydro	M-C	Ca-Fe	full - hydro		0.7				100
	Kidd Creek	Visit 1999	M-S	69	48	full - hydro	M-C	Ca-Fe	part - hydro	SiO ₂ fluxing					50
	Miami	Visit 1999	ISA	56.9	45	no	P-S + H.	F	no		0.5	0.522	0.34	0.138	132
	Hayden	Visit 1999	I. FSF	60	96	no	P-S	F	full		0.3				340
	Altonorte	Visit 1999	Rev.	50	21	no	P-S + Inj	F	no	concentrate injection	0.8		0.518	0.486	267
	Caletones	Visit 1999	Rev.	52	21	no	P-S	F	part - hydro	soda fluxing	0.6				170
	Gaspé	2000	Rev.	41	21	no	P-S + Inj	F	part	concentrate injection	0.8	0.13	0.43	0.44	210
	Onahama	Visit 1999	Rev.	42	21	no	P-S + Inj	F	part	concentrate injection	1.0				100
	Potrerrillos	Visit 1999	Rev.	47.2	21	no	P-S	F	part	soda fluxing					133

INDUSTRIAL AVERAGE*

0.7 0.22 0.30 0.49 265

STDEVATION

0.3 0.20 0.15 0.23 244

*The industrial average should be used with great care as minor element distributions change to a great extent with operating conditions (Chapter 4)

ANTIMONY

			Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
	Smelter name	Data source	Furnace type	Matte grade (%Cu)	%O2	Dust Bleed	Type	Type of slag	Dust bleed		D ^{matte/slag}	p ^{gas}	p ^{matte}	p ^{slag}	Anode (ppm)
D A T A F R O M L I T E R A T U R E	Kosaka	Temaya et al., 1993	Out. FSF	52.5	42	full - hydro	P-S	F	full - hydro	overblowing with SiO ₂ & CaCO ₃	0.7	0.105	0.325	0.57	480
	Chuquicamata-Out FSF	Mendoza et al., 1995	Out. FSF	60	50	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting		0.442	0.476	0.082	
	Saganoseki	Hino et al., 1995	Out. FSF	60	81.3	part - hydro	P-S	F	full - hydro			0.509	0.481		
	Chuquicamata-CT	Mendoza et al., 1995	T.C.	71.1	30	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting		0.514	0.189	0.297	
	Teniente global	Harris, 1999	T.C.	75.7	32	n/a						0.51	0.19	0.3	
	Las Ventanas	Diaz, et al., 1997	T.C.	75	33	part	P-S	F				0.49	0.26	0.23	
	Noranda - Horne	Harris, 1999	Nor. R.	70	42	n/a						0.54	0.15	0.31	
	Kidd Creek	Chenier et al., 1992	M-S	69	48	full - hydro	M-C	Ca-Fe	part - hydro	SiO ₂ fluxing		0.06	0.21	0.71	
	Naoshima	Ajima et al., 1995	M-S	67	47.5	part - hydro	M-C	Ca-Fe	full - hydro		0.59	0.125			
	Naoshima	Suzuki et al., 1977	Rev.	45	21	no	P-S	F	full - hydro		1.4				
	Onahama	Saitoh et al., 1994	Rev.	39.2	21		P-S Inj.	F		concentrate injection	2.0				

BISMUTH

	Smelter name	Data source	Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
			Furnace type	Matte grade (%Cu)	%O ₂	Dust Bleed	Type	Type of slag	Dust bleed		D ^{matte/slag}	p ^{gas}	p ^{matte}	p ^{slag}	Anode (ppm)
D A T A F R O M I N D U S T R I A L V I S I T S	Chuquicamata - FSF	Visit 1999	O. FSF	60	50	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting					109
	Kennecott	Visit 1999	O. FSF	70	75	part - hydro	K-O. FCF	Ca-Fe	part - hydro	SiO ₂ fluxing	1.2	0.591	0.325	0.084	400-600
	Kosaka	Visit 1999	O. FSF	56	45	full - hydro	P-S	F + Ca	full - hydro	overblowing with SiO ₂ & CaCO ₃			0.178		500
	La Caridad	Visit 1999	O. FSF	63	50	no	P-S	F	no	CaCO ₃ at the end of converting	3.7				190
	Saganoseki	Visit 1999	O. FSF	65	71	no	P-S	F	full - hydro		2	0.474	0.361	0.164	100
	Tamano	Visit 1999	O. FSF	63	47.5	no	P-S	F	full				0.675		60
	Toyo	Visit 1999	O. FSF	61	44	no	P-S	F	no		4				300
	Caletones	Visit 1999	T.C.	75	33	part	P-S	F	part - hydro	soda fluxing	1				
	Chuquicamata	Visit 1999	T.C.	74	36	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting					109
	La Caridad	Visit 1999	T.C.	73	31	part	P-S	F	no	CaCO ₃ at the end of converting	1.3				190
	Las Ventanas	Visit 1999	T.C.	75	33	part - hydro	P-S	F							130
	Horne	2000	Nor. R.	70	40	part - hydro	NCV	F	no	soda fluxing	2.8	0.7	0.16	0.14	150
	Naoshima	Visit 1999	M-S	67	57	part - hydro	M-C	Ca-Fe	full - hydro		3.8				150
	Kidd Creek	Visit 1999	M-S	69	48	full - hydro	M-C	Ca-Fe	part - hydro	SiO ₂ fluxing					40
	Miami	Visit 1999	ISA	56.9	45	no	P-S + H.	F	no		0.7	0.481	0.404	0.115	13
	Hayden	Visit 1999	I. FSF	60	96	no	P-S	F	full		4	0.199	0.723	0.078	130
	Altonorte	Visit 1999	Rev.	50	21	no	P-S + Inj.	F	no	concentrate injection					20
	Gaspé	2000	Rev.	41	21	no	P-S + Inj.	F	part	concentrate injection	4.7	0.31	0.59	0.1	80
	Onahama	Visit P.L. - '99	Rev.	42	21	no	P-S + Inj.	F	part	concentrate injection					40
INDUSTRIAL AVERAGE*											2.7	0.46	0.43	0.11	156
STDEVATION											1.5	0.18	0.22	0.03	143

*The industrial average should be used with great care as minor element distributions change to a great extent with operating conditions (Chapter 4)

BISMUTH

			Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
	Smelter name	Data source	Furnace type	Matte grade (%Cu)	%O ₂	Dust Bleed	Type	Type of slag	Dust bleed		D ^{matte/slag}	p ^{gas}	p ^{matte}	p ^{slag}	Anode (ppm)
D A T A F R O M L I T E R A T U R E	Kosaka	Tenmaya et al., 1993	O. FSF	52.5	42	full - hydro	P-S	F	full - hydro	overblowing with SiO ₂ & CaCO ₃		0.5	0.491	0.009	110
	Chuquicamata-Out FSF	Mendoza et al., 1995	O. FSF	60	50	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting		0.548	0.369	0.083	
	Magma	Young & Um, 1992	O. FSF	61.5	65	no	P-S	F	part - hydro			0.742	0.245	0.013	41
	Chuquicamata-CT	Mendoza et al., 1995	T.C.	71.1	30	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting		0.37	0.227	0.403	
	Teniente global	Harris, 1999	T.C.	75.7	32	n/a						0.152	0.22	0.628	
	Las Ventanas	Diaz, et al., 1997	T.C.	75	33	part	P-S	F				0.3	0.37	0.33	
	Noranda - Horne	Harris, 1999	Nor. R.	70	42	n/a						0.79	0.09	0.12	
	Kidd Creek	Chenier et al., 1992	M-S	69	48	full - hydro	M-C	Ca-Fe	part - hydro	SiO ₂ fluxing		0.68	0.24	0.06	
	Naoshima	Ajima et al., 1995	M-S	67	47.5	part - hydro	M-C	Ca-Fe	full - hydro		3.03	0.55			
	Naoshima	Suzuki et al., 1977	Rev.	45	21	no	P-S	F	full - hydro						
	Nchanga	Hanks et al., 1979	Rev.	60.7	21		P-S	F			3.2				

LEAD

			Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
	Smelter name	Data source	Furnace type	Matte grade (%Cu)	%O2	Dust Bleed	Type	Type of slag	Dust bleed		D ^{matte/slag}	p ^{gas}	p ^{matte}	p ^{slag}	Anode (ppm)
D A T A F R O M I N D U S T R I A L V I S I T S	Chuquicamata - FSF	Visit 1999	O. FSF	60	50	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting					120
	Hidalgo	Visit 1999	O. FSF	62.5	40	no	P-S	F	no	-	1.4	0.123	0.056	0.821	
	Kennecott	Visit 1999	O. FSF	70	75	part - hydro	O. FCF	Ca-Fe	part - hydro	SiO ₂ fluxing	1.2	0.239	0.362	0.399	2500-4000
	Kosaka	Visit 1999	O. FSF	56	45	full - hydro	P-S	F + Ca	full - hydro	overblowing with SiO ₂ & CaCO ₃			0.406		2600
	La Caridad	Visit 1999	O. FSF	63	50	no	P-S	F	no	CaCO ₃ at the end of converting					840
	Saganoseki	Visit 1999	O. FSF	65	71	no	P-S	F	full - hydro	-	2.4				120
	Tamano	Visit 1999	O. FSF	63	47.5	no	P-S	F	full	-					950
	Toyo	Visit 1999	O. FSF	61	44	no	P-S	F	no	-	2.8				600
	Chuquicamata	Visit 1999	T.C.	74	36	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting					120
	La Caridad	Visit 1999	T.C.	73	31	part	P-S	F	no	CaCO ₃ at the end of converting					840
	Las Ventanas	Visit 1999	T.C.	75	33	part - hydro	P-S	F	-	-					330
	Hernan Videla Lira	Visit 1999	T.C.	72.9	35	no	P-S	F	no	-					800
	Potrerrillos	Visit 1999	T.C.	72.2	29	part	P-S	F	part	soda fluxing					133
	Horne	2000	Nor. R.	70	40	part - hydro	NCV	F	no	soda fluxing	2.8	0.35	0.35	0.3	1250
	Naoshima	Visit 1999	M-S	67	57	part - hydro	M-C	Ca-Fe	full - hydro	-	2.4				4000
	Kidd Creek	Visit 1999	M-S	69	48	full - hydro	M-C	Ca-Fe	part - hydro	SiO ₂ fluxing					1500
	Miami	Visit 1999	ISA	56.9	45	no	P-S + H.	F	no	-	2.6				129
	Hayden	Visit 1999	I. FSF	60	96	no	P-S	F	full	-	1.7				110
	Altonorte	Visit 1999	Rev.	50	21	no	P-S + Inj.	F	no	concentrate injection	3.9	0.204	0.669	0.127	30
	Caletones	Visit 1999	Rev.	52	21	no	P-S	F	part - hydro	soda fluxing	2.8				
	Gaspé	2000	Rev.	41	21	no	P-S + Inj.	F	part	concentrate injection	3.5	0.2	0.65	0.15	350
	Onahama	Visit 1999	Rev.	42	21	no	P-S + Inj.	F	part	concentrate injection	3.8				260

INDUSTRIAL AVERAGE*

2.6 0.22 0.42 0.36 917

STDEVIATION

0.9 0.08 0.23 0.28 1125

*The industrial average should be used with great care as minor element distributions change to a great extent with operating conditions (Chapter 4)

LEAD

			Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
	Smelter name	Data source	Furnace type	Matte grade (%Cu)	%O ₂	Dust Bleed	Type	Type of slag	Dust bleed		D ^{matte/slag}	p ^{gas}	p ^{matte}	p ^{slag}	Anode (ppm)
D A T A F R O M L I T E R A T U R E	Kosaka	Teruya et al., 1993	O. FSF	52.5	42	full - hydro	P-S	F	full - hydro	overblowing with SiO ₂ & CaCO ₃	4.1	0.308	0.542	0.15	
	Chuquicamata-Out FSF	Mendoza et al., 1995	O. FSF	60	50	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting		0.329	0.512	0.155	
	Toyo	Kimura et al., 1994	O. FSF	61.3	42.3	no	P-S	F	no	-	4.1				
	Saganoseki	Hino et al., 1995	O. FSF	60	81.3	part - hydro	P-S	F	full - hydro	-			0.771	0.229	
	Chuquicamata-CT	Mendoza et al., 1995	T.C.	71.1	30	part - hydro	P-S	F	part - hydro	soda fluxing + CaCO ₃ at the end of converting		0.529	0.22	0.251	
	Teniente global	Harris, 1999	T.C.	75.7	32	n/a	-	-	-	-		0.54	0.22	0.24	
	Las Ventanas	Diaz, et al., 1997	T.C.	75	33	part	P-S	F	-	-		0.42	0.31	0.27	
	Noranda - Horne	Harris, 1999	Nor. R.	70	42	n/a	-	-	-	-		0.73	0.13	0.14	
	Kidd Creek	Chenier et al., 1992	M-S	69	48	full - hydro	M-C	Ca-Fe	part - hydro	SiO ₂ fluxing		0.42	0.32	0.26	
	Naoshima	Ajima et al., 1995	M-S	67	47.5	part - hydro	M-C	Ca-Fe	full - hydro	-	2.65	0.5			
	Naoshima	Suzuki et al., 1977	Rev.	45	21	no	P-S	F	full - hydro	-	7.1				
	Onahama	Saitoh et al., 1994	Rev.	39.2	21	-	P-S + Inj.	F	-	concentrate injection	4.2				

NICKEL

			Smelting				Converting			Special treatment for minor elements (except dust bleed)	Smelting furnace				
	Smelter name	Data source	Furnace type	Matte grade (%Cu)	%O2	Dust Bleed	Type	Type of slag	Dust bleed		D _{matte/slag}	p _{gas}	p _{matte}	p _{slag}	Anode (ppm)
D A T A F R O M I N D U S T R I A L V I S I T S	Kennecott	Visit 1999	O. FSF	70	75	part - hydro	Kennecott Outokumpu FCF	Ca-Fe	part - hydro	SiO ₂ fluxing					215
	Kosaka	Visit 1999	O. FSF	56	45	full - hydro	Peirce-Smith	fayalite + Ca	full - hydro	overblowing with SiO ₂ & CaCO ₃					1200
	La Caridad	Visit 1999	O. FSF	63	50	no	Peirce-Smith	fayalite	no	CaCO ₃ at the end of converting					220
	Saganoseki	Visit 1999	O. FSF	65	71	no	Peirce-Smith	fayalite	full - hydro						880
	Tamano	Visit 1999	O. FSF	63	47.5	no	Peirce-Smith	fayalite	full						700
	Toyo	Visit 1999	O. FSF	61	44	no	Peirce-Smith	fayalite	no						1100
	La Caridad	Visit 1999	T.C.	73	31	part	Peirce-Smith	fayalite	no	CaCO ₃ at the end of converting					220
	Hernan Videla Lira	Visit 1999	T.C.	72.9	35	no	Peirce-Smith	fayalite	no						290
	Potrerrillos	Visit 1999	T.C.	72.2	29	part	Peirce-Smith	fayalite	part	soda fluxing					71
	Horne	2000	Nor. R.	70	40	part - hydro	Noranda Continuous Cv	fayalite	no	soda fluxing	4.5	0.01	0.65	0.34	1750
	Kidd Creek	Visit 1999	M-S	69	48	full - hydro	Mitsubishi-C	Ca-Fe	part - hydro	SiO ₂ fluxing					3500
	Miami	Visit 1999	ISA	56.9	45	no	PS + Hoboken	fayalite	no		14.6				514
	Hayden	Visit 1999	I. FSF	60	96	no	Peirce-Smith	fayalite	full		5				
	Altonorte	Visit 1999	Rev.	50	21	no	Peirce-Smith + concentrate inj.	fayalite	no	concentrate injection					116
	Caletones	Visit 1999	Rev.	52	21	no	Peirce-Smith	fayalite	part - hydro	soda fluxing	8.9				
	Gaspé	2000	Rev.	41	21	no	Peirce-Smith + concentrate inj.	fayalite	part	concentrate injection	2.6	0.02	0.78	0.2	640
	Onahama	Visit 1999	Rev.	42	21	no	Peirce-Smith + concentrate inj.	fayalite	part	concentrate injection					115

INDUSTRIAL AVERAGE*

7.12 0.02 0.72 0.27 769

STDEVATION

4.8 0.01 0.09 0.10 898

*The industrial average should be used with great care as minor element distributions change to a great extent with operating conditions (Chapter 4)

L I T E R A T U R E	Kosaka	Yemaya et al., 1993	O. FSF	52.5	42	full - hydro	Peirce-Smith	fayalite	full - hydro	overblowing with SiO ₂ & CaCO ₃					520
	Teniente global	Harris, 1999	T.C.	75.7	32	n/a					0.01	0.8	0.19		
	Las Ventanas	Diaz, et al., 1997	T.C.	75	33	part	Peirce-Smith	fayalite			0.04	0.63	0.33		
	Noranda - Horne	Harris, 1999	Nor. R.	70	42	n/a					0.01	0.78	0.21		
	Naoshima	Ajima et al., 1995	M-S	67	47.5	part - hydro	Mitsubishi-C	Ca-Fe	full - hydro						
	Naoshima	Suzuki et al., 1977	Rev.	45	21	no	Peirce-Smith	fayalite	full - hydro						

APPENDIX B

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APPENDIX A – TABLE OF RESULTS

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