

MINOR ELEMENT BEHAVIOR  
IN THE INCO CRED PROCESS

by

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## ABSTRACT

In INCO's Copper Refinery Electrowinning Department (CRED) the copper sulfide residue containing precious metals (referred as the first stage cake), is subjected to an oxidative pressure leach. The leach – referred as second stage leaching, produces a copper sulfate solution and basic copper sulfate. The basic copper sulfate is releached with spent electrolyte from copper electrowinning containing sulfuric acid to produce impure copper sulfate solution and a precious metals residue.

A sample of first stage cake from INCO CRED was shipped to UBC and treated under second stage leaching conditions. The minor element behavior in the process was the objective of the study. The minor elements include cobalt, iron, arsenic, antimony, bismuth, selenium, tellurium and tin. Four important factors that might affect the behavior of minor elements were investigated: Cu/Acid ratio in the feed, Cu/S ratio in the feed, impurity levels in the feed and degree of oxidation. Four series of experiments were performed with filtrate solutions and solid residues analyzed by ICP scan for chemical compositions.

Selenium was the minor element of greatest interest due to the difficulty in removing Se from the CRED impure leach solution. Selenium species if present will contaminate copper cathodes and therefore must be removed. The two principal forms of selenium in the CRED streams are believed to be selenite ( $\text{Se}^{\text{IV}}$ ) and selenate ( $\text{Se}^{\text{VI}}$ ), respectively. INCO CRED had a great concern about selenium speciation in the second stage leaching, which will help to understand the behavior of selenium better and remove it more efficiently. A method for selenium analysis was developed, which was based on Atomic Fluorescence Spectrometry with Hydride Generation (AFS-HG). A pretreatment process was applied to suit the samples in the project and eliminate interferences in Se analysis caused by sulfate and cations. This method was initially applied to samples generated in the UBC lab work. In addition, some samples were taken from INCO CRED plant and analyzed by this method.

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## CHAPTER 1 INTRODUCTION

Hydrometallurgy technology has become an important process for extracting metals from ores or concentrates. At INCO CRED (Inco Ltd.'s Copper Refinery Electrowinning Department) pressure hydrometallurgy is used in the acid leaching of copper.

About 80% of the world's supply of copper is present as sulphidic ores. The recovery of copper from sulphide ores has been practiced for many centuries traditionally using pyrometallurgical technology. Until recently with the higher demand of environment protection, hydrometallurgical technique has been making great progress because of its specific advantages.

Potential advantages and disadvantages of hydrometallurgical processes [1] are shown as follows:

### A. Advantages

1. In comparing capital costs, expenditures of hydrometallurgy are usually less than that of pyrometallurgical processes.
2. Hydrometallurgical processes have the flexibility for treatment of complex ores and for production of a variety of by-product metals.
3. Hydrometallurgical operations are generally performed at lower temperatures and many use less energy compared to the high temperatures often employed in pyrometallurgical operations.
4. Hydrometallurgical processes generally do not produce gases (such as sulfur dioxide, which must be converted to sulfuric acid or disposed of by other ways), and if they do, the container can be made gas-tight easily. Hydrometallurgical processes reduce air pollution caused by smelter emissions.

## B. Disadvantages

1. Hydrometallurgical plants require more sophisticated control schemes to maintain satisfactory operation.
2. Engineering of hydrometallurgical plants is more complex and requires the full understanding of scaleup relationships as well as processing requirements.
3. Hydrometallurgical processes can produce significant amounts of liquid or solid wastes that may cause serious disposal problems. Sometimes even the separation of solid and liquid may ruin a hydrometallurgical procedure.

In hydrometallurgy, the leaching process plays a very important role, in which valuable metals can be dissolved into solution for further processing. In general, leaching methods can be classified into percolation leaching and agitated leaching shown in figure 1.1. These methods should be chosen according to the nature of ores and mineral deposits.

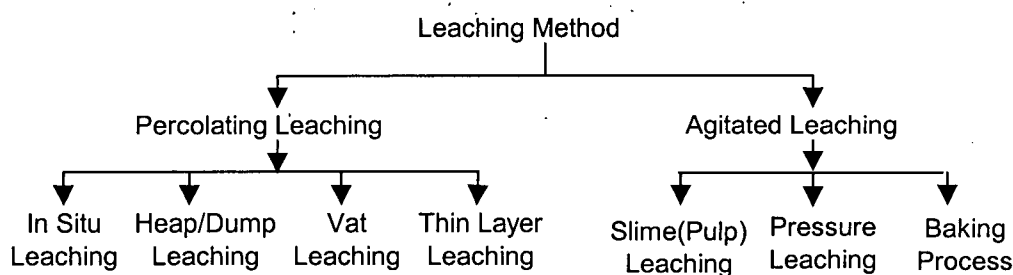


Figure 1.1 Classification of leaching methods [1]

The common sulfide minerals of copper such as chalcocite, chalcopyrite and covellite are not as such soluble in dilute sulfuric acid. However, they readily dissolve in  $\text{H}_2\text{SO}_4$  in the presence of oxidizing agents such as oxygen, ferric ion and bacteria. Pressure leaching is used worldwide for copper and nickel recovery, particularly in the treatment of copper-nickel matte.

At INCO CRED, a sulfide residue is produced from its first stage leaching, which mostly contains chalcocite ( $\text{Cu}_2\text{S}$ ) as well as small amounts of Ni, Co, Fe, As, Sb, Se, Te and precious metals. This residue was shipped to UBC for experimental work to investigate minor element behavior during second stage leaching. In the laboratory the industrial

operating conditions were imitated in small scale tests and the minor element behavior in the system was studied by analyzing the distribution of each element during the leaching process.

Minor element behavior in leaching processes is a significant concern at INCO CRED because these impurity elements may have a deleterious impact on copper electrowinning. So, a deep investigation of the behavior of minor elements is essential. Selenium is especially important during the second stage leaching. It must be largely removed prior to electrowinning in order to reduce its contamination of the copper cathode product. Therefore, a feasible analytical method for Se species needs to develop, which is suitable to the samples at INCO CRED. In this study two tasks were included: (1) study of minor element behavior, and (2) development of Se analytical method. Chapter 2 contains a literature review and the background. Chapter 3 presents the experimental methods and Chapter 4 shows the results and discussions. Chapter 5 offers some conclusions and recommendations. In each chapter above, the main activities of minor element behavior and Se speciation are discussed separately.

## CHAPTER 2 BACKGROUND AND LITERATURE REVIEW

This Chapter includes two parts: Part One -- INCO-CRED Minor Elements; and Part Two -- Selenium Speciation Analysis.

In part one, a brief background of INCO-CRED is provided. Also this part contains a literature survey on the behavior of minor elements during the second stage leaching at CRED—cobalt, iron, arsenic, antimony, bismuth, selenium, tellurium and tin. Copper and nickel were included in this part. In part two, the determination of selenium species ( $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$ ) is reviewed. The available analytical methods are mostly used in the field of environmental protection and medicine or food. Therefore, an analytical method is developed for selenium species in the solutions with high concentrations of sulfate and copper ion in the INCO CRED process.

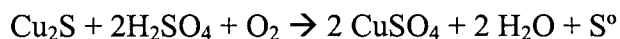
### Part One: INCO-CRED Minor Elements

#### 2.1 Introduction

INCO Ltd's Copper Refinery Electrowinning Department (CRED) in Copper Cliff, Ontario, is a hydrometallurgical operation, which processes copper-rich sulfidic residues produced by the INCO Pressure Carbonyl (IPC) process. Figure 2.1 shows the general processing at CRED.

The INCO-CRED plant became operational in the early 1970's and the procedure has changed gradually for better leaching and recovery of valuable metals. The process mainly includes two stages of leaching – first stage leaching and second stage leaching. This project was focused on second stage leaching.

Second stage leaching was originally designed to leach chalcocite ( $\text{Cu}_2\text{S}$ ) completely in the presence of excess sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and under oxygen pressure at 110 °C:



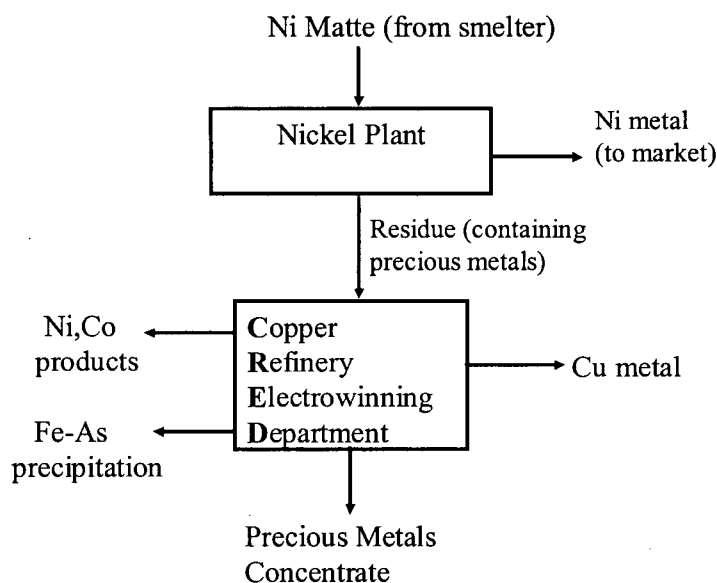


Figure 2.1 Schematic of CRED plant operations

The products of leaching were  $\text{CuSO}_4(\text{aq})$  and elemental sulfur. In this case, the acid and copper concentrations were not critical factors in the leaching rate. Studies found the reaction proceeds rapidly to form elemental sulfur with iron in solution. However, without iron in solution, the reaction was slow and consumed more oxygen according to the reaction:



The initial leaching condition forming elemental sulphur complicated the downstream recovery of precious metals. After a few years, the leaching process was changed to make all the sulfide sulfur oxidized to form sulfate rather than elemental sulfur by leaching in a low-acid solution. This leaching process produces a solid of basic copper sulfate ( $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ ) in a solution of copper sulfate. The basic copper sulfate slurry is mixed with spent copper electrowinning electrolyte containing sulfuric acid to dissolve the basic copper sulfate and produce a final residue containing precious metals and impurities. This procedure is performed at 150 psi oxygen pressure at 105°C. The second stage leaching is a batch operation and the pulp density in the batch feed is ~40% solids. The feed includes the first stage cake, spent electrolyte, sulfuric acid and water, as well as copper and iron in the solution. The process was continually changed to be improved and eventually became a total oxidative pressure leaching process. The leaching temperature was switched to 115 °C, and

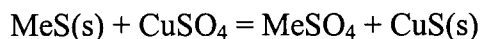
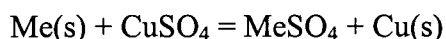
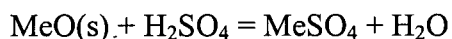
the total pressure in the autoclave was set at 150 psi (oxygen partial pressure of about 140 psi). Usually complete second stage batch leaching should take 5 hours, but the leaching sometimes encounters a problem known as “slow cook” in which the leaching time is extended up to 20 hours or copper is leached incompletely. Obviously this problem reduces production rate and affects plant revenues. Much work had been done trying to investigate its reasons. It was found that higher solids density feeds and high arsenic levels in solution lowered the leaching rate of copper due to higher viscosity of the slurry, which hindered the gas-solids mass transfer [2,3,4]. The agitation speed of the slurry in the autoclave also was a critical factor that is linked with oxygen dispersion in the leaching slurry.

In this part, the details of INCO-CRED process are reviewed. Some critical aspects of copper sulfide leaching are surveyed. Some Eh-pH diagrams of minor elements are also analyzed.

## 2.2 Overview of the INCO-CRED Process

INCO-CRED deals with the residue from INCO Pressure Carbonyl (IPC) process. The IPC Residue contains approximately 55-60 wt.% Cu, 4-9 wt.% Fe, 6-10 wt.% Ni, 4-8 wt.% Co and 13-19 wt.% S, as well as trace amounts of As, Bi, Pb, Se, Te and Sn. Approximately fifty metric tons of IPC residue are processed daily. At CRED, two successive batch leach unit operations are performed to produce copper sulfate solution and a residue containing precious metals. A simplified flowsheet for the operations is illustrated in Figure 2.2 and described below [5].

The IPC residue is initially treated in a pressure leaching step to dissolve nickel, cobalt, iron and arsenic. A small amount of copper also remains in solution. This is called first stage leaching. The operation conditions are as follows:  $\text{H}_2\text{SO}_4$  100-200 g/L, copper sulfate 40-90 g/L and temperature  $150^\circ\text{C}$ . The reactions in the first stage leaching step are shown below.



Where Me = Ni, Co, Fe



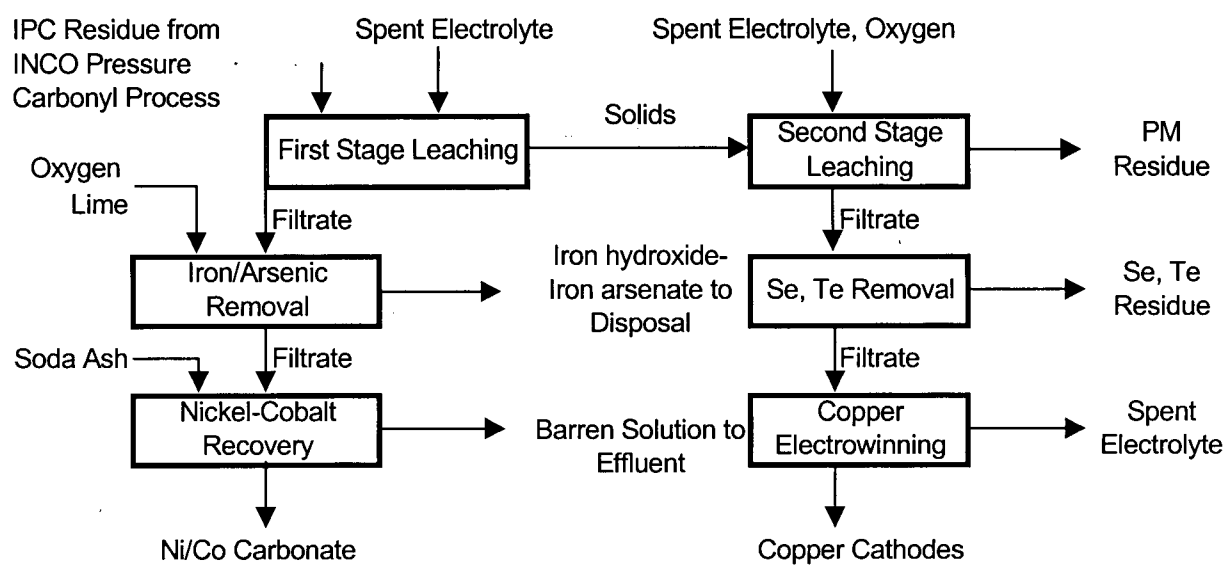
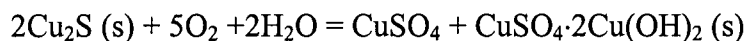


Figure 2.2 Simplified flowsheet at INCO-CRED

Approximately 95-98% of the Ni, Co and Fe are leached out of the solids. Copper is precipitated and is predominantly present as chalcocite ( $\text{Cu}_2\text{S}$ ) or other Cu-S species and passes through to second stage leaching. The equipment in this stage is comprised of a batch makeup tank, autoclaves, vacuum filters, and holding vessels for the storage of autoclave discharge slurry and first stage filtrate. Figure 2.3 shows the flowsheet of first stage leaching at CRED.

Residue from the first stage leaching is essentially chalcocite or digenite and enters the second stage leaching. The purpose of the second stage leaching is to convert chalcocite into basic copper sulphate:



The slurry is then mixed with spent copper electrowinning electrolyte to dissolve the basic copper sulphate:



Selenium and tellurium also dissolve in this leach process. They must be removed from the pressure filter filtrate prior to copper electrowinning. Figure 2.4 shows the second stage leaching flowsheet.

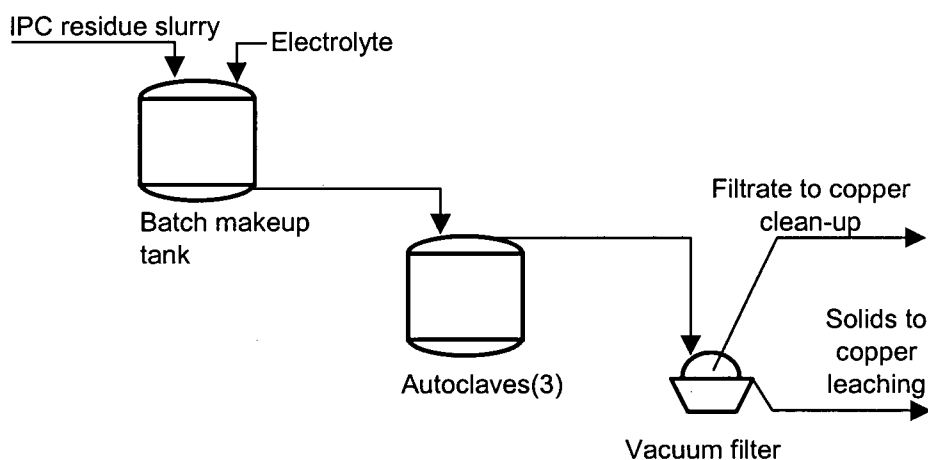


Figure 2.3 First stage leaching at CRED

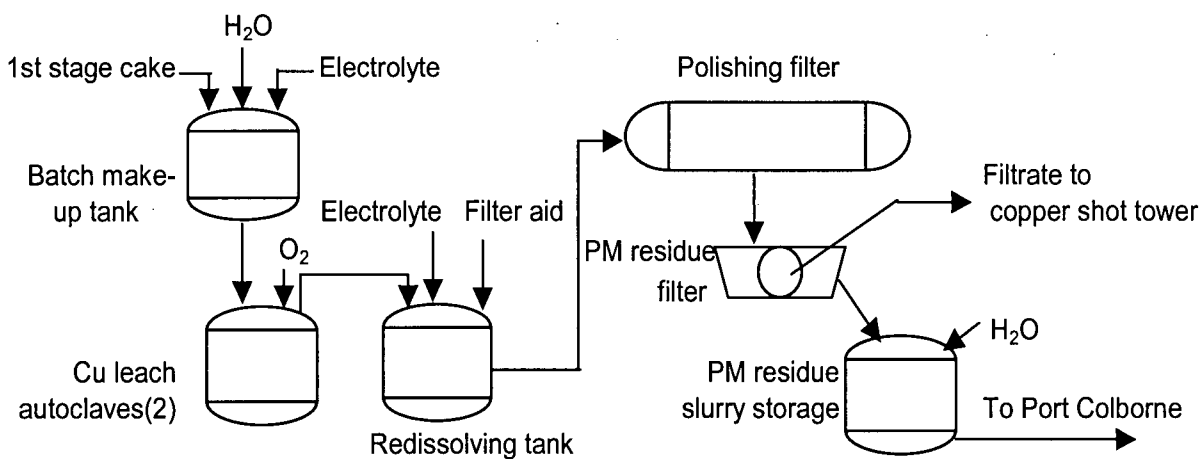


Figure 2.4 Flowsheet of second stage leaching at CRED

Filtrate from the second stage pressure filters is sent to the electrowinning tankhouse for copper recovery. Because selenium and tellurium could co-deposit and contaminate the cathodes, the filtrate must first be purified prior to electrowinning. This process is conducted at the temperature of over 95 °C by passing impure solution through a column containing

copper shot. In the copper shot column, the dissolved selenium and tellurium are converted to copper selenides and tellurides at high temperature. They are insoluble and precipitate as fine black particulates. The solution and solids then pass through four large aging towers where the solids are settled. The selenium and tellurium concentrations in the purified solution can be reduced to less than 1mg/L. The overflow from the final aging tower passes through polishing filters before going to the electrowinning circuit. The settled solids from these towers are underflowed to a small vacuum drum filter and transferred to the Silver Refinery for further processing. Figure 2.5 shows this process.

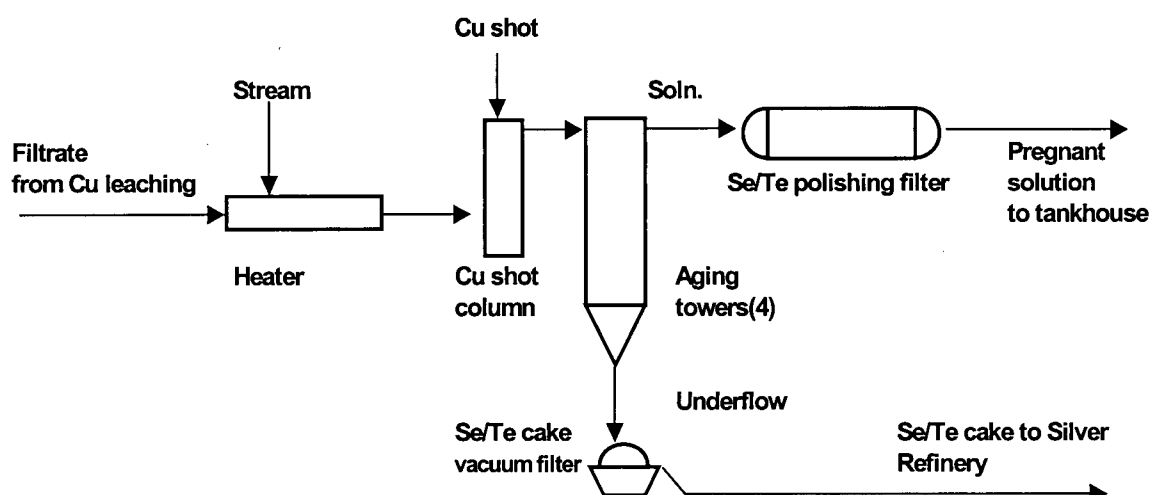


Figure 2.5 Selenium and tellurium removal flowsheet at CRED

The major factors that affect selenium and tellurium removal include solution temperature, contact time, copper bed depth, bed channeling, acid concentration and aging time.

After the first stage leaching, the slurry is filtered and the solids sent to second stage of leaching. The first stage filtrate is then processed through a series of unit operations to precipitate and recover the residual copper for processing with the first stage cake; precipitate iron and arsenic as a gypsum-ferric hydroxide-ferric arsenate precipitate which is discarded to tailings; and precipitate nickel and cobalt as a bulk carbonate feed material for INCO's cobalt refinery.

In this project the focus was on the behavior of minor elements during the second stage leaching at CRED. Other units (such as electrowinning, copper clean-up, removal of

iron/arsenic and nickel/cobalt recovery) were not studied in this project and are not discussed in detail here.

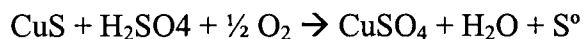
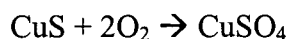
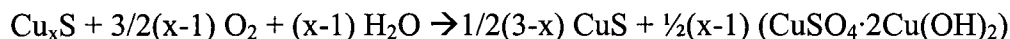
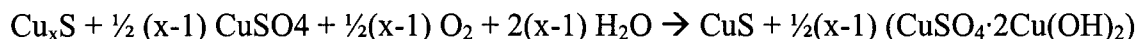
## 2.3 The UBC Screening Model

In order to evaluate possible metallurgical causes of the “slow cook” encountered during the second stage leaching, in which leaching times are greatly extended and /or copper is leached incompletely, Dreisinger and Peters [6] developed a mathematical model trying to explain this “slow cook” phenomenon. From this model we can better understand the reactions proceeding in the process. The following describes some assumptions of this model, and main reactions in the oxidative pressure leaching process.

The model was developed on a number of important assumptions as follows:

- $\text{Cu}_2\text{S}$  leaches very quickly to  $\text{CuS}$
- The  $\text{CuS}$  produced by leaching  $\text{Cu}_2\text{S}$  tends to fracture and become finely disseminated.
- $\text{Cu}_2\text{S}$  conversion to  $\text{CuS}$  proceeds very quickly relative to the leaching of  $\text{CuS}$ .
- A small amount of iron in solution promotes elemental sulphur formation during leaching. The leaches with no iron showed little or no elemental sulphur in the leach residue.

In developing the model, a number of discrete leaching reactions were proposed which would proceed sequentially depending on the prevailing solution conditions and the character of the unleached solids. The chemical reactions and their corresponding solution conditions are:



The value of  $x$  in  $\text{Cu}_x\text{S}$  refers to the average  $\text{Cu/S}$  mole ratio of the solids being leached in the feed. The CRED second stage feed material usually has  $\text{Cu/S}$  mole ratios in excess of 2, indicating the presence of elemental or oxide copper.

Prior work by Grewal [2] verified that reactions in second stage leaching proceed nearly sequentially.

## 2.4 Copper Sulfides

The first stage cake from INCO CRED consists mainly of chalcocite ( $\text{Cu}_2\text{S}$ ) and other minor elements (Ni, Co, Fe, As, etc.). In this part some copper sulfide compounds are discussed, such as chalcocite and covellite ( $\text{CuS}$ ).

Chalcocite is an important copper mineral ore. It has been mined for centuries and is one of the most profitable copper ores. The reason for this is its high copper content (67% atomic ratio and nearly 80% by weight) and the ease at which copper can be separated from sulfur.

Covellite ( $\text{CuS}$ ) is usually found as an oxidative product of chalcocite or other primary copper sulfides like chalcopyrite as a zone of secondary enriched copper deposit. The oxidation of chalcocite does not lead to the direct formation of covellite. The decomposition process produce many intermediate sulfides such as djurleite ( $\text{Cu}_{1.96}\text{S}$ ), digenite ( $\text{Cu}_{1.76-1.83}\text{S}$ ), blue-remaining covellite ( $\text{Cu}_{1.1-1.4}\text{S}$ ) and covellite ( $\text{CuS}$ ) [7].

In chalcocite and djurleite, the sulphur species are arranged in a hexagonal close packed structure [8]. The copper ions are located near the triangular faces of the tetrahedral sites as opposed to being in the center of the tetrahedral interstices. The structure of digenite is a cubic close packed arrangement of the sulphur species and the copper ions are located off-center in the tetrahedral interstices. One eighth of the tetrahedral positions are unoccupied. Natural digenite has 1% iron to maintain a stable solid solution composition but a stable iron-free "low digenite" called anilite ( $\text{Cu}_{1.75}\text{S}$ ) is also found.

## 2.5 Gas-Liquid Mass Transfer in Oxidative Leaching

The second stage leach includes an oxidative pressure leaching in an autoclave. Many studies have shown that gas-liquid mass transfer plays a critical role in the leaching process.

For oxidative pressure leaching processes, Peters [9] has offered the following four general mechanisms to describe oxidative leach process using oxygen gas. These are described briefly below and illustrated in figure 2.6.

1. Oxygen introduced in gaseous form, dissolves, and directly reacts with the particle at the particle-solution interface (Figure 2.6a).
2. Dissolved oxygen reacts homogeneously with an aqueous reduced species (R) which results in the formation of a surrogate oxidant species (R<sup>+</sup>) which then affects the oxidation process at the mineral surface (Figure 2.6b). If high concentrations of the reduced (and thus surrogate oxidant) species are present significant increases in leaching rates may be incurred.
3. Oxygen reacts at the gas-liquid interface with a reducing agent formed from the mineral leaching process to form a surrogate oxidant which then reacts with the mineral (Figure 2.6c). This is a possible model for the Arbiter ammonial leach for the treatment of copper concentrates [10] in which the reduced species is the cuprous-ammine complex,  $\text{Cu}(\text{NH}_3)_2^{2+}$ .
4. Oxygen reacts in the gas phase to generate a gaseous surrogate oxidant species that has a higher solubility than oxygen (Figure 2.6d). This mechanism has been proposed by Peters [9] to account for the nitric acid catalysis of the oxygen pressure leaching of pyrite ( $\text{FeS}_2$ ) and arsenopyrite ( $\text{FeAsS}$ ) feeds. Nitric acid is consumed to produce reduced N-O species which are re-oxidized by oxygen to regenerate a soluble oxidant (probably nitrosyl,  $\text{NO}^+$ ).

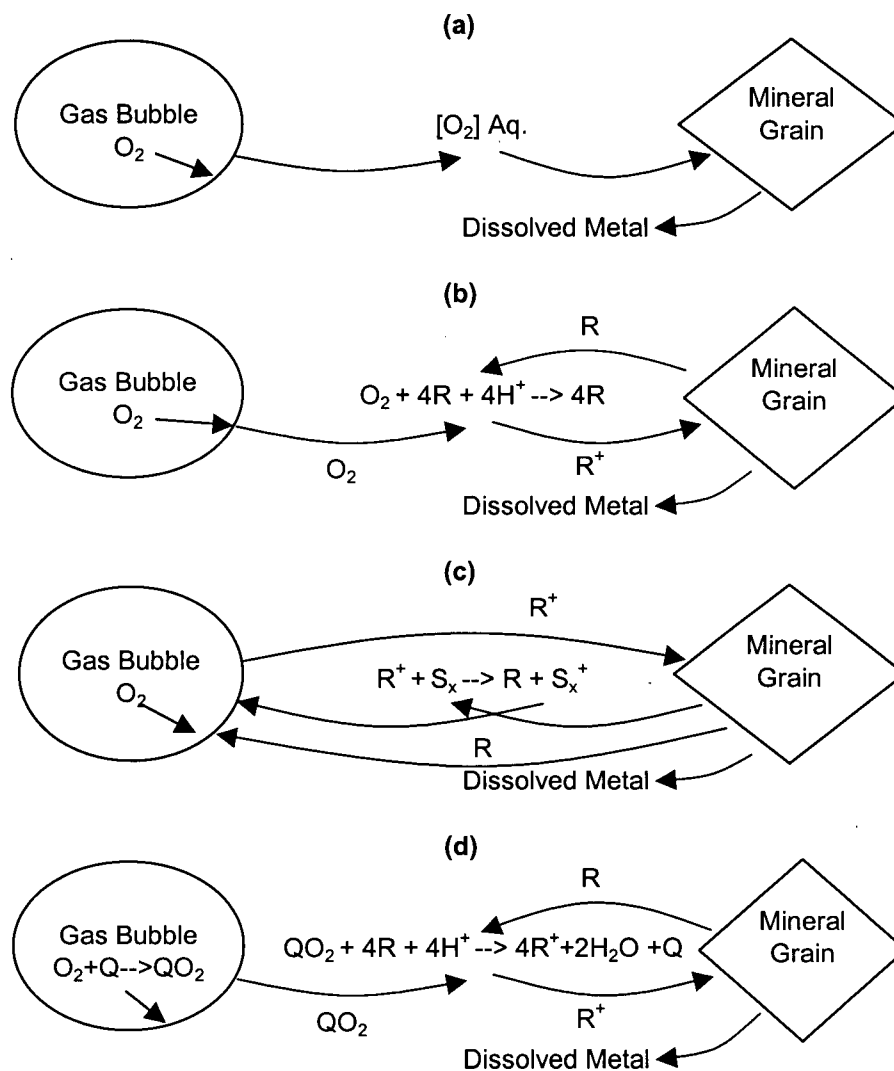
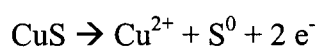
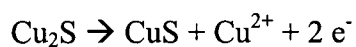


Figure 2.6 Models for oxygen absorption during oxidative leaching [9]

## 2.6 Leaching of Chalcocite and Covellite

The leaching of chalcocite has often been reported as a two-step process according to the following reaction sequence:



A variety of leaching processes have been investigated in the laboratory and classified according to the leaching steps and the types of reagents used. The most common oxidizing agents are:

- Ferric sulfate in acid
- Ferric chloride in acid
- Oxygen in sulfuric acid
- Oxygen in ammoniacal solutions
- Nitric acid

There are other oxidizing agents but they have not received much attention, because of their cost and commercial availability. There are many works done with the leaching of chalcocite.

Chu Yong Cheng and Frank Lawson [11] studied the kinetics of leaching chalcocite in acidic oxygenated sulphate-chloride solutions. The leaching process was found to occur in two steps. In the first rapid leaching stage, cuprous ions diffuse through the solid to the particle surface and are oxidized to divalent state. The rate-limiting step is the diffusion of oxygen through the liquid boundary layer around the particle to the reaction surface. This stage of leaching is completed when the surface has been converted to covellite (CuS). The second stage leaching is much slower. The leaching rate of covellite is initially limited by surface chemical reactions and in the late second stage by both the surface chemical reactions and pore diffusion processes. The study showed that over 97% of copper in the chalcocite was leached out in a 0.5 M H<sub>2</sub>SO<sub>4</sub>/0.5 M NaCl with pure oxygen bubbling at 85 °C in 3 h. About 1 % of the sulfide sulphur was oxidized to sulphate while the remainder was converted to solid elemental sulphur extractable with xylene.

Zhang et al. [12] studied the kinetics of sulfuric acid pressure leaching of chalcocite in the presence of iron in the solution. Their experiments showed that the presence of a small amount of iron accelerates the rate of leaching. The catalytic effect of iron is considered to act as an oxygen carrier. The yield of elemental sulfur was increased with the increase of iron concentration.

Chmielewski and Lekki [13] studied the initial stage of leaching of chalcocite in oxygenated aqueous sulphuric acid at 368 K and found that chalcopyrite can accelerate the leaching of chalcocite due to grain contact between chalcocite and chalcopyrite.

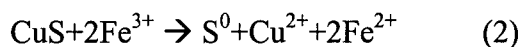
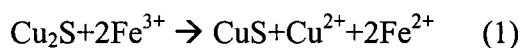


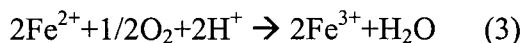
Pilarczyk et al. [14] used pyridine-hydrochloric acid mixtures and pyridine solutions of pyridine hydrochloride to recovery copper from natural chalcocite. Total copper recovery is reached after 15 minutes at 60°C.

Bioleaching technology has become well established for the exploitation of copper sulfide ores. Also, it has been applied to treat chalcocite. But in many operations the rate of copper extraction is rather slow. Much work has been done in this field.

Dixon et al. [15] studied the dynamics of chalcocite heap bioleaching. Chalcocite is leached by a two-stage mechanism. The first stage is rapid, whereas the second stage has a high activation energy and proceeds slowly at ambient temperatures. A comprehensive column bioleaching study of a chalcocite ore has shown that the chalcocite columns are leached in a zone-wise fashion. The first zone corresponds to the first stage of chalcocite leaching, where all ferric produced by the bacteria is immediately consumed and all acid entering with the feed solution is consumed within a relatively narrow band. The second stage of chalcocite leaching proceeds much more slowly in the wake of the first stage, within a zone that grows gradually over the entire length of the column. The overall rate of leaching is thus determined by the rate of acid supply into the column rather than by mineral or bacterial kinetics, at least until the entire column is engaged in second-stage chalcocite leaching. Thus, the rate of chalcocite oxidation in heaps is governed by sideways diffusion rather than downward migration.

Palencia et al. [16] studied the treatment of secondary copper sulfide (chalcocite and covellite) by the BRISA process (Biolixiviación Rápida Indirecta con Separación de Acciones: Fast Indirect Bioleaching with Actions Separation). This process is based on bioleaching by the indirect contact mechanism. According to this mechanism, metallic sulphides are chemically oxidized by ferric sulphate leading to elemental sulphur and copper in solution (Eqs. (1) and (2)). The ferrous iron resulting from Eq. (1) is oxidized by ferrooxidant bacteria—as *Thiobacillus ferrooxidans*—thus regenerating the ferric iron (Eq.(3))





In the BRISA process, developed to improve the kinetics of bioleaching, the bioleaching process is performed in two separate stages: (a) a chemical stage based on (1) and (2), and (b) a biological stage based on Eq. (3) for the biooxidation of ferrous iron and reuse of the ferric iron consumed in the chemical stage (Figure 2.7).

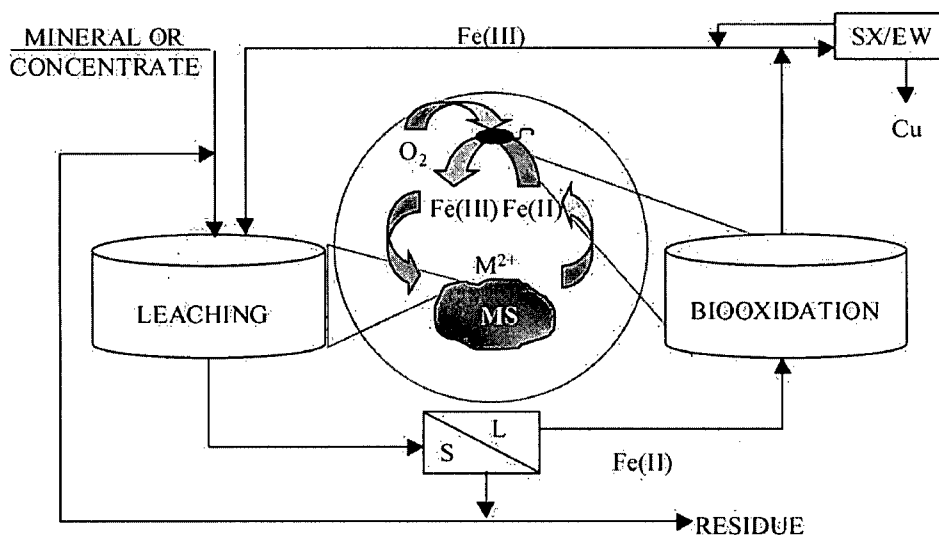


Figure 2.7 The BRISA process

## 2.7 Eh-pH Diagrams

Many processes used in the field of hydrometallurgy are concerned with the adjustment of conditions so as to control the stability of a solid with respect to a solution containing a number of reagents. For example, leaching is a very common operation in hydrometallurgy and involves decomposition of a solid so that some component (or the whole of it) dissolves. Most of the reactions of interest need to show stability of each species, and Eh-pH diagrams can meet this requirement.

Eh-pH diagrams are also called Pourbaix diagrams [17]. M. Pourbaix developed this method around 1965 to use in the field of corrosion studies. And this simple graphical manner has already proved extremely useful.

In this study, minor elements exist in the reaction process. In order to better understand the behavior of these elements, Eh-pH diagrams of these elements may be investigated at experimental temperatures and pressures. During the second stage leaching, the materials are first processed in an autoclave at 115°C, 150 psig (total); and then basic copper sulfate produced from the autoclave is dissolved with sulfuric acid at room temperature. A software – Outokumpu HSC 5.1 – was used to draw Eh-pH diagrams. Due to the complexity of reactions performed during the pressure leaching, the diagrams at 115 °C and 150 psi cannot reflect the real situations in the process. Therefore, we only investigate Eh-pH diagrams for each element at 25°C and unit pressure.

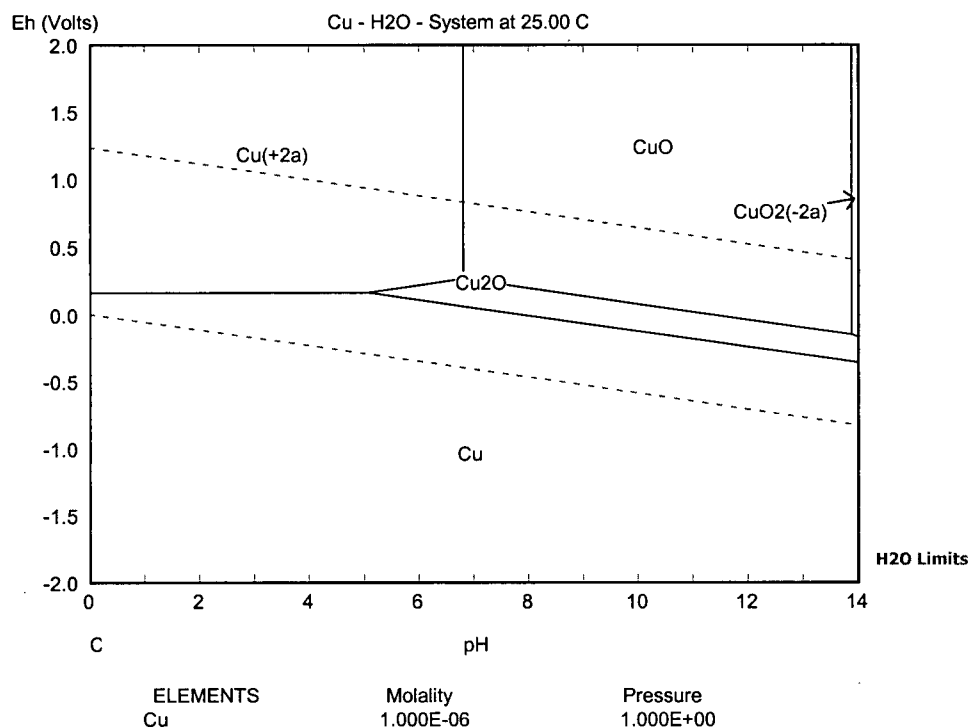
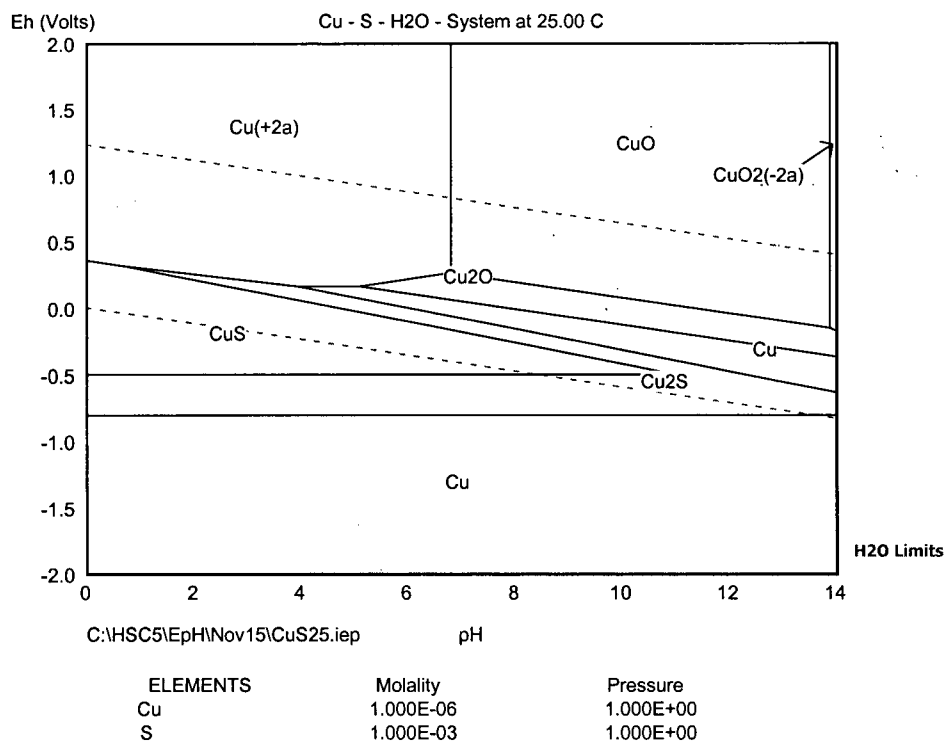
Copper, nickel, cobalt, iron, arsenic, antimony, bismuth, selenium, tellurium and tin were studied in the leaching process. The followings are the detailed Eh-pH diagrams for each element.

### 2.7.1 Cu-S-H<sub>2</sub>O system

In the Cu-H<sub>2</sub>O system, the stable species under ambient conditions are presented in Figure 2.8. When sulfur is added to the system, the Cu-H<sub>2</sub>O system is modified and several new stable species appear (see Figure 2.9 and Figure 2.10).

The Cu-H<sub>2</sub>O Eh-pH diagram is shown in Figure 2.8. A molality of Cu = 10<sup>-6</sup> is assumed. Native copper oxidizes to cupric ion under acidic pH. Cu<sub>2</sub>O oxidizes to CuO under higher Eh conditions. At high pH, CuO dissolves to form CuO<sub>2</sub><sup>2-</sup>, and Cu<sub>2</sub>O oxidizes to CuO<sub>2</sub><sup>2-</sup> as well. From Cu-S-H<sub>2</sub>O system at 25 °C (Figure 2.9), chalcocite and covellite both occupy significant parts of the Eh-pH diagram. The fields of Cu<sub>2</sub>O, CuO, CuO<sub>2</sub><sup>2-</sup> and most of Cu<sup>2+</sup> are identical to those shown in Figure 2.8.

Previous work by Saito [4] reported the Eh-pH diagram of Cu-S-H<sub>2</sub>O system at 115 °C. The diagram shows that the leaching of Cu<sub>2</sub>S in sulfuric acid media to form cupric requires potentials above 400 mV<sub>SHE</sub>. The average basic copper sulfate slurry pH observed in Grewal's work [2] was 2.8. Under the acid deficient conditions of second stage leaching, when temperature reaches 115 °C, from Figure 2.10 [4] it can be seen that at around pH 2.8, basic copper sulfate is formed at high Eh.

Figure 2.8 Eh-pH diagram for Cu-H<sub>2</sub>O system at 25 °CFigure 2.9 Eh-pH diagram for Cu-S-H<sub>2</sub>O system at 25 °C

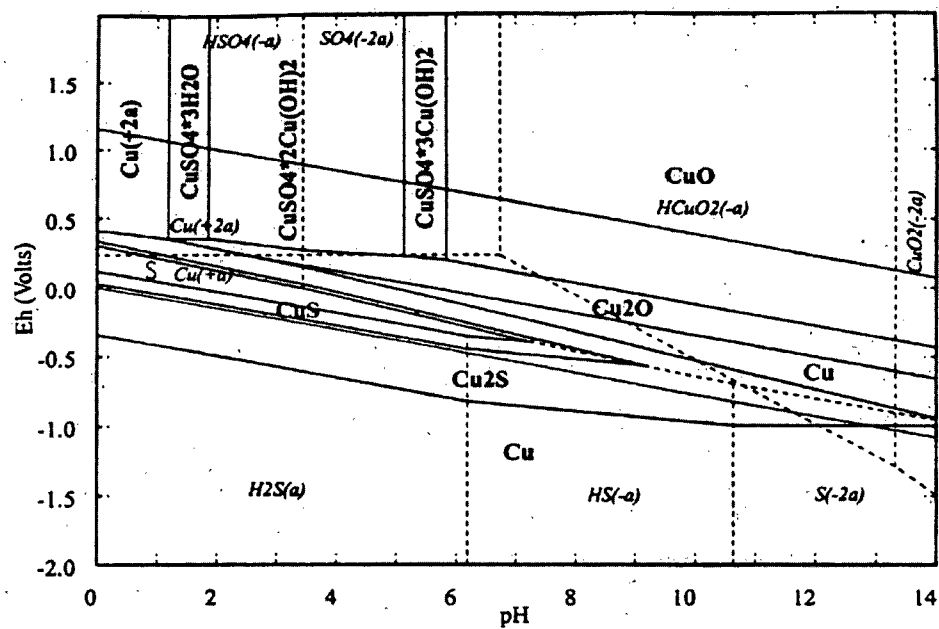


Figure 2.10 Eh-pH diagram for Cu-S-H<sub>2</sub>O system at 115 °C [4]

### 2.7.2 Ni-S-H<sub>2</sub>O System

In the Ni-H<sub>2</sub>O system assuming the Ni molality is  $10^{-6}$ , a fairly narrow field of Ni(OH)<sub>2</sub> separates a large field of Ni<sup>2+</sup> from HNiO<sub>2</sub><sup>-</sup> (Figure 2.11).

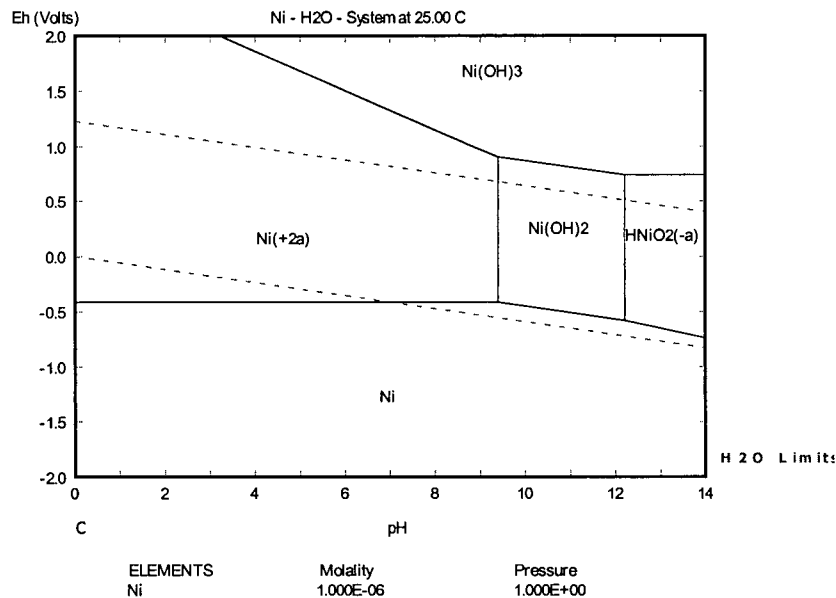


Figure 2.11 Eh-pH diagram for Ni-H<sub>2</sub>O system at 25 °C

When S is introduced in the system, a large field of millerite (NiS) occurs in the diagram (Figure 2.12).

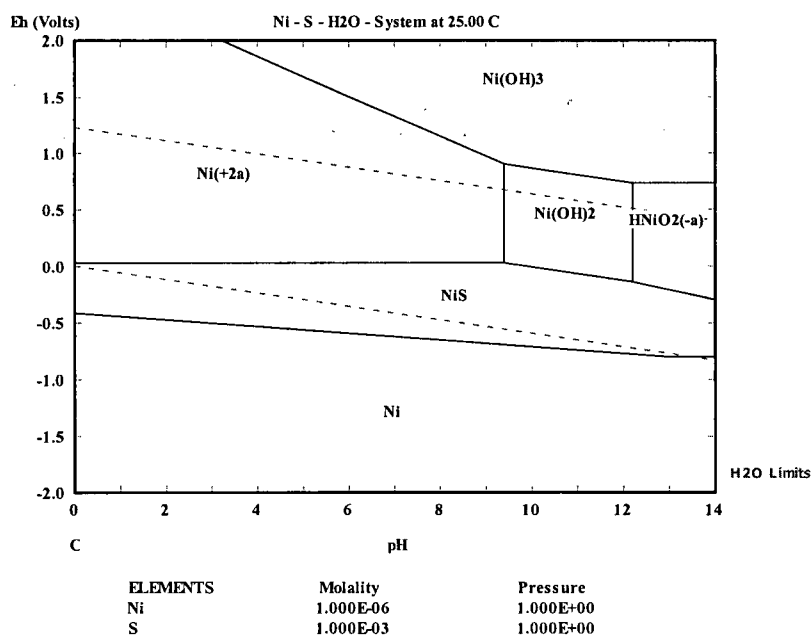


Figure 2.12 Eh-pH diagram for Ni-S-H<sub>2</sub>O system at 25 °C

### 2.7.3 Co-S-H<sub>2</sub>O System

The Eh-pH diagrams for cobalt species are shown in Figure 2.13 and 2.14 (assumed molality of Co is  $10^{-6}$  and that of S is  $10^{-3}$ ). From these diagrams it can be seen that  $\text{Co}_3\text{O}_4$  and  $\text{Co}(\text{OH})_3$  occupy a large field under oxidizing conditions from neutral to basic pH. In addition, under oxidizing and acidic conditions,  $\text{Co}^{2+}$  is stable.

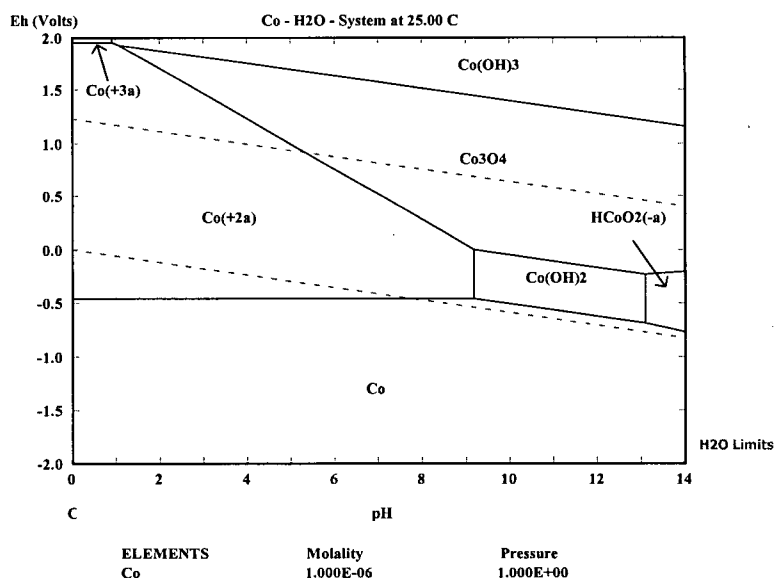


Figure 2.13 Eh-pH diagram for Co-H<sub>2</sub>O system at 25 °C

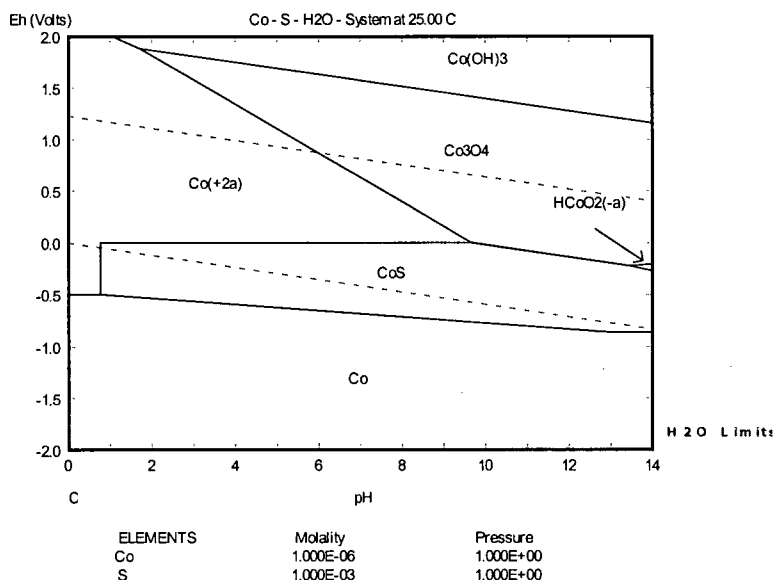


Figure 2.14 Eh-pH diagram for Co-S-H<sub>2</sub>O system at 25 °C

### 2.7.4 Fe-S-H<sub>2</sub>O System

Figure 2.15 is characterized by a large field of Fe<sub>2</sub>O<sub>3</sub> and Fe<sup>2+</sup>. In Figure 2.16, hematite (Fe<sub>2</sub>O<sub>3</sub>) is still shown as the stable Fe<sup>3+</sup> phase, since both Fe(OH)<sub>3</sub> and FeO·OH will age to Fe<sub>2</sub>O<sub>3</sub> (although very slowly) [17]. And in Figure 2.16 FeS<sub>2</sub> and FeS also have a large stable area.

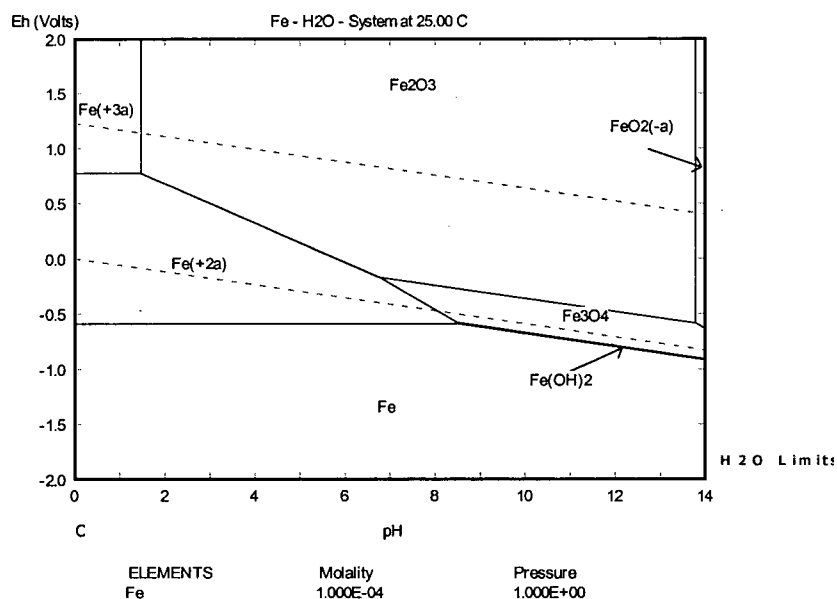


Figure 2.15 Eh-pH diagram for Fe-H<sub>2</sub>O system at 25 °C

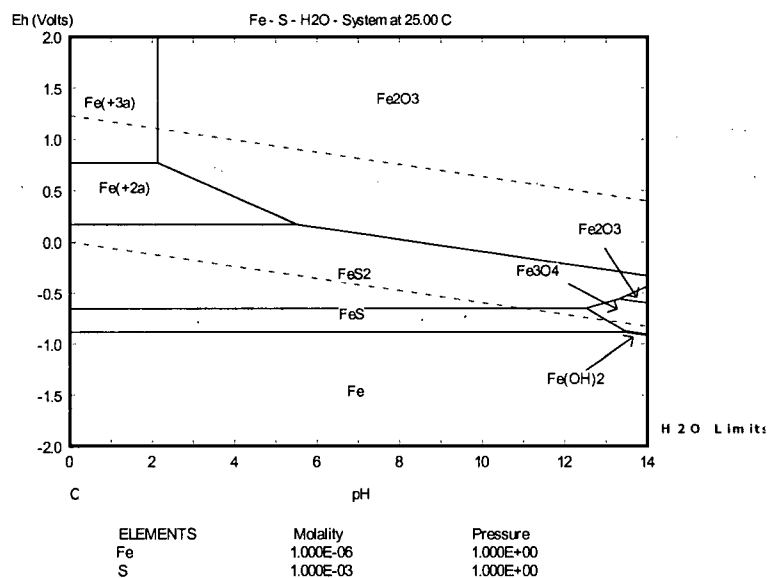


Figure 2.16 Eh-pH diagram for Fe-S-H<sub>2</sub>O system at 25 °C



### 2.7.5 As-S-H<sub>2</sub>O System

Figure 2.17 shows the Eh-pH relationships in the As-H<sub>2</sub>O system assuming a molarity of  $10^{-6}$  for dissolved arsenic. Figure 2.18 shows the effect of sulfur on the arsenic system. Arsenic acid and its ionization products are stable over a wide range of pH and Eh.

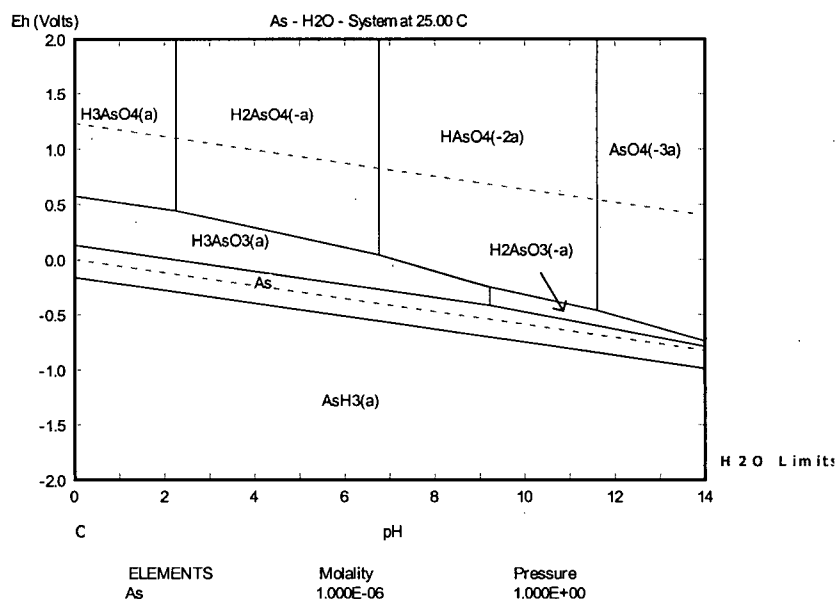


Figure 2.17 Eh-pH diagram for As-H<sub>2</sub>O system at 25 °C

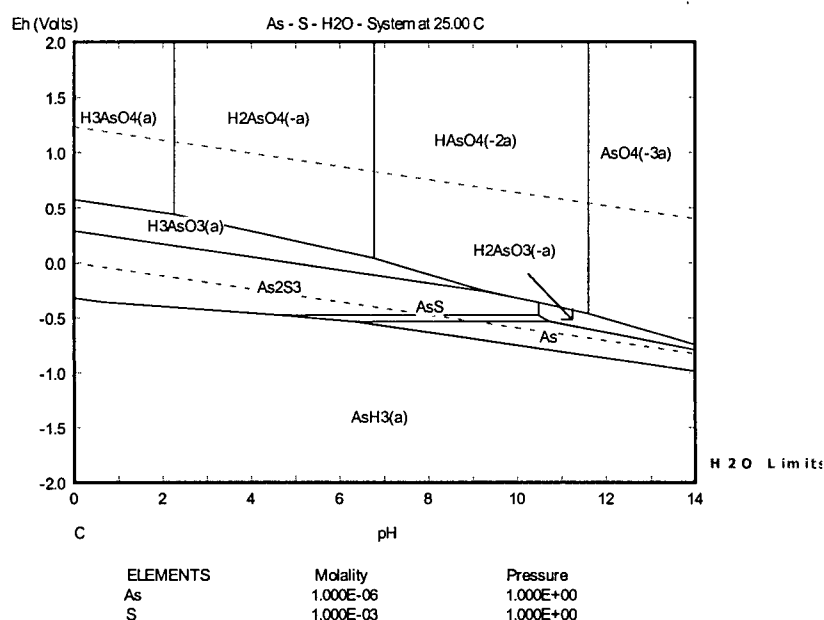


Figure 2.18 Eh-pH diagram for As-S-H<sub>2</sub>O system at 25 °C

### 2.7.6 Sb-S-H<sub>2</sub>O System

Figure 2.19 and 2.20 show fields for various antimony oxides and sulfides. At high Eh levels, Sb<sub>2</sub>O<sub>5</sub> and Sb<sub>2</sub>O<sub>4</sub> occupy a large field. Under reducing conditions and in the presence of sulfur (assumed molarity =  $10^{-3}$ ), Sb<sub>2</sub>S<sub>3</sub> forms and occupies a large field.

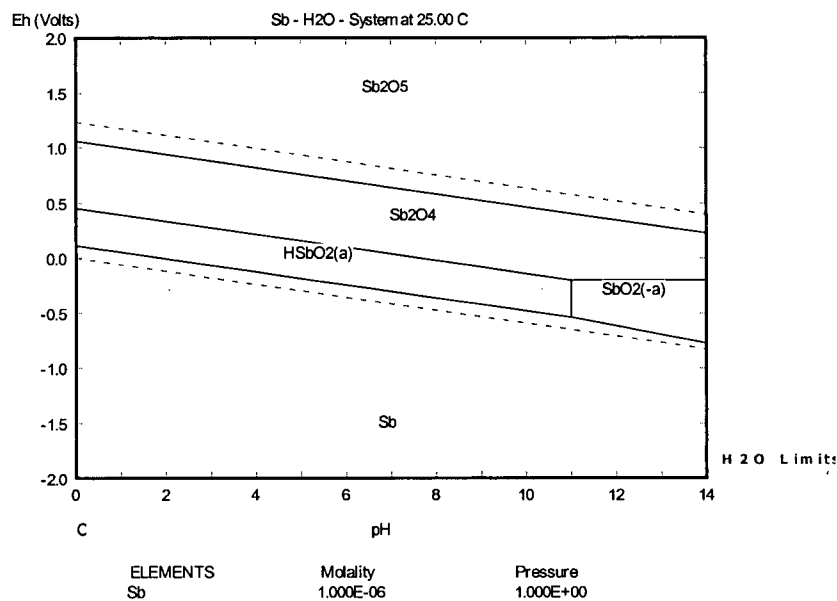


Figure 2.19 Eh-pH diagram for Sb-H<sub>2</sub>O system at 25 °C

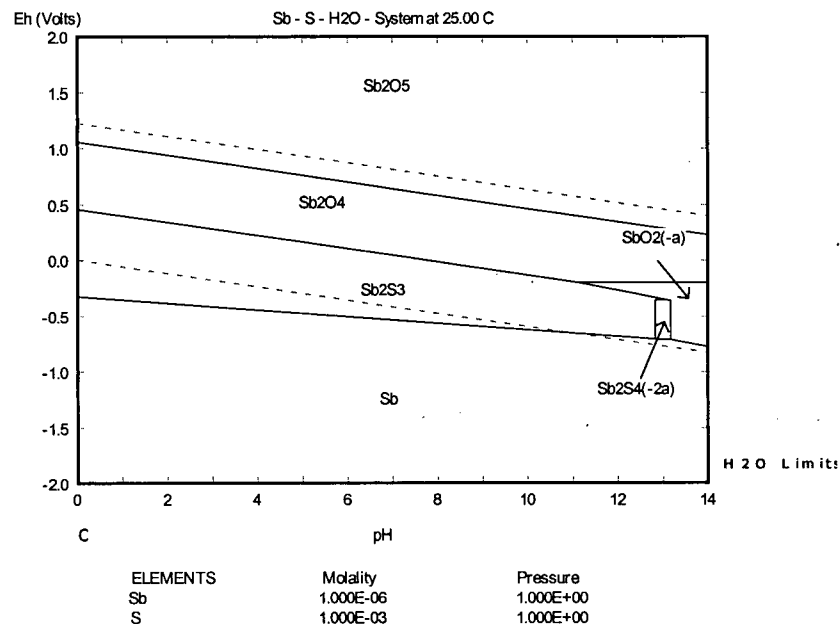


Figure 2.20 Eh-pH diagram for Sb-S-H<sub>2</sub>O system at 25 °C

### 2.7.7 Bi-S-H<sub>2</sub>O System

Aqueous species of bismuth are complex. In Figure 2.21 and Figure 2.22, the oxide  $\text{Bi}_2\text{O}_3$  occupies much of the Eh-pH field. In Bi-S-H<sub>2</sub>O system, bismuthinite ( $\text{Bi}_2\text{S}_3$ ) occupies most of the space under sulfide stable conditions.

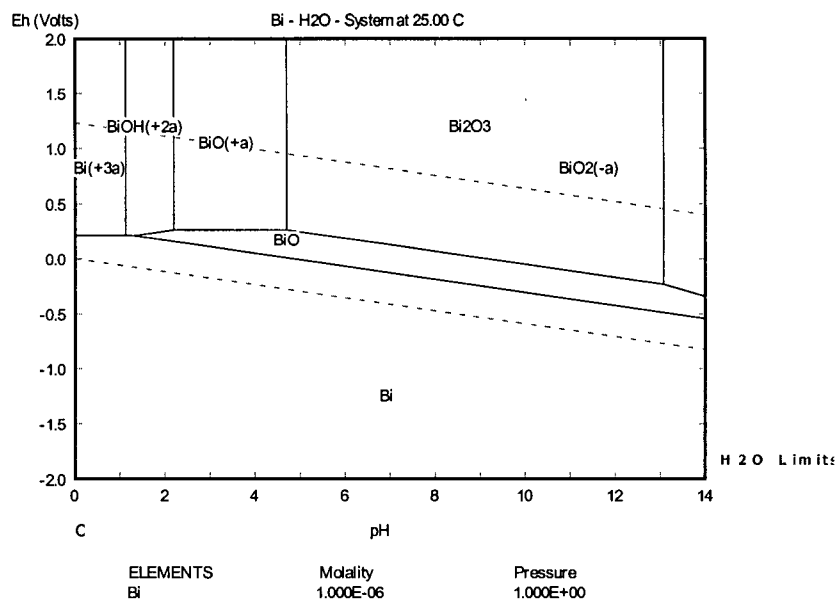


Figure 2.21 Eh-pH diagram for Bi-H<sub>2</sub>O system at 25 °

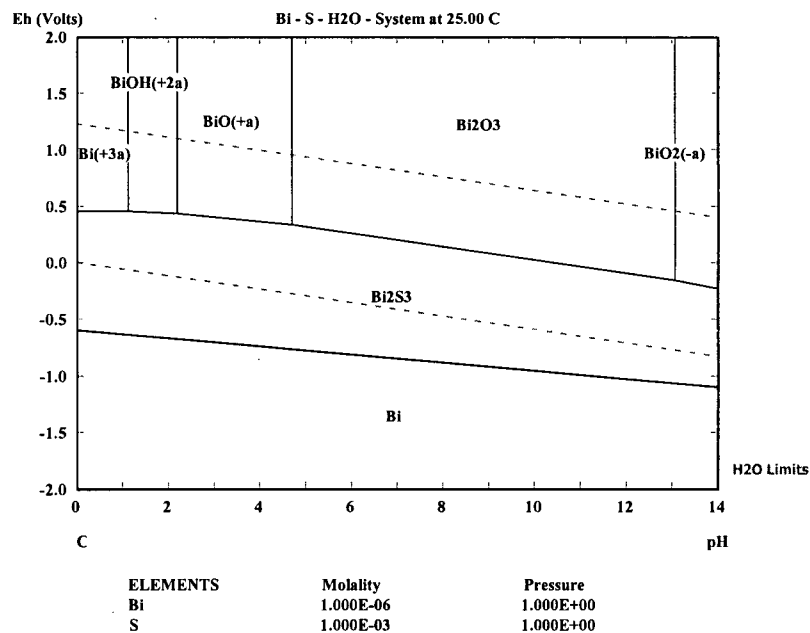


Figure 2.22 Eh-pH diagram for Bi-S-H<sub>2</sub>O system at 25 °C

### 2.7.8 Se-H<sub>2</sub>O System

The Eh-pH diagram presented here is on the basis of assumed molality of dissolved selenium of  $10^{-6}$ . Figure 2.23 shows large stability fields of native selenium,  $\text{HSeO}_3^-$ ,  $\text{SeO}_3^{2-}$  and  $\text{SeO}_4^{2-}$ . The field of native selenium will increase with increased Se activity and diminish with decreased Se activity [17]. Selenite and selenate are believed to be main forms of Se species under oxidative conditions.

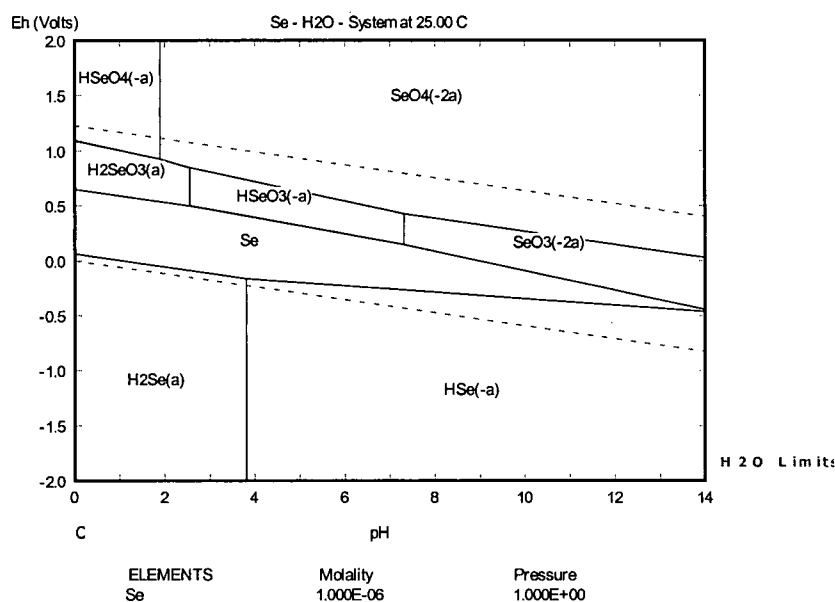


Figure 2.23 Eh-pH diagram for Se-H<sub>2</sub>O system at 25 °C

### 2.7.9 Te-H<sub>2</sub>O System

In the Te-H<sub>2</sub>O system (assumed activity of dissolved Te=10<sup>-6</sup>), a large field of native tellurium occupies the reducing Eh-pH space of Figure 2.24 [17]. Smaller activities of dissolved Te will cause the field of native Te to shrink. There are two main forms of Te, Te(IV) and Te(VI), existing in the oxidized solution. From low to high pH, native Te oxidizes to Te(IV) forming TeO·OH<sup>+</sup>, TeO<sub>2</sub>, HteO<sub>3</sub><sup>-</sup> and TeO<sub>3</sub><sup>2-</sup>. And Te(IV) oxidizes to Te(VI) to form H<sub>2</sub>TeO<sub>4</sub>, HTeO<sub>4</sub><sup>-</sup> and TeO<sub>4</sub><sup>2-</sup> as shown in Figure 2.24.

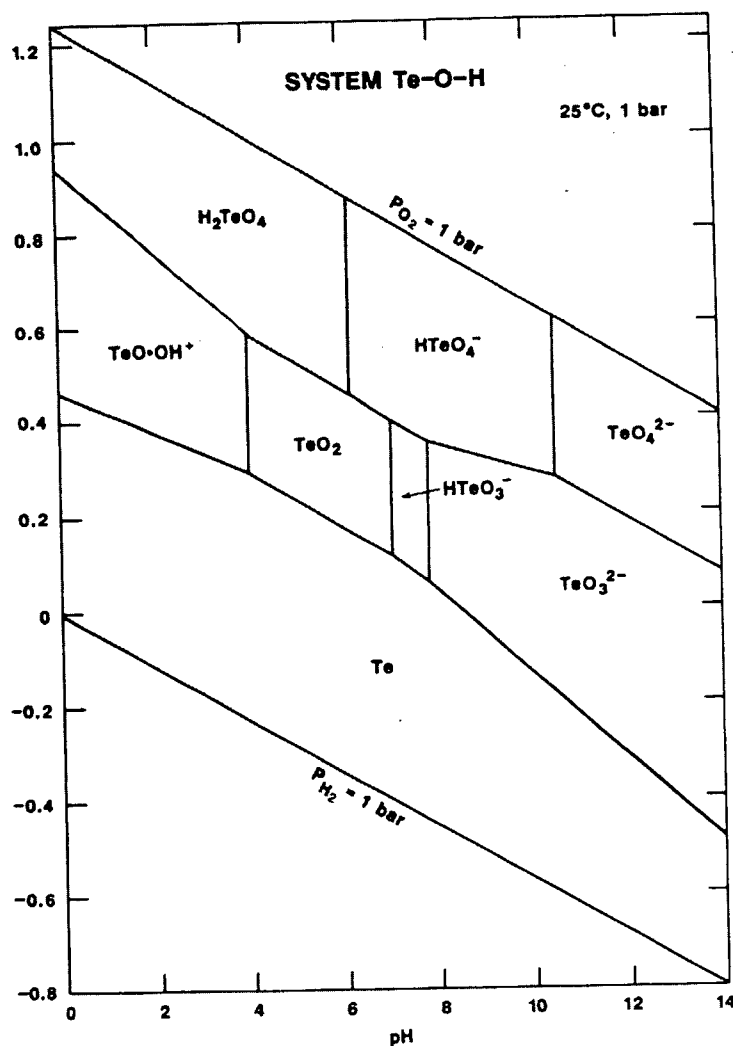


Figure 2.24 Eh-pH diagram for Te-H<sub>2</sub>O system at 25 °C [17]

### 2.7.10 Sn-S-H<sub>2</sub>O System

Figures 2.25 and 2.26 show tin species in Sn-H<sub>2</sub>O system and Sn-S-H<sub>2</sub>O system, respectively. SnO<sub>2</sub> occupies most of the Eh-pH space. And under very acidic pH, SnO<sub>2</sub> will dissolve to Sn<sup>4+</sup>. In Sn-S-H<sub>2</sub>O system, a large field of SnS<sub>2</sub> and SnS occur in the diagrams.

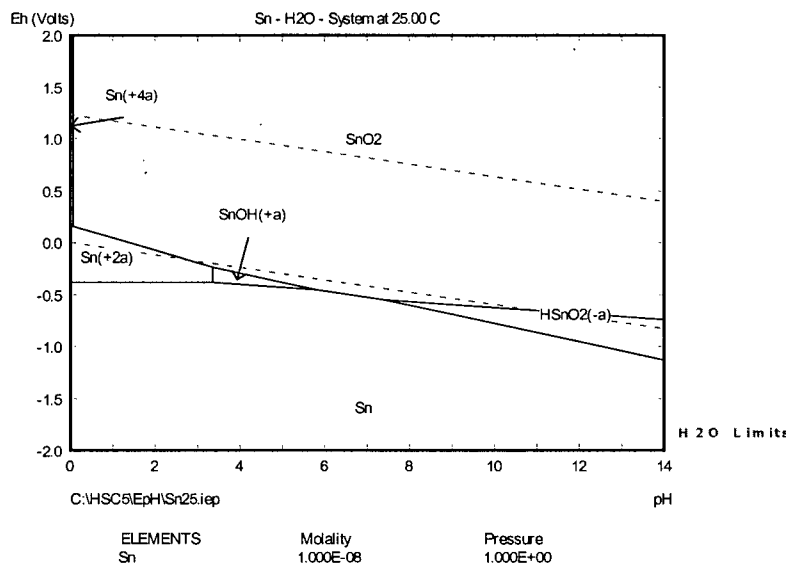


Figure 2.25 Eh-pH diagram for Sn-H<sub>2</sub>O system at 25 °C

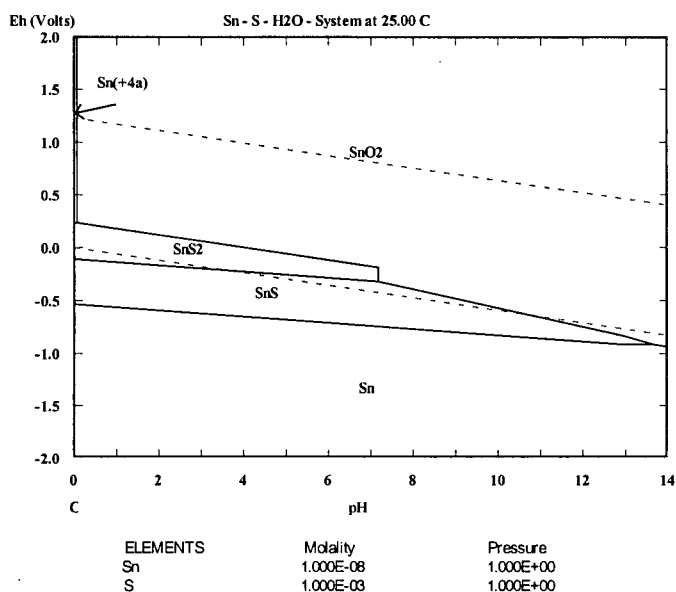


Figure 2.26 Eh-pH diagram for Sn-S-H<sub>2</sub>O system at 25 °C

### 2.7.11 Summary of Eh-pH diagrams

Eh-pH-diagrams can be used to estimate the prevailing species in aqueous solutions as a function of pH and chemical potential. In this study, the oxidation pressure leaching is conducted at the temperature of 115°C and the total pressure of 150 psig followed by a releaching at the pH of 0.5. Because of the uncertainty of Eh-pH diagrams at higher temperatures and pressures, all the Eh-pH diagrams in this study were drawn for 25°C (298.15 K) and 1 bar ( $10^5$  Pa) pressure. And all Eh-pH diagrams in this study are drawn on the basis of assumed molality of minor elements =  $10^{-6}$ ,  $S = 10^{-3}$ . Though above diagrams cannot completely reflect real situations of leaching process, they do provide rough outline and guidance for the research work.

## Part Two: Selenium Speciation Analysis

### 2.8 Introduction

Selenium occurs in various concentrations as an accompanying element in many sulfidic ores. Most copper concentrates contain selenium and are hence the most important sources of selenium. Selenium production is therefore closely linked to copper production. At INCO CRED, selenium comes from INCO Pressure Carbonyl (IPC) residue as heavy-metal selenides such as copper selenide.

The term speciation analysis refers to the analytical activity of identifying and measuring species [18]. Speciation of selenium in the process of second stage leaching at INCO CRED plant is of interest because selenium can co-deposit with copper during electrowinning and contaminate the cathodes. To reduce the effect of selenium, a copper shot tower and several aging towers are applied to remove selenium as much as possible. The specific form -- Se(IV) can be reduced more rapidly than Se(VI) in the removal process. On the other hand, selenium is a toxic trace element at excess level for humans, and may cause some diseases. Therefore, it is important to determine the concentration of selenium species during the leaching stage.

The analytical techniques used for selenium speciation analysis involves many methods. Several techniques have been used for selenium species detection, such as graphite furnace atomic absorption spectrometry (GFAAS) [19], inductively coupled plasma-mass spectrometry (ICP-MS) [20], hydride generation atomic absorption spectrometry (HG-AAS) [21] and HG-atomic fluorescence spectrometry (HG-AFS) [22].

However, the above studies were used to detect selenium species in food, potable water, plants and the blood of human beings. No studies have been performed with selenium speciation in the leaching process of copper. INCO has worked on this for many years trying to obtain an ideal method. In CRED solution samples there are high concentrations of sulfate, copper ( $\text{Cu}^{2+}$ ) and other cations, which may interfere with the analytical results. One of the



objectives of this work was to develop a practical method for speciation of selenium without interference by other ions.

## 2.9 Selenium Chemistry

Selenium is an element which is widely distributed in small concentrations in the earth's crust, having an abundance around  $7 \times 10^{-5}$  wt %. As a member of Group VIA of the periodic table, selenium displays a number of similarities to sulfur and tellurium in many of its properties. Figure 2.27 shows the structure of selenium.

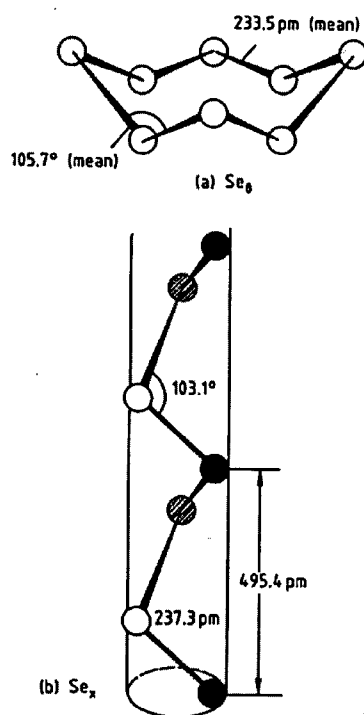


Figure 2.27 Structures of selenium

a)  $\text{Se}_8$  molecule in red  $\alpha$ -,  $\beta$ - and  $\gamma$ -selenium; b) Helical chains in hexagonal gray selenium [23]

## 2.10 Selenium analysis

The analytical chemistry of selenium is quite well defined both with respect to the determination of macro as well as micro amounts of the element. Its common association

with tellurium presents no serious problems since it can be readily separated by volatilization or selective precipitation. The traditional gravimetric and volumetric methods are commonly used for macro determinations of selenium. In INCO's CRED process, selenium exists in micro concentration and these traditional methods are not suitable.

Speciation is mainly applied in the environmental field, especially to soil, water, and airborne particles and to biology and medicine. Therefore there are many studies of determination for selenium speciation in those fields. The most common means of accomplishing element speciation consist of combined and coupled systems, in which species are first separated, and subsequently the elements of the species are selectively detected. In recent decades many new instruments were used to analyze the species of selenium, currently liquid chromatography is widely employed, which is coupled on-line with very sensitive, element specific detection methods such as inductively coupled plasma mass spectrometry (ICP-MS), hydride generation atomic fluorescence spectrometry (HG-AFS), hydride generation atomic absorption spectrometry (HG-AAS), hydride generation ICP atomic emission spectrometry (HG-ICP-AES), or HG-ICP-MS.

M. J. Ahmed [24] et al. developed a spectrofluorimetric method for the simultaneous determination of selenium(IV) and (VI) as selenite-selenate by flow injection analysis (FIA). The method is based on the selective oxidation of the non-fluorescent reagent 2-( $\alpha$ -pyridyl) thioquinaldinamide (PTQA) in acidic solution (1.5–3.0 M  $\text{H}_2\text{SO}_4$ ) by Se(IV) to give an intensely fluorescent oxidation product. Selenium (VI) is reduced on-line to Se(IV) in a reduction coil installed in a photo-reactor, which is then treated with PTQA and the fluorescence due to the sum of Se(IV) and Se(VI) is measured; Se(VI) is determined from the difference in fluorescence values. The calibration graphs were rectilinear for 0.1–2.4  $\mu\text{g ml}^{-1}$  of SeVI and 10 ng  $\text{ml}^{-1}$ –2.2  $\mu\text{g ml}^{-1}$  of Se(IV), respectively. The method was applied to the determination of Se in several Standard Reference Materials (alloy, sediments and tea), as well as in some environmental waters (tap and surface water), food samples (flour and egg), a biological sample (human hair), soil sample and in synthetic mixtures. Figure 2.28 shows the simplified set-up.

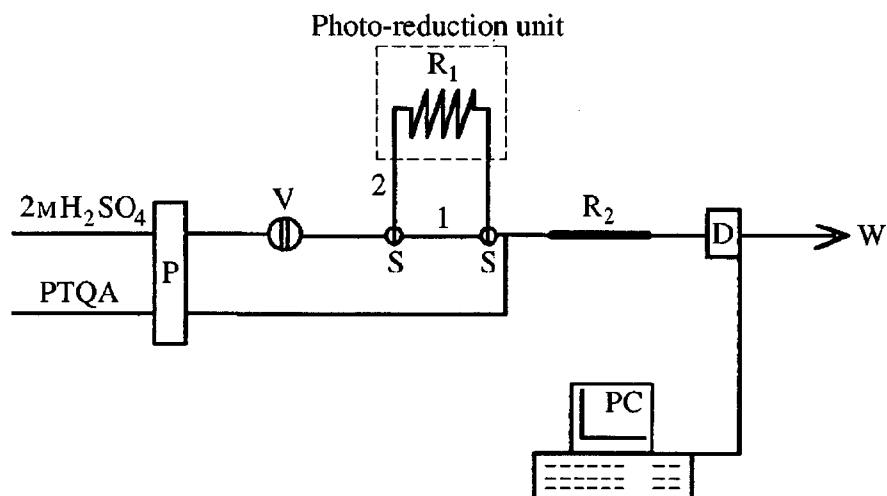


Figure 2.28 Schematic of FIA for the simultaneous determination of  $\text{Se}^{\text{IV}}$  and  $\text{Se}^{\text{VI}}$  [24]

(PTQA, 2-( $\alpha$ -pyridyl) thioquinaldinamide ; FIA, Flow Injection Analysis ; P, Pump; V, valve; S, Selector valve; R1, photoreduction coil; R2, single bead string reactor (SBSR); D, Detector; W, Waste; and PC, Personal Computer.)

Ion chromatography (IC) is now a well-established methodology for the analysis of ionic species. Ion Chromatography can readily determine selenate and selenite species in water in the absence of interferences [25]. However, the chromatographic peaks for the species of selenium will usually be completely obscured by other anions. Hoover and Yager [26] have discussed the determination of selenite and selenate together with arsenite in potable and ground waters by ion chromatography.

In their study, a Dionex Model 10 ion chromatograph was equipped with a AG-1 guard column. They found that major ions might interfere the results of trace determination. In the case of selenite, the major interferent is nitrate. And for selenate, however, the critical interference is from sulfate. Figure 2.29 shows the peaks of selenium species interfered by sulfate. In INCO CRED's samples, sulfate is also a main interferent.

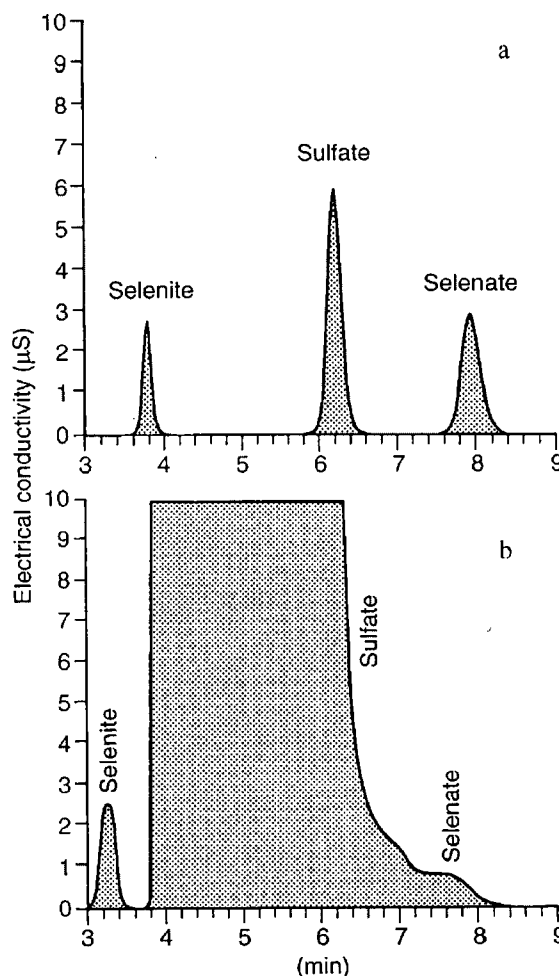


Figure 2.29 Ion chromatograms for Se speciation with different sulfate levels [27]

**a** distinct peak separation (20 mg/l of selenite-selenate and sulfate),

**b** shifting and overlapping of peaks (4270 mg/l sulfate)

HPLC-ICP-MS is an efficient method to detect elemental species. The combination of separation methods with element-selective detection methods finally leads to coupled systems in which the element-selective detector is directly (on-line) connected to the separation system. Figure 2.30 shows the schematic diagram of an HPLC-ICP-MS system [28]. These on-line systems provide the advantage of giving easier and faster results than those obtained with off-line modules. Additionally, the risk for contamination or losses is reduced, avoiding the need for fraction collection and storage (in possibly contaminating containers) [29].

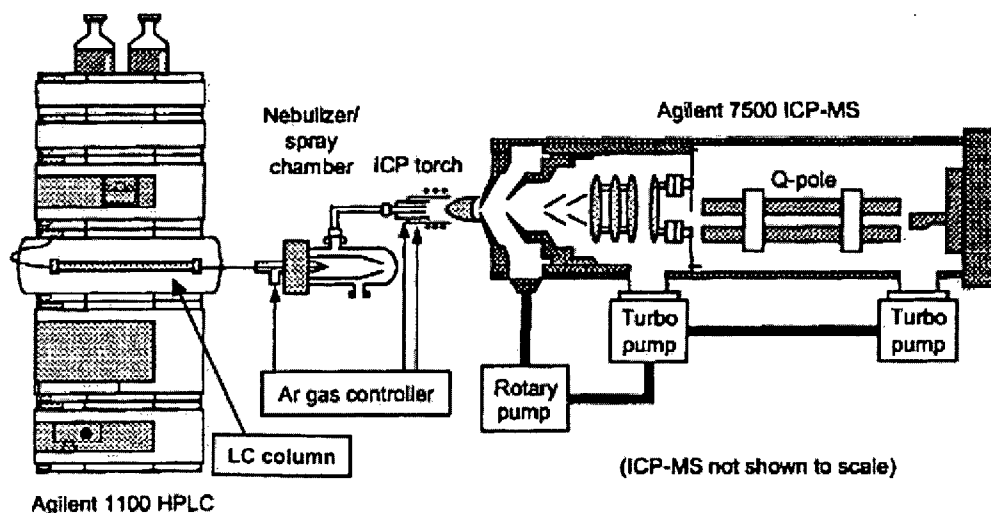


Figure 2.30 Schematic diagram of a HPLC-ICP-MS system [28]

T. Guerin et al. [30] used HPLC-ICP-MS to detect selenium species along with arsenic, antimony and tellurium speciation directly and simultaneously. Yong Cai et al. [31] used this method to determine selenite and selenate from water matrices. Gammelgaard et al [32] investigated urine samples for Se species. Birringer et al [33] investigated Se yeast and Se garlic with LC-ICP-MS. Quijano et al [34] also used this method to examine seafood for Se speciation. More recently, Michalke et al [35] provided an anion-exchange-ICP-MS method to analyze six Se standard compounds. It was an enlightenment to pretreat refractory samples for further analysis.

Atomic absorption spectroscopy (AAS) and atomic fluorescence spectroscopy (AFS) are two of the commonest instrumental methods for analyzing metals and some metalloids. A lot of analytical methods for some elements (such as Se, As, etc.) have been developed.

Ipolyi et al. [36] detected the speciation of arsenic and selenium simultaneously by three instrument combinations. HPLC-USN-AFS, HPLC-HHPN-AFS and HPLC-HG-AFS are compared. (HPLC -- High Performance Liquid Chromatography, USN -- UltraSonic Nebulisation, HHPN -- Hydraulic High Pressure Nebulisation, HG -- Hydride Generation.). The results show that the HPLC-HG-AFS provides the best detection limits. Figure 2.31 shows the schematic diagram of the analytical system.

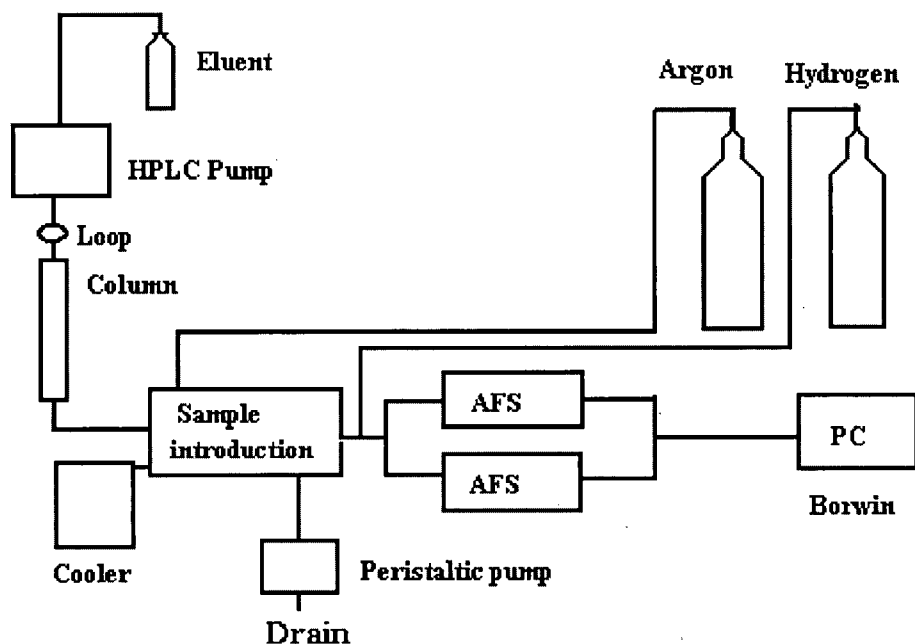


Figure 2.31 Schematic of HPLC-HG-AFS [36]

Sharmasarkar et al [35] compared two methods to detect selenite and selenate using atomic absorption spectroscopy with hydride generation (AAS-HG) and ion chromatography (IC) methods. The result showed that the AAS-HG method could analyze Se as low as 0.002 mg/L, which was below the detection limit of IC. During their study, they also found high concentration of  $\text{SO}_4^{2-}$  caused a problem by shifting or overlapping Se peaks ( Figure 2.29), resulting in the difficulty to detect selenium species. Under such circumstances spectroscopy is the better analytical choice.

American Society for Testing and Materials (ASTM) published standard test methods for selenium in water [37]. These two methods covered the determination of dissolved and total recoverable selenium in most waters and wastewaters. Both test methods utilize atomic absorption procedures such as Gaseous Hydride AAS and Graphite Furnace AAS.

## 2.11 Summary of Selenium Species Analysis

Inductively coupled plasma (ICP) is a powerful analytical, instrumental method for selenium and other elements but its much higher cost limits its widespread use as compared to AFS-HG or IC. Hydride generation atomic fluorescence spectrometry (HG-AFS) has been used for determination of hydride-forming elements because of its high sensitivity, simplicity, and low costs, but most of such work has been concentrated on water and medical analysis, and reports dealing with industrial sample determination by AFS-HG are rare. PSA Ltd. submitted the Millennium Excalibur method for selenium in drinking, surface, ground, saline and industrial & domestic waste waters in its manual, which is attached as Appendix 1.

Because of the concentrated solution character of CRED samples, it is not possible to adopt a known method to analyses of Se(IV) and Se(VI) in CRED samples. The instruments – Ion chromatography and Hydride Generation Atomic Fluorescence Spectrophotometer were available for this work. According to the accessibility of the analytical instruments, the present work focuses on these two instruments in order to develop a feasible method for selenium species analysis suitable to CRED solution analysis.

## CHAPTER 3 EXPERIMENTAL METHODS

In the experimental section of this thesis, two main parts are again included. Part one: Minor element behavior in the second stage leaching process; Part two: Development of the analytical method for selenium species.

### Part One: Minor Element Behavior

#### 3.1 Research Goals

The objective of this research was to investigate the distribution of minor elements—Ni, Co, Fe, As, Sb, Bi, Se, Te and Sn, during the second stage leaching. As a main composition element, copper was studied as well.

1. The effect of Cu/Acid ratios (mol:mol.) on the behavior of minor elements in pressure leaching

The oxidative pressure leaching is acid deficient, in order to produce sulfate rather than elemental sulfur. In plant operations, the composition of the first stage cake varies from batch to batch, resulting in some fluctuation of copper content in the feed. This series of experiments tried to clarify to what degree the Cu/Acid ratio affects the leaching process and the behavior of minor elements.

2. The effect of Cu/S ratios (wt.:wt.) on the behavior of minor elements in pressure leaching

Cu/S ratio in the feed also varies from batch to batch. The first stage cake consists mostly of chalcocite and the theoretical Cu/S ratio should be 4. Because copper metal or covellite may exist in the cake, and other sulfides also remain in the cake, the Cu/S ratio may vary from 3.8 to 4.4. This series of experiments were performed to check if Cu/S ratio has some distinct effects on the leaching process.



3. The effect of impurity additives on the behavior of minor elements in pressure leaching

During leaching process in CRED, spent electrolyte is recycled and added in the feed of pressure leach, which contains many impurities such as As, Sb, Bi, Pb, Fe and Sn. Some of these impurities may affect the leaching process greatly. In this study the effect of these impurities on the leaching process was investigated by adding salts of the impurities to the batch makeup.

4. The effect of degree of oxidation on the behavior of minor elements in pressure leaching

The CRED second stage leach is a batch process. The initial feed material is unoxidized and the final residue, fully oxidized. In this series of experiments, the batch leach was stopped at intermediate oxidation level to learn more about the impurity element behavior as a function of oxidation and batch leach time.

### 3.2 Experimental flowsheet

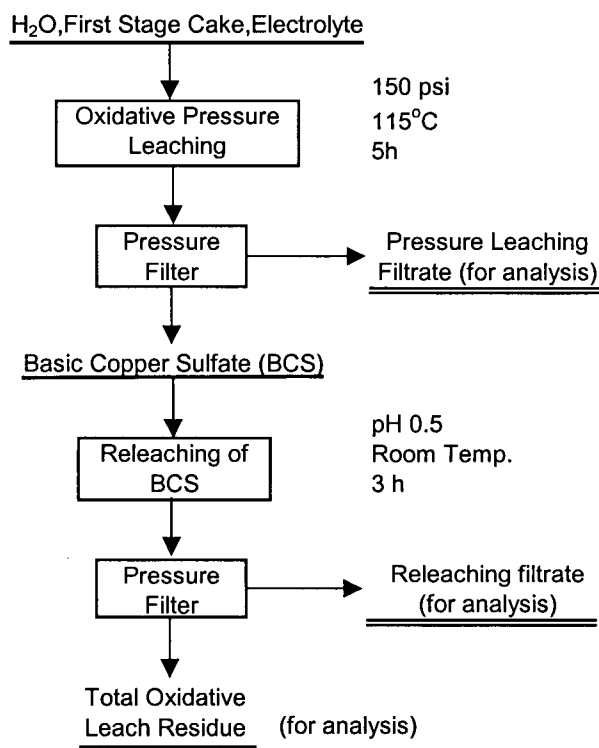


Figure 3.1 Schematic flowsheet of second stage leaching experimental method

The second stage leaching was divided into two steps: oxidative pressure leaching in an autoclave and re-leaching of basic copper sulfate formed in the prior step. Figure 3.1 shows the simplified flowsheet of these two steps for performing laboratory work.

In the first step, a filtrate mainly bearing copper sulfate (referred to as oxidative pressure leaching sample) and a solid (basic copper sulfate) were produced. In the second step, basic copper sulfate was dissolved to form copper sulfate solution (referred to as re-leach solution sample) and an unleached solid (referred to as total oxidative leach residue sample). All these three samples were collected and sent to IPL (International Plasma Laboratories, Vancouver) for chemical analysis.

### 3.3 Experimental Variables

This study investigated four variables in the oxidative pressure leach experiments listed below.

1. Cu/Acid ratios. Cu/Acid ratio is the short form of  $\text{Cu}_2\text{S}/\text{H}_2\text{SO}_4$  ratio (mole basis) in the feed to pressure leaching. Chalcocite ( $\text{Cu}_2\text{S}$ ) is the main composition of the feed to leaching process. The copper content in the first stage cake used as feeds varies from batch to batch. The acid ( $\text{H}_2\text{SO}_4$ ) used in the second stage leaching came from the spent electrolyte of electrowinning at CRED. Because the reactions are occurring in an acid deficient leaching process, the Cu/Acid ratio may affect the behavior of minor elements. The higher the Cu/Acid ratio, the more acid demand occurs during leaching and therefore the greater the degree of acid deficiency. According to the fluctuating range of Cu/Acid ratios in plant operations at CRED, several ratios were chosen by adding different amounts of chalcocite in the feeds while the acid was kept the same (the volume of electrolyte was consistent). Table 3.1 shows the ratios selected in this series of experiments.

Table 3.1 Selected  $\text{Cu}_2\text{S}$ /Acid ratios in oxidative pressure leaching

Feed No.	$\text{Cu}_2\text{S}$ /Acid (mol:mol)	$\text{Cu}_2\text{S}$ g	Acid* g	Liquid/Solid Ratio
1	2.0	398.84	100	2.84
2	2.2	438.73	100	2.56
3	2.4	478.61	100	2.33
4	2.6	518.50	100	2.14
5	2.8	558.38	100	1.98
6	3.0	598.26	100	1.83
7	3.2	638.15	100	1.71

\*Note: Acid used here comes from synthetic spent electrolyte, which contains

Cu 40 g/L,  $\text{H}_2\text{SO}_4$  200 g/L,  $\text{Fe}(2+)$  5 g/L, As 2 g/L.

2. Cu/S Ratios. In general Cu:S ratio (wt./wt.) is around 4 (assuming most material in the first stage is chalcocite). The prior studies [4, 16] showed that high Cu:S ratio would result in more basic copper sulfate precipitation and high slurry viscosity. The assays of the feeds used in the oxidative pressure leaching shows that Cu/S ratios (wt.:%:wt.:%) had a varying value. Because of the existence of elemental copper or covellite ( $\text{CuS}$ ) and other sulfides in the first stage cake, Cu:S ratios may vary around 4. In this series experiments, the first stage cake used as feeds contains Cu 64.14% and S 16.97%, in which Cu: S ratio is around 3.8. In this study several Cu:S ratios were selected by adding certain amounts of powder copper (Fisher, 99%) in the feeds. The size of powder copper was -100 mesh (10% -325 mesh). The higher copper levels are achieved by adding fine copper powder to the 1<sup>st</sup> stage cake. Table 3.2 presents the ratios and relative weight of fine copper powder added.

Table 3.2 Selected Cu/S ratios and the weight of Cu added

Feed No.	Cu:S (wt:wt)	Cu powder added g
1	3.8	0
2	4	19.07
3	4.2	36.38
4	4.4	53.69

Note: The first stage cake used in this series experiments came from INCO CRED and original label was "April 17-2", which contains Cu 64.14 wt %, S 16.97 wt %. The moisture in the cake is 25%.

3. Impurity Addition. In CRED plant spent electrolyte is added to feeds to perform the second stage leaching. In order to investigate the effects of these impurities on the leach, a series of contrast experiments for each impurity at low and high concentrations, respectively, were completed. When one impurity was studied, other concentrations of impurities were kept at the average level. The range of typical composition (low and high) and average level of the spent electrolyte are presented in Table 3.3.

Table 3.3 Typical composition of the spent electrolyte at CRED\*

	Cu	H <sub>2</sub> SO <sub>4</sub>	As	Bi	Fe	Pb	Sb	Sn
	gpl	gpl	gpl	ppm	gpl	ppm	ppm	ppm
Low	40	190	0.5	100	2	5	20	1
High	50	230	1.5	500	10	20	80	5
Average	40	200	1	300	5	10	50	3

\*Note: The composition of spent electrolyte came from CRED plant operation data.

4. Degree of Oxidation. Monitoring of oxygen flow rate can be used to identify degree of oxidation in progress. In this series of experiments several levels of oxygen consumption were chosen by shutting down the oxygen valve during leach progress. As soon as the oxygen supply was terminated the experiment was stopped.

### 3.4 Experimental Apparatus

The second stage leaching of the first stage cake was conducted in a pressure autoclave. The main apparatus is a Parr 2 L titanium autoclave. Other appliances include temperature/rotation speed controller, oxygen mass flow meter and cooling system. Figure 3.2 shows the experimental setup.

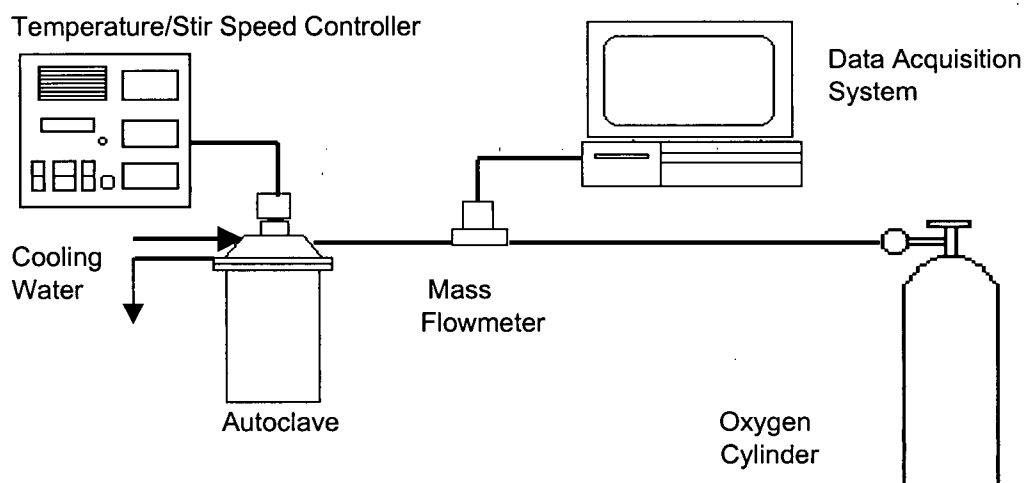


Figure 3.2 Experimental Setup in oxidative pressure leaching

The leach temperature was controlled by a temperature/agitation (Parr 4842) controller, which monitored the desired temperature using a thermocouple probe and maintained the set points by external heating and internal cooling coils. Agitation was performed by two, 4-bladed (45° pitch) down-draft impellers connected to a magnetic drive unit, which is also controlled by the above Parr controller unit. Oxygen was introduced into the autoclave below the slurry level and was monitored by an OMEGA mass flowmeter and recorded using the Labtech Notebook software.

### 3.5 Feeds Preparation

In CRED plant the second stage leaching applied the spent electrolyte of electrowinning to leach the first stage cake. In our research the electrolytes were synthetically prepared by

dissolving analytical grade chemicals in de-ionized water. The standard electrolyte composition was set as follows: Cu 40 g/L (as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), Fe 5 g/L (as  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ),  $\text{H}_2\text{SO}_4$  200 g/L and As 2 g/L (as  $\text{NaAsO}_2$ ). The standard electrolyte was used in Cu/Acid series, Cu/S series experiments. In the Impurity Addition series and Oxygen Consumption series experiments, impurities were added in the prepared electrolyte at average level (shown as Table 3.3). For Impurity Addition series experiments, the specific element concentration was set as low and high level, respectively, whereas other element concentrations were maintained the average level.

The first stage cakes were provided by the CRED plant. Four bags of sample were shipped to UBC in a drum. They were labeled as April 17-1, April 17-2, April 23 and April 25. The cakes were respectively remixed for uniformity and stored moist inside airtight plastic bags until used. A moisture analysis was performed on each residue using a vacuum desiccator equipped with a silicon trap and a "cold trap", and chemical compositions were determined using Inductively Coupled Plasma (ICP) scan by International Plasma Laboratories (IPL) in Vancouver. The assays of those samples will be presented in chapter 4.

### 3.6 Experimental Procedure

The feed slurry for a standard pressure leach test was usually prepared by adding 510 g of first stage cake (dry basis) with 500 ml of prepared electrolyte. De-ionized water was added to reach a total volume of 1.2 L. The pulp density was controlled around 30 wt.%. Then the autoclave was sealed and heated to the leach temperature. Moderate agitation (450 rpm) was maintained throughout heating to ensure uniform temperature distribution and to prevent solids setting during oxidative leaching. When the desired temperature was achieved (115 °C), the oxygen feed to the autoclave was engaged and monitored using an electronic mass flow meter connected to a data acquisition system. The pressure was maintained at a total gauge pressure of 150 psi (1034 kPa).

In the Cu/Acid series, Cu/S series and Impurity Addition series experiments, the leaching was allowed to proceed completely until the oxygen flow rate dropped to zero. The total oxygen consumed at the leach end was considered to be all the oxygen needed for complete

oxidative leaching. The value may vary according to different feed compositions. And the leaching time also may extend to more than 7 hours.

In the various oxidation series of experiments, experiments were shut down at intermediate levels of oxygen consumption. This was accomplished by shut down of the oxygen flow to the autoclave, rapidly quenching the slurry to a temperature of 80 °C and bleeding excess oxygen out of the autoclave quickly. In this series of experiments, all the feeds had the same composition.

For all experiments, after the autoclave was cooled below the temperature of 80 °C and excess oxygen was bled out of the autoclave, the autoclave was opened and the slurry was filtered hot using a pressure filter. Then the internal parts of the autoclave were washed completely into the pressure filter to avoid mass loss. The solids (basic copper sulfate) were washed by pouring hot water (>90°C) over them, which will help to speed the filtration process by dissolving crystal of copper sulfate formed when temperature drops. The filtrate and wash water were analyzed via an ICP scan.

The formed solids in the pressure leaching were slurried in deionized water (Liquid /Solid ratio: ~4) and sulfuric acid was added to dissolve all the basic copper sulfate. The acid was added slowly until the slurry pH reached a value of 0.5. The retention time was 1 hour. The slurry was then filtered again using a pressure filter to separate the unleached solids from the solution. Filter aid was added to the leach slurry as “body feed” prior to pressure filtration. No filter aid usually resulted in a poor filtration performance. The filter aid was supplied by CRED and contained mostly amorphous alumina silicate. 5 g of filter aid was added prior to filtration.

After leaching, leach solution and releach solution were collected and stored in 100 ml plastic bottles. In order to avoid crystallization of copper sulfate, some solutions (leach solutions) required dilution before being stored. The final unleached solids were dried in a vacuum desiccator to prevent further oxidation and then stored in plastic bags. All these samples were sent to IPL for chemical analysis. The solution samples were analyzed for selenium species via atomic fluorescence spectrometry with hydride generation (AFS-HG). The analysis of Se speciation will be discussed in detail below.

## Part Two: Analysis of Se Speciation

In this study a reliable analytical method was developed especially for CRED second stage leaching solutions. The AFS-HG method developed was applied to samples from the lab study as well as samples from the CRED plant.

### 3.7 Goals

The goals of this work were to:

- develop a reliable method for Se speciation analyses
- verify the reliability of the AFS-HG selenium analysis, and
- provide data about selenium concentration and speciation in the process stream to electrowinning at the CRED plant.

### 3.8 Apparatus

#### 3.8.1 AFS-HG

The Atomic Fluorescence Spectrometry with Hydride Generation (AFS-HG) was used in the measurements of Se speciation. A hydride generator module (P. S. Analytical, Orpington, Kent, England), Model 10.004, was used to pump the reagents needed for hydride generation. Detection was performed with a P. S. Analytical Model Excalibur atomic fluorescence spectrometer equipped with a Se-boostered hollow cathode lamp (current intensities: primary = 20.0; boost = 25.0). Figure 3.3 shows the analytical system.

The instrument consists of two pumps with two peristaltic pump heads each for feed solutions and sample, a mixing valve, a gas-liquid separator, a gas dryer, a flame, a booster discharge hollow cathode selenium lamp and a detector. The instrument requires reagent solutions of 4.8 M HCl (trace metal grade) and 7 g/L NaBH<sub>4</sub> (99%, Sigma-Aldrich) in 0.1 M NaOH (certified ACS grade, Fisher Scientific). The NaOH helps to slow decomposition of the borohydride. The solution must be prepared fresh daily and it was filtered through 0.45 µm nylon membrane filters using Pyrex glass apparatus. Solutions were stored in



polyethylene bottles. The HCl solution is fed to the instrument at 8-10 mL/min and the borohydride solution is pumped at 4-5 mL/min. The flame is maintained by the reaction of borohydride and acid that generate hydrogen.

The instrument is controlled by a software -- Avalon. The analysis employs three stages. Sample is flushed through the valve and lines (15 sec), then it is mixed with borohydride for analysis (10 sec) and finally the system is flushed with the blank 4.8 M HCl solution (60 sec). The corresponding time periods are termed delay, analysis and memory. The signal is indicated as a peak which approaches a steady state height, which can be calculated by the software.

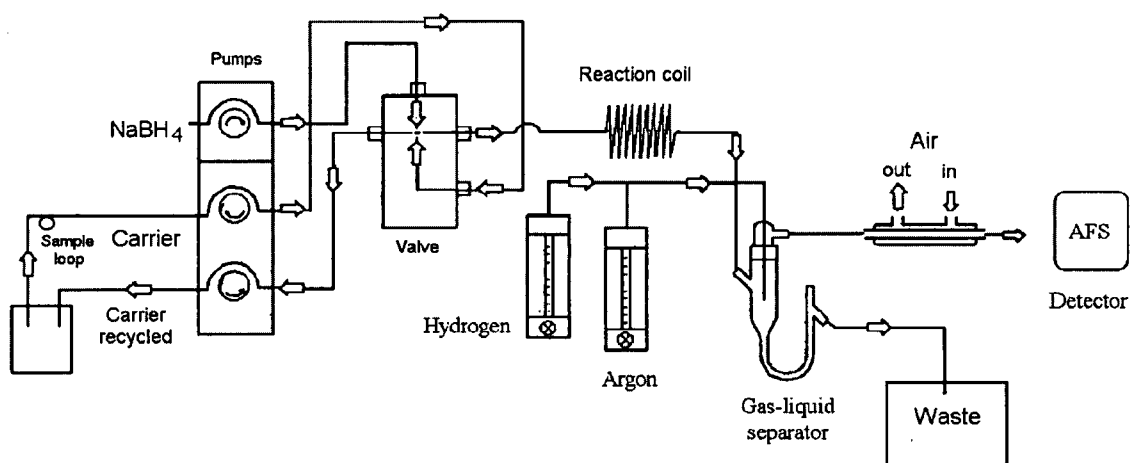


Figure 3.3 Analytical system of AFS-HG

### 3.8.2 IX and Reflux Instruments

The samples contain high concentrations of copper and other cations, which interfere with analytical results for selenium speciation by the hydride generation technique. Therefore, ion exchange is necessary to remove cations in the samples prior to performing AFS-HG analysis. An ion exchange column (15 ml) with cation ion exchange resin was used to conduct this work. The column was made by cutting a part of volumetric burette and connected with a pump that can control the flowrate of the sample solution and wash water. Figure 3.4 shows the set-up.

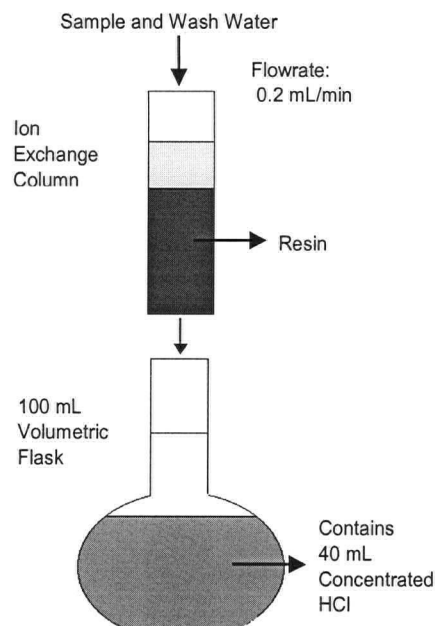


Figure 3.4 Schematic of IX setup

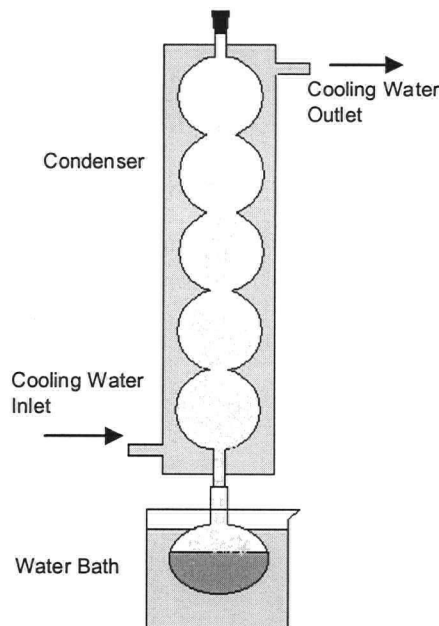


Figure 3.5 Simplified reflux setup for conversion of Se(VI)

AFS-HG can only detect selenite ( $\text{Se}^{\text{IV}}$ ), which forms the hydride,  $\text{H}_2\text{Se}$ , that can be detected by AFS. It is believed that selenite and selenate are the principal forms of selenium that exist in CRED solutions. The total selenium may be determined as the sum of Se(IV) and Se(VI) following the conversion of all Se(VI) to Se(IV). Total selenium ( $\text{SeO}_3^{2-} + \text{SeO}_4^{2-}$ ), and selenite ( $\text{SeO}_3^{2-}$ ) are determined in two separate runs. Selenate ( $\text{SeO}_4^{2-}$ ) was calculated by difference. Therefore, AFS-HG provides a direct measure of selenite and an indirect analysis for selenate.

The conversion process was performed using a reflux condenser, which reduces the loss of volatile selenium compounds. A schematic diagram of the setup is shown in Figure 3.5. In this process, the acidified sample solution (4.8 M HCl) is boiled gently for 45 minutes in a water bath and the hydrochloric acid digestion ensures that selenium(VI) is quantitatively converted to selenium (IV). The reaction is shown below:



During digestion volatile selenium-chloride species may form and cause selenium loss in an open vessel. Therefore, a reflux condenser with a rubber stopper was used to avoid selenium

loss. The apparatus should be periodically vented during the initial warm-up to release pressure.

### 3.9 Regents and Standards

All the solutions were prepared by using de-ionized water. All chemicals used in analysis were ultra-pure reagents at all times. And calibration solutions were prepared daily by diluting stock solutions.

High purity hydrochloric acid (35 ~ 37 % m/m) was used in all cases. In this study, tracemetal grade hydrochloric acid (Fisher, Pittsburgh, PA, USA) was used, which contains selenium below 0.1 ppb.

The selenite standard stock solution, 1000 mg l<sup>-1</sup> Se(IV), was obtained from Spex Inc. (Spex, Metuchen, NJ, USA). The selenate standard stock solution, 1000 g/L Se(VI), was prepared by dissolving 1.197 g sodium selenate (99%) (Aldrich, Milwaukee, WI, USA) in a 500-ml volumetric flask. Solutions of NaBH<sub>4</sub> were prepared in 0.1 mol/L NaOH aqueous solution, and the solution was filtered through a 0.45 µm Nylon membrane. This solution was prepared daily and could not be kept in a closed bottle because of pressure build-up due to hydrogen evolution.

### 3.10 Procedure

1) All solution samples from the second stage leaching were pretreated by ion exchange. The cation exchange resin Rexyn 101, analytical grade, H<sup>+</sup> form (Fisher Scientific) was used. Five millilitre portions of resin were packed in water in glass columns equipped with Teflon stopcocks. Glass wool was used to support the resin bed. Samples from the second stage leaching tests were diluted 10 times and typically 2.00 mL aliquots were used. Larger volumes were used for more dilute samples. The sample was allowed to flow through the resin and the column was then washed with ~30 mL deionized water in three portions. The flow rates were controlled at the speed of about 0.2 mL/min. The solution exiting the column was collected into a 100 mL volumetric flask containing 20 mL of water and 20 mL of concentrated HCl (Trace metal grade, Fisher Scientific). After

the wash a further 20 mL of concentrated HCl was added. The solution was diluted to the mark with deionized water. Usually the total dilution factor was 500. Samples were stored in borosilicate glass containers that had been cleaned using 1+1 nitric acid.

2) For total selenium (Se(IV)+ Se(VI)), Se(VI) was digested with high concentration HCl at elevated temperature and converted to Se(IV), then total Se can be detected by determination of total Se(IV). This can be pretreated by a flask connected with a reflux condenser which helps to avoid selenium loss. The flask was heated to  $\sim 100\text{ }^{\circ}\text{C}$  using a water bath. The reflux time was about 45 minutes and the pretreated solution was transferred to a glass bottle and stored in a fridge at  $4\text{ }^{\circ}\text{C}$ .

3) All pretreated samples were analyzed with AFS-HG. First, calibration standards were prepared and the range of standards were 0—200  $\mu\text{g/L}$ ; then the calibration curve was obtained and samples were analyzed. A standard was checked periodically to ensure that the instrument was stable.

4) After analysis, all glassware was soaked with nitric acid (1+1) for 24 hours, then rinsed with de-ionized water 3 times and soaked with hydrochloric acid for another 24 hours, finally rinsed with de-ionized water again prior to use.

## CHAPTER 4 RESULTS AND DISCUSSION

This chapter presents the results and discussion surrounding the two major topics covered in this thesis: Part I: Minor element behavior; Part II: Se speciation analyses.

In part I, four experimental factors of the second stage leaching were studied. They were Cu/Acid ratio, Cu/S ratio, impurity addition and degree of oxidation in the CRED process. These are the main factors that can possibly affect the behavior of minor elements. In part II of this chapter, the development and application of the AFS-HG method of selenium speciation is discussed in detail. This method was applied to analysis of solution samples from the second stage leaching experiments performed at the University of British Columbia and to samples taken from the CRED plant.

### 4.1 Samples Assay

There were four bags of first stage cake shipped to UBC from INCO-CRED plant. They were labeled as "April 17-1", "April 17-2", "April 23" and "April 25". The cakes were respectively remixed for uniformity and stored moist inside airtight plastic bags until use. The chemical analysis was performed after drying the samples using a vacuum desiccator equipped with a silica gel trap and a liquid nitrogen cold trap. The silica trap was used to dry the cake, and the liquid nitrogen cold trap could condense the moisture in the airflow that may cause damage to the vacuum pump. This instrument was used to dry the feed cake or final unleached solids to avoid further oxidation of samples. Table 4.1 presents the analyses for these four samples. The mineralogical composition is presented in detail in a CANMET MMSL report and not discussed here [38].

Table 4.1 Chemical composition of the first stage cake (ppm)

Sample* No.	Cu(%)	S(tot) %	Se	Te	Al	Sb	As	Ba
1	64.98	16.71	482	585	<100	121	6110	<2
2	64.14	16.97	642	542	<100	115	5403	<2
3	67.61	16.27	512	608	<100	98	5530	<2
4	68.52	16.82	361	717	<100	138	9079	<2
Sample* No.	Bi	Cd	Ca	Cr	Co(%)	Fe	La	Pb
1	206	<0.2	184	14	1.9	13939	<2	5577
2	207	<0.2	191	13	2	13954	<2	5217
3	252	<0.2	459	12	1.9	14264	<2	6198
4	247	<0.2	153	8	1.4	8491	<2	6787
Sample* No.	Mg	Mn	Hg	Mo	Ni(%)	P	K	Sc
1	<100	3	<3	14	2.1	<100	9639	5
2	<100	3	<3	14	2.1	<100	6856	5
3	<100	4	<3	11	2.5	<100	5609	5
4	<100	2	<3	12	1.7	<100	4401	5
Sample* No.	Sn	Ag	Na	Sr	Tl	Ti	W	V
1	1464	400	190	<1	<10	<100	<5	3
2	1462	300	205	<1	<10	<100	<5	3
3	1309	200	231	<1	<10	<100	<5	2
4	868	300	162	<1	<10	<100	<5	2
Sample* No.	Zn	Zr						
1	663	<1						
2	623	<1						
3	666	<1						
4	708	<1						

\*Note: Sample 1 – April 17-1; Sample 2 – April 17-2;

Sample 3 – April 23; Sample 4 – April 25

## 4.2 Cu/Acid ratio in the feed

Cu/Acid ratio is the short form of Copper/Acid ratio (mol/mol) in the feed used for pressure leaching. “Cu” represents the copper contained in the first stage cake added to the autoclave, and “Acid” represents sulfuric acid in the electrolyte added to the autoclave batch. In the CRED plant, spent electrolyte is recycled to leach the first stage cake in an autoclave. The electrolyte contains 200 g/L H<sub>2</sub>SO<sub>4</sub>, 40 g/L Cu<sup>2+</sup> and other dissolved salts. Because the composition of spent electrolyte used in the CRED plant is fairly constant, the different Cu/Acid ratios were achieved by changing the amount of the first stage cake.

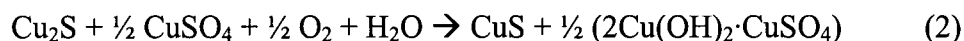
### 4.2.1 Minor Element Behavior

In general there are three products of the lab experimentation during leaching process. These are:

- an oxidative pressure leach solution from the autoclave oxidation (Ox L);
- a releach solution (R L) obtained by acid releaching of the primary autoclave solids;
- a final solid residue (S) containing the precious metals.

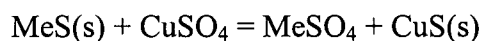
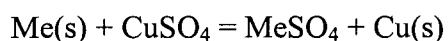
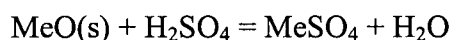
#### Copper

By analyzing copper distribution in the second stage leach process (Figure 4.1), it can be seen that with an increase in the Cu/Acid ratio, from 2.0 to 3.2, the copper distribution to the oxidative pressure leach (OPL) solution decreases gradually from 62% to 38%, while the distribution to the releach solutions (RL) increases from 38% to 62% (Figure 4.1). The final unleached solids (S) are nearly free of copper. This means that the oxidative pressure leaching was complete and that copper from first stage cake was transferred to soluble copper sulfate and solid basic copper sulfate. According to the UBC screening model for the CRED process, the reactions in the autoclave proceed nearly sequentially through reaction (1) to (3) below. Reaction (4) represents the releach process. With an increase of the Cu/Acid ratios, the acid was increasingly depleted and more basic copper sulfate would be formed during oxidative pressure leaching. This of course results in higher distribution of copper to the releach solution.



### Nickel and Cobalt

The leaching behavior of nickel and cobalt is very similar (Figures 4.2 and 4.3). From the distribution of these two elements, it can be seen that both metals stay in the leach solution without any appreciable precipitation. The reactions for nickel and cobalt in this stage are shown below.



Where Me = Ni, Co

So in theory all nickel and cobalt should be soluble and exist in the leach solution. But, because of incomplete washing after oxidative pressure leaching, a small amount these of metals report to the releach solution. Neither metal is thought to affect the leaching process significantly at the levels at which they are present in the system.

### Iron

As described in the literature review, iron plays a very important role in the chalcocite leaching process. It was found to increase the leaching rates in most studies primarily by acting as a charge carrier between the oxygen and the copper sulfide particles. Iron is also believed to have an important effect on the precipitation behavior of basic copper sulfate. From the pH-Eh diagram, it is obvious that iron could be leached into solution during the oxidative pressure leaching process. But only 4 - 5 % of iron remains in the oxidative pressure leach solution whereas more than 92 % of it stays in the releach solution (Figure 4.4). Grewal [2] studied the iron leaching process and found that most of iron in solution precipitates rapidly with the basic copper sulfate to a stable level by the 25% oxygen consumption point. The experiments reported by Grewal [2] with no iron in solution showed



that the resulting basic copper sulfate slurry was much more viscous and the agglomerate size of the precipitate was finer.

### Arsenic

In this series of experiments the synthetic spent electrolyte contains 2 g/L of arsenic (as sodium arsenite). From Figure 4.5 it can be seen that more than 80% of the initial soluble arsenic reports to the re-leach solution. The total oxidative leach residue (final unleached solids) contains less than 20% of the total arsenic. The experiments also showed that there is little arsenic in the oxidative pressure leaching solution, which means that arsenic was precipitated along with basic copper sulfate. The arsenic may be precipitated as basic copper arsenate or as a ferric precipitate.

A previous study on the final unleached solids [38] revealed that the Sn arsenate ( $\text{SnAsO}_4(\text{OH})$ ) likely precipitated during the leaching process. The Sn arsenate phase may also contain variable amounts of Au, PGMs, Sb, Te, Se and Bi. The tin arsenate phase is insoluble under CRED re-leach conditions and remains in the final residue.

### Antimony

Antimony has a similar behavior to arsenic. Figure 4.6 shows that more than 80% of antimony exists in the re-leach solution and less than 20% of it was left in the final unleached solids. The experiments showed that there is little antimony in the oxidative pressure leaching solution, which means that antimony precipitated in the presence of basic copper sulfate during pressure leaching process.

### Bismuth

From Figure 4.7 it can be seen more than 99% of bismuth was left in the final unleached solids. In the oxidative pressure filtrate and the re-leach filtrate the concentration of bismuth was too low to be detected (beyond detection limit) by ICP scans. A previous study showed

that the bismuth arsenate ( $\text{BiAsO}_4$ ) occurs as tiny crystals in association with tin arsenate ( $\text{SnAsO}_4$ ) [38].

### Selenium

The selenium behavior in the second stage leaching process is a significant concern at INCO's CRED plant. Selenium in solution will have a deleterious impact on copper electrowinning (Se contaminates Cu and has a negative impact on Cu quality). It must be largely removed prior to electrowinning in order to meet required product specifications. The two principal forms of selenium in the CRED streams are believed to be selenite ( $\text{SeO}_3^{2-}$ ) and selenate ( $\text{SeO}_4^{2-}$ ), respectively. A practical analytical method has been developed in this study for selenium speciation, which is discussed in a later section. At this point only the behavior of total selenium during leaching process is investigated.

According to the Figure 4.8, almost 60 percent of selenium reports to the leach solution while one third of the selenium was leached out during oxidative pressure leaching. Less than 10 % of selenium was left in the final unleached solids. This is believed to be unleached copper selenide that is left in the final residue. A general study of second stage CRED residues [38] showed that some complex precipitates (Cu-Ag-Te-Se phase and Cu-Te-S-Se-O phase) were also detected in the final unleached solids.

### Tellurium

Though tellurium and selenium have some similar properties in some aspects, they had very different behavior during the leaching process. Nearly 90% of tellurium was leached reported to the leach solution and the rest of the tellurium was left in the unleached solids (Figure 4.9). This means almost all tellurium precipitated with basic copper sulfate during oxidative pressure leaching. During leach process Cu telluride ( $\text{Cu}_2\text{Te}$ ) was found, which was identified by the X-ray diffraction analyses [38]. Some very complex phases, such as Cu-Te-

S-O, Cu-Te-Sn-As-O, Cu-O-Te, Cu-Ag-Te-Se and Cu-Te-S-Se-O phases, were detected in the final unleached solids in an earlier study of CRED residues [38].

### Tin

Most of tin was left in the final unleached solids (Figure 4.10). The form of tin in the final unleached solids is basic tin arsenate ( $\text{SnAsO}_4(\text{OH})$ ) [38]. It was believed the basic tin arsenate likely precipitated during leaching process [2]. The basic tin arsenate contains variable amounts of Au, PGMs, Sb, Te, Se and Bi.

#### **4.2.2 Summary**

In this series of experiments, with the increase of Cu/Acid ratios, there was little change of distribution of minor elements during leaching process. This means that there is little effect of Cu/Acid ratios on the distribution of minor elements.

With the increase of Cu/Acid ratios, the oxidative pressure leaching process encountered “slow cook” conditions which require extended leach times for complete oxidation. Figure 4.11 shows the time changes needed for complete oxidative pressure leaching, which shows that the reactions of oxidative pressure leaching could be accomplished within 3 hrs at the  $\text{Cu/Acid} = 2 \sim 2.4$ . With higher Cu/Acid ratios, more time and more oxygen were required to complete oxidative reactions (Figure 4.12). The oxygen volume ranges from 103 liters (at  $\text{Cu/Acid} = 2$ ) to 168 liters (at  $\text{Cu/Acid} = 3.2$ ).

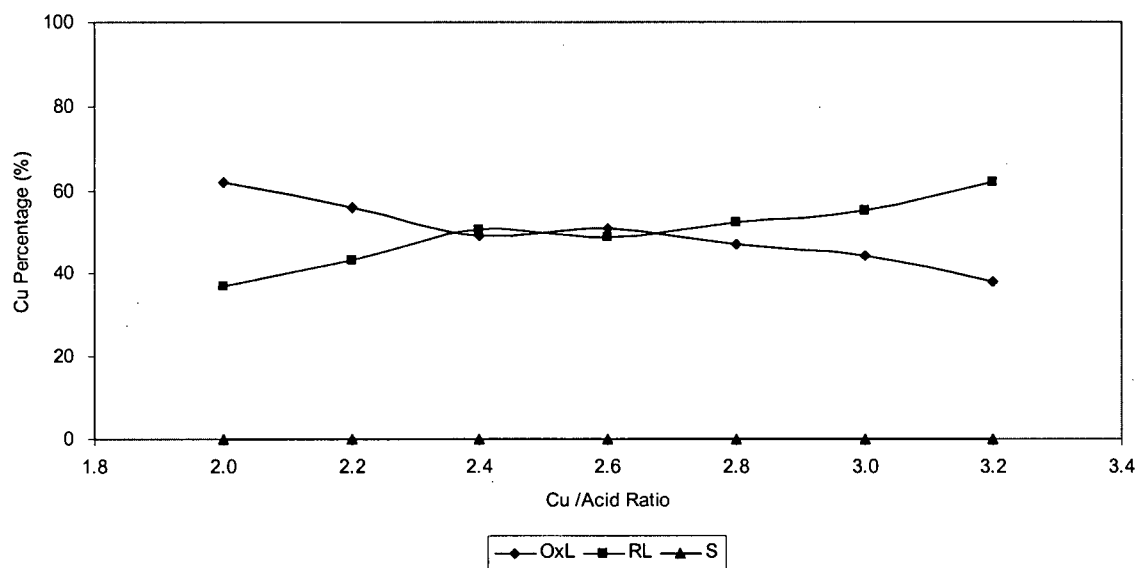


Figure 4. 1 Cu distribution as a function of various Cu/Acid ratios in the batch test feed

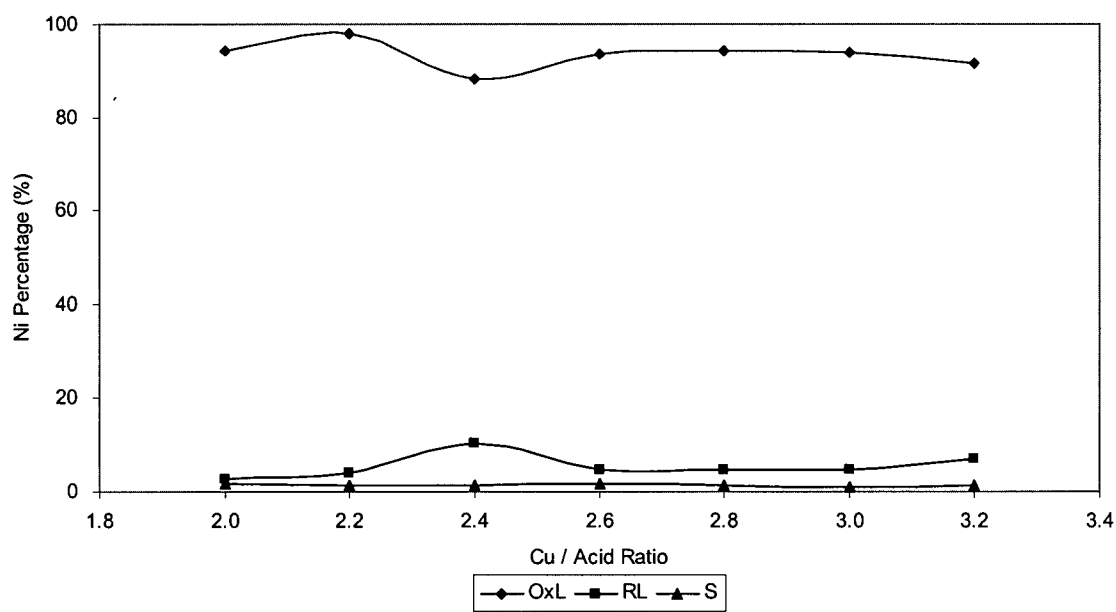


Figure 4.2 Ni distribution as a function of various Cu/Acid ratios in the batch test feed

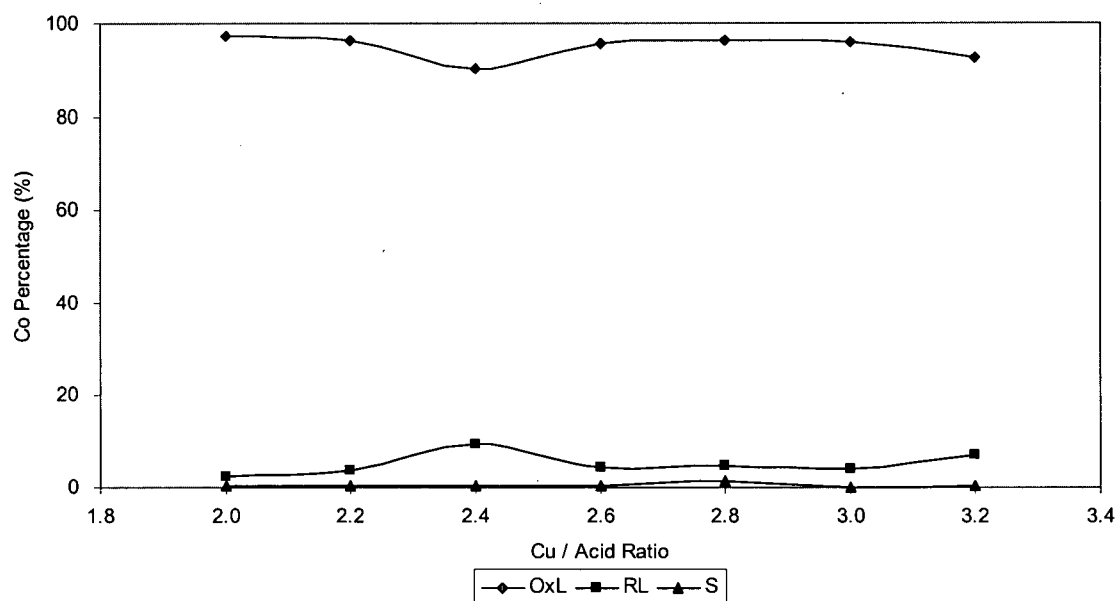


Figure 4.3 Co distribution as a function of various Cu/Acid ratios in the batch test feed

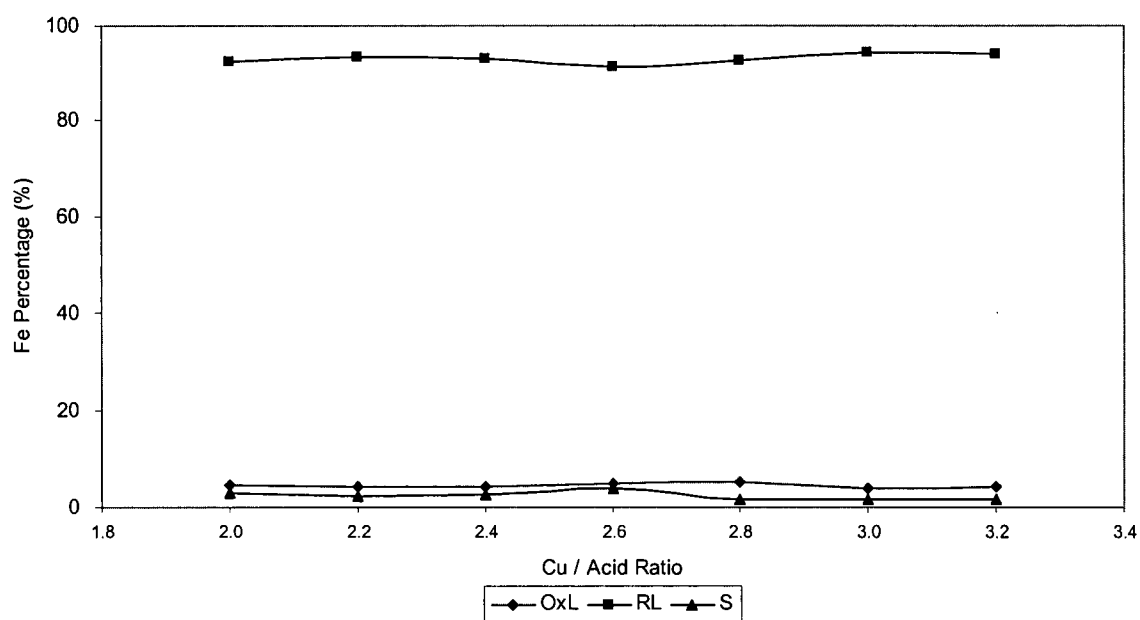


Figure 4.4 Fe distribution as a function of various Cu/Acid ratios in the batch test feed

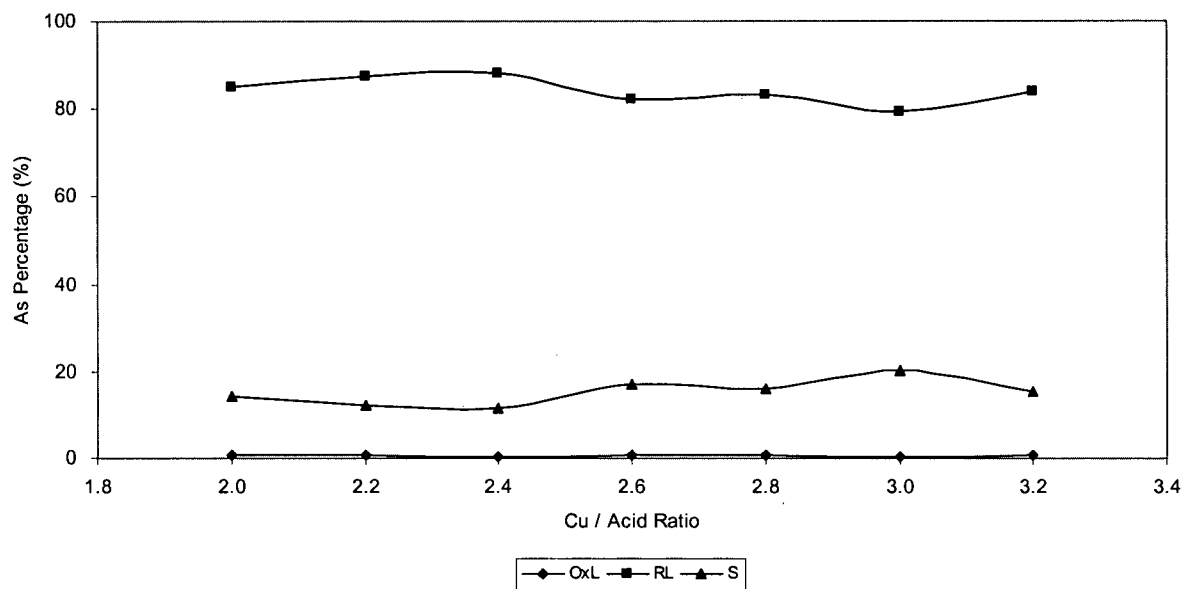


Figure 4.5 As distribution as a function of various Cu/Acid ratios in the batch test feed

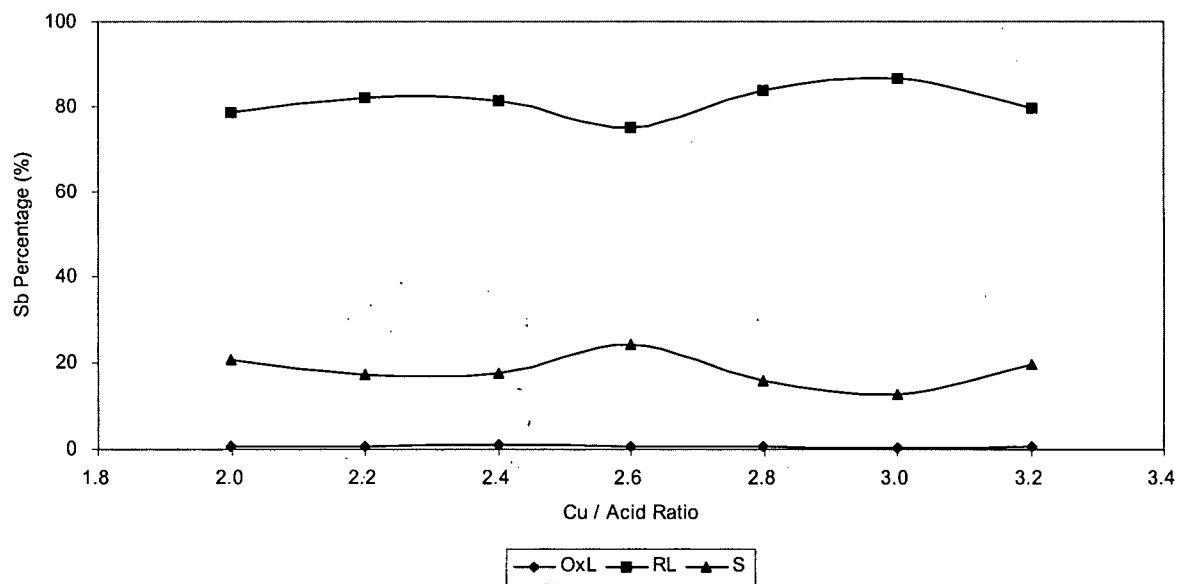


Figure 4.6 Sb distribution as a function of various Cu/Acid ratios in the batch test feed

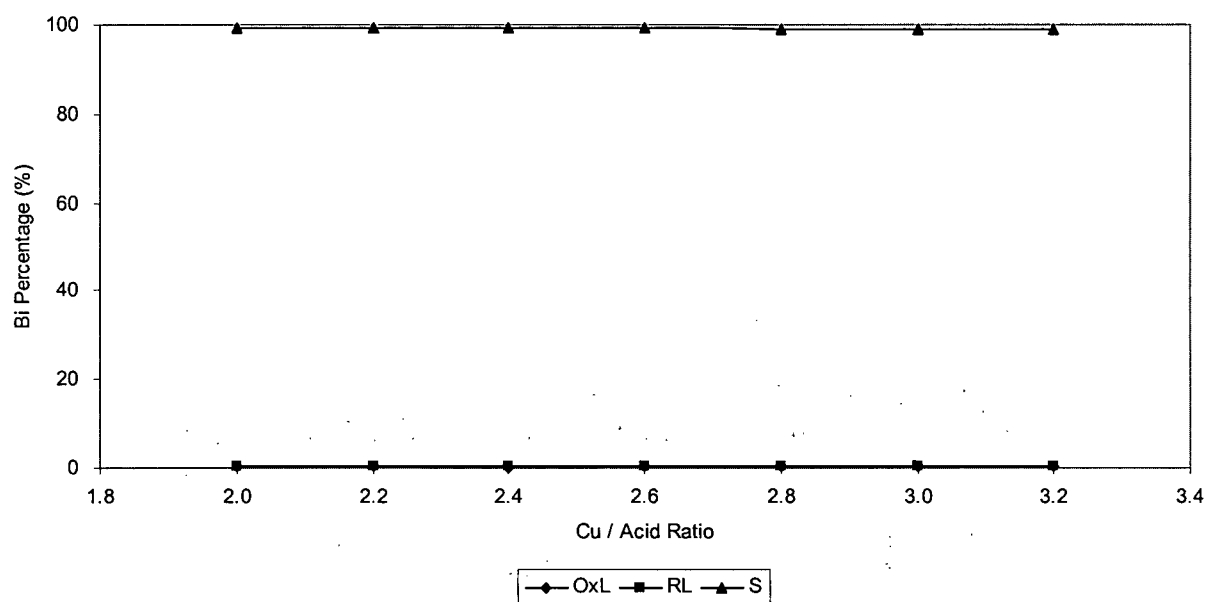


Figure 4.7 Bi distribution as a function of various Cu/Acid ratios in the batch test feed

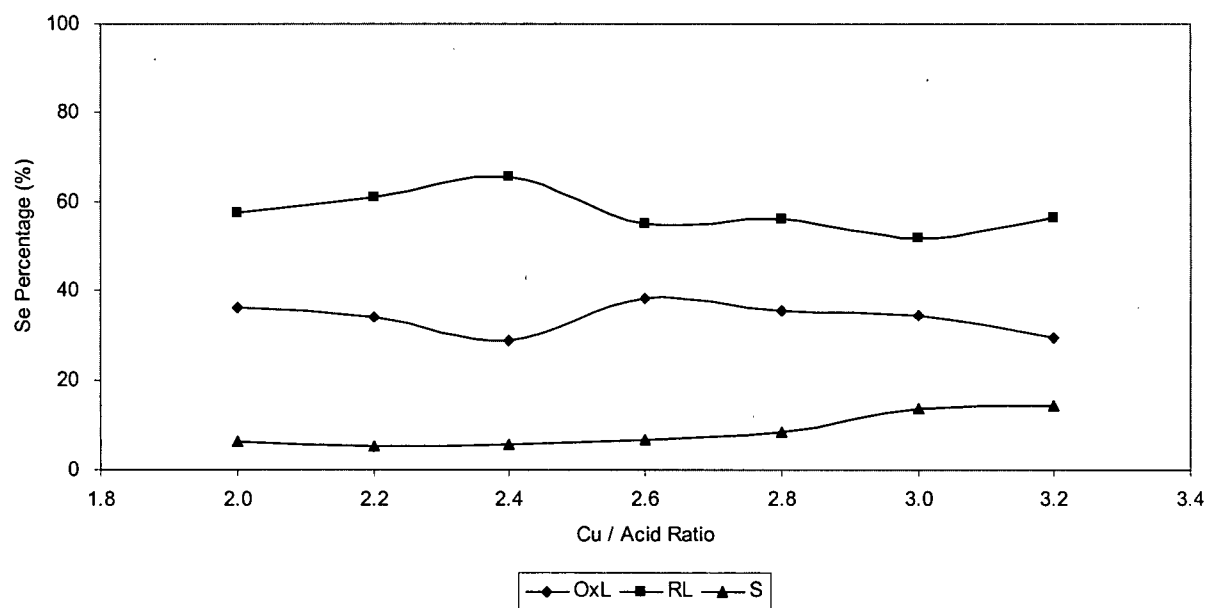


Figure 4.8 Se distribution as a function of various Cu/Acid ratios in the batch test feed

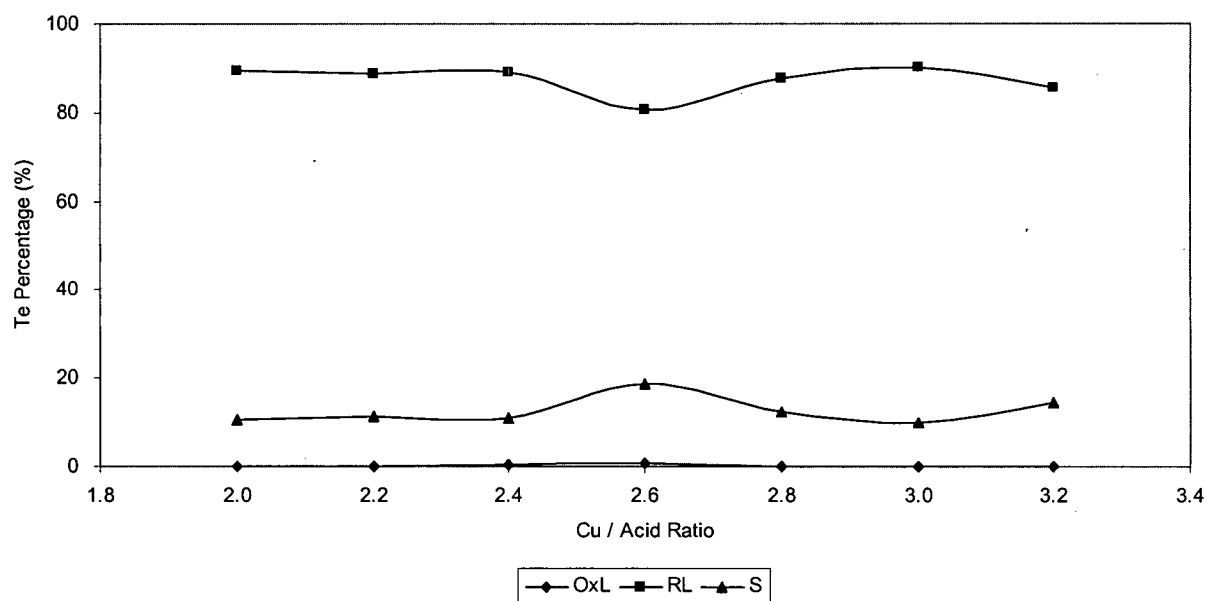


Figure 4.9 Te distribution as a function of various Cu/Acid ratios in the batch test feed

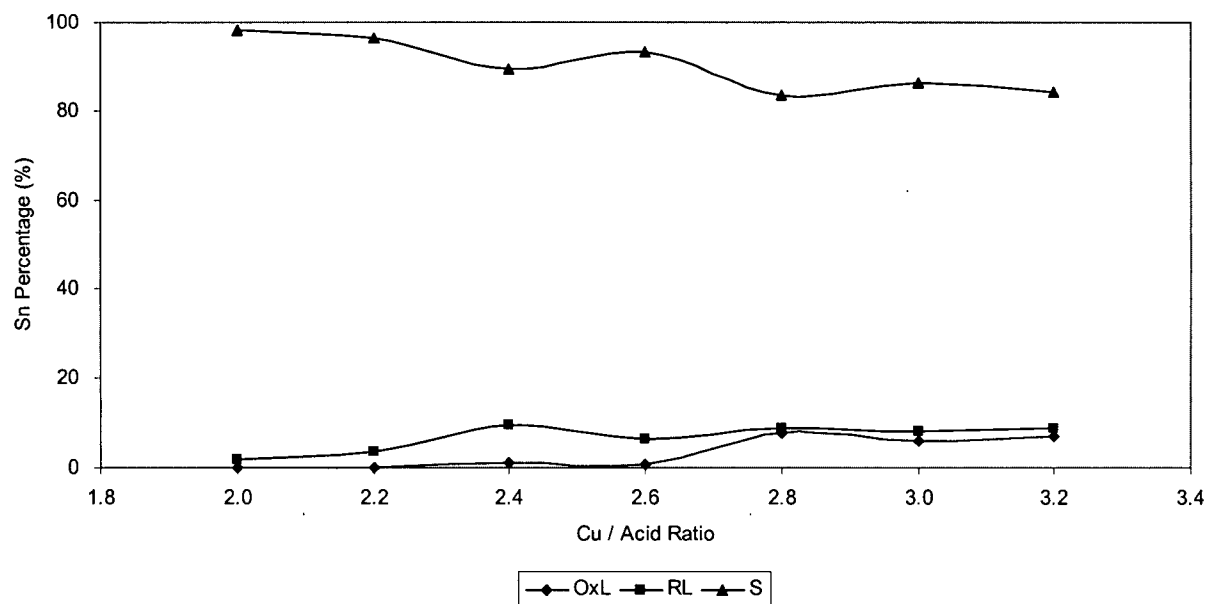


Figure 4.10 Sn distribution as a function of various Cu/Acid ratios in the batch test feed



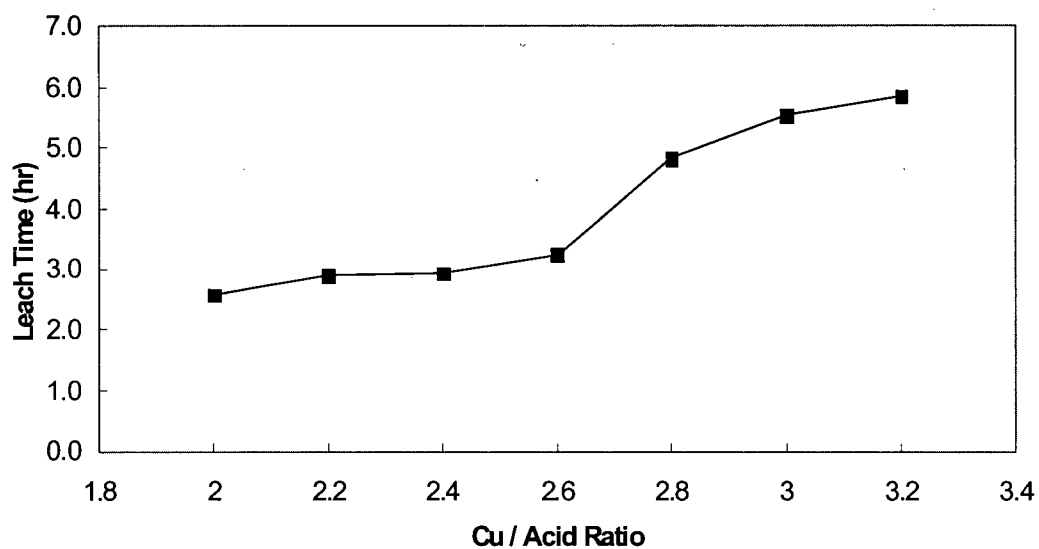


Figure 4.11 Leach time required completing oxidative pressure leaching

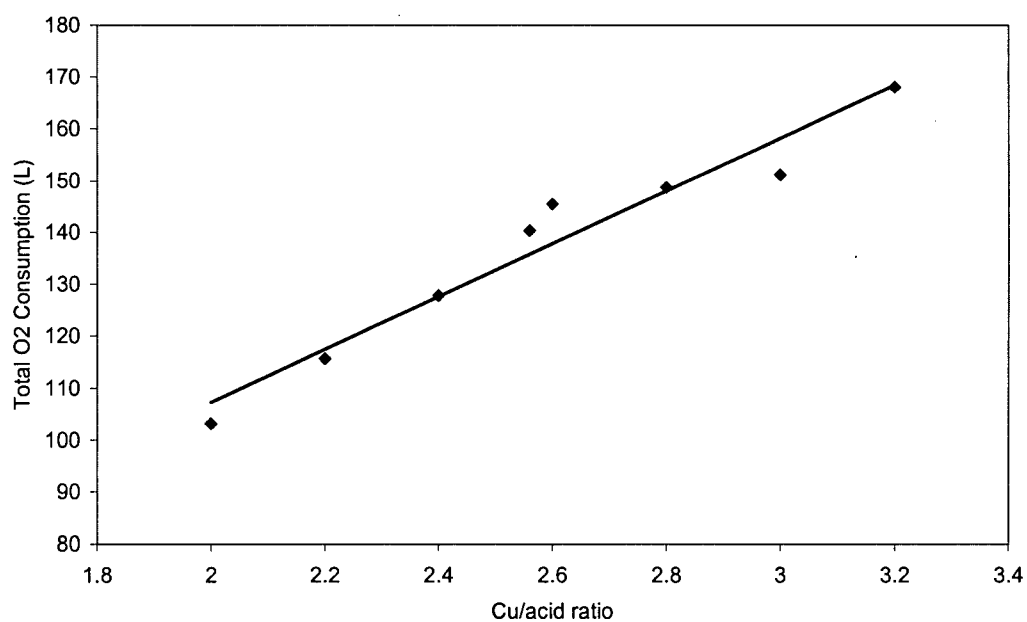


Figure 4.12 Oxygen required in oxidative pressure leaching at various Cu/Acid ratios

### 4.3 Cu/S Ratio Series

In general Cu:S ratio (wt./wt.) is around 4 (assuming most material in the first stage is chalcocite). In this series of experiments, the first stage cake used as feeds (labeled as April 17-2) contains Cu 64.14% and S 16.97%, in which Cu: S ratio is around 3.8. In this study four Cu:S ratios were selected by adding certain amounts of metallic copper powder (99%, -100 mesh, 10% -325 mesh) to the batch leach feed. The higher copper levels are achieved by adding fine copper powder to the 1<sup>st</sup> stage cake. The results are presented below.

#### 4.3.1 Minor Elements Behavior

The behavior of minor elements has little change with different Cu/S ratios except selenium and tellurium (Figure 4.13 – Figure 4.22). Because other elements have same distribution as the Cu/Acid series above, here only selenium and tellurium are discussed.

##### Selenium

With an increase in the Cu/S ratio, selenium in oxidative pressure leach solution remains constant (Figure 4.20). However the distribution of selenium to the releach solution drops from more than 60% to about 15%, resulting in more selenium reporting to the final unleached solids (from 4% to 48%).

It is possible that copper selenide was unleached or was formed during leaching process by Se precipitation. Also the increasing formation of some complex precipitates (Cu-Ag-Te-Se phase and Cu-Te-S-Se-O phase) may have increased the portion of selenium in the final unleached solids.

##### Tellurium

When the Cu/S ratio was held below 4.2, the distribution of Te was fairly constant. But, when more copper was added to feeds and the Cu/S ratio reached 4.4, there was a sudden

decrease of Te in leach solution and more tellurium was left in the final unleached solids (Figure 4.21).

It is possible that the very high Cu/S ratio could force even more tellurium into final unleached solids. During the leach process more Cu telluride ( $\text{Cu}_2\text{Te}$ ) and complex precipitates ( $\text{Cu-Te-S-O}$ ,  $\text{Cu-Te-Sn-As-O}$ ,  $\text{Cu-O-Te}$ ,  $\text{Cu-Ag-Te-Se}$  and  $\text{Cu-Te-S-Se-O}$ ) may have been formed.

#### 4.3.2 Summary

In Cu/S series experiments, Cu/S ratios had little effect on the distribution of minor elements during leaching process except Se and Te. For Se and Te, there are fairly stable distributions of them in the oxidative pressure leaching solution. With the increase of Cu/S ratios, the portions of them in leach solution decrease and more Se and Te were left in final unleached solids. According to the previous study [38], this is because Se and Te could form copper selenides or tellurides or other complex precipitates with copper and report to the final unleached solids.

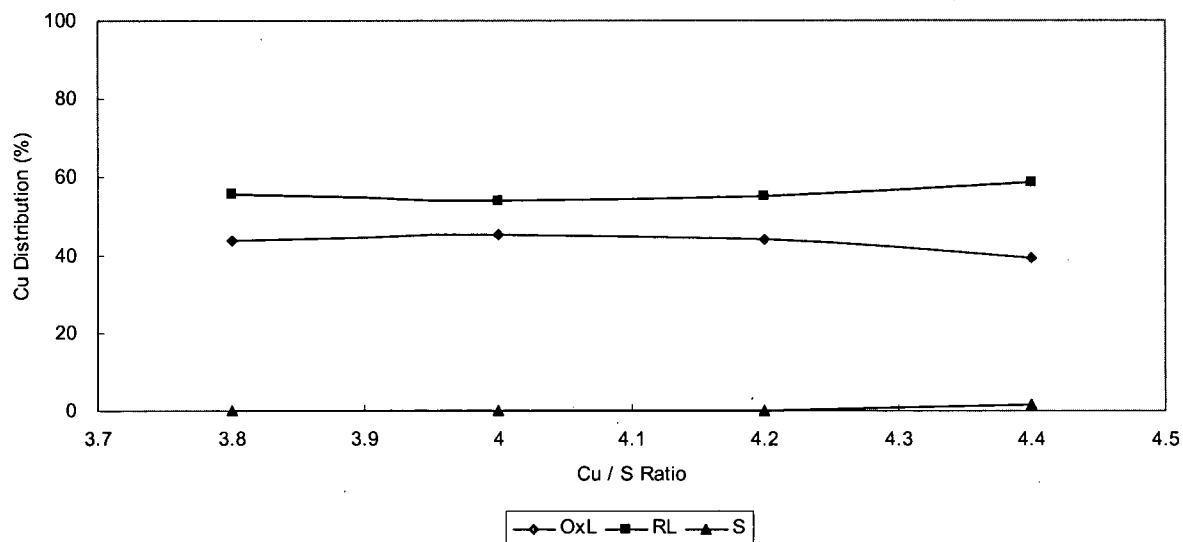


Figure 4.13 Cu distribution as a function of various Cu/S ratios in the batch test feed

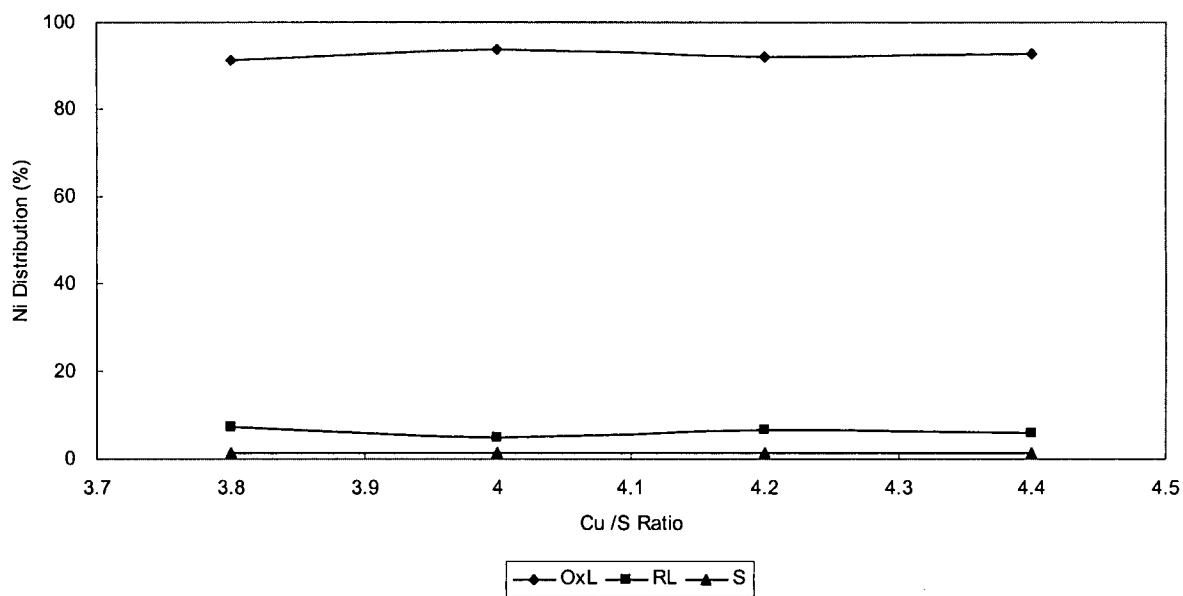


Figure 4.14 Ni distribution as a function of various Cu/S ratios in the batch test feed

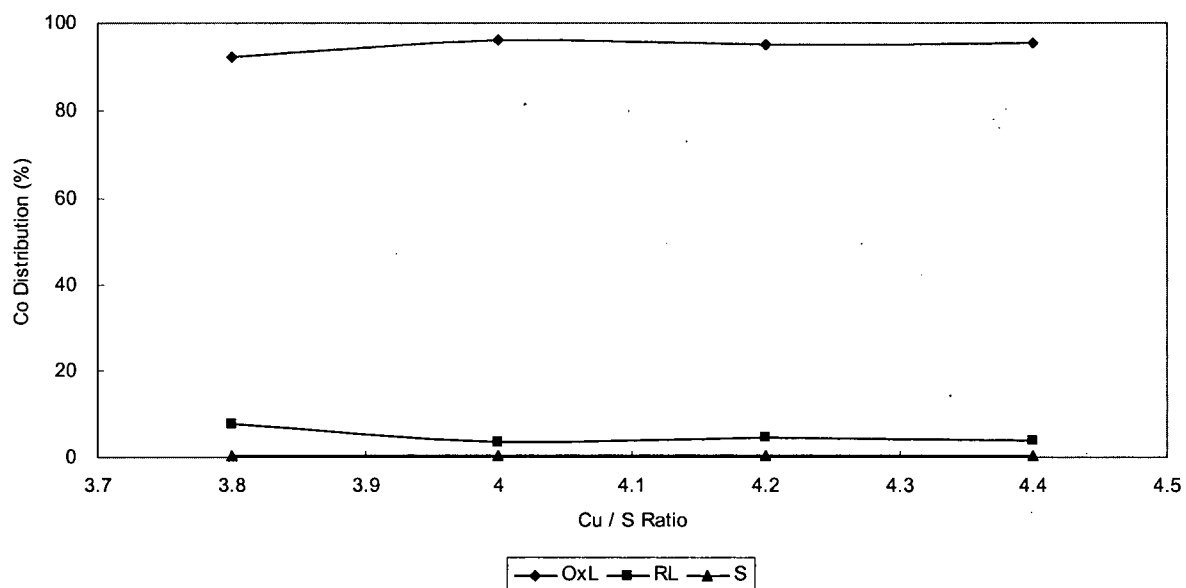


Figure 4.15 Co distribution as a function of various Cu/S ratios in the batch test feed

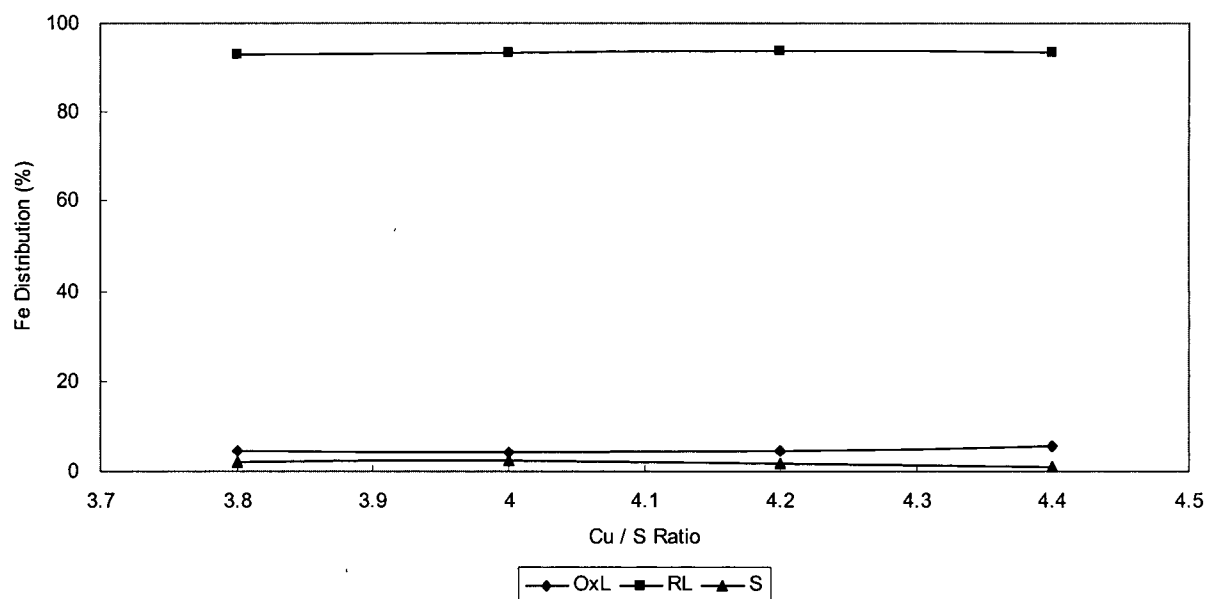


Figure 4.16 Fe distribution as a function of various Cu/S ratios in the batch test feed

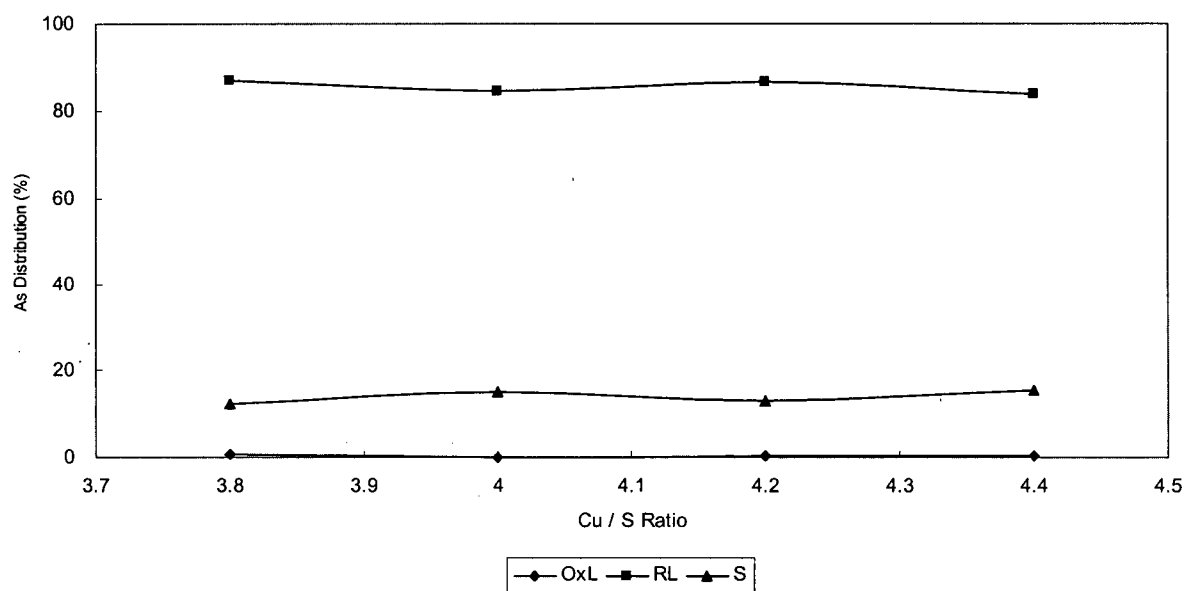


Figure 4.17 As distribution as a function of various Cu/S ratios in the batch test feed

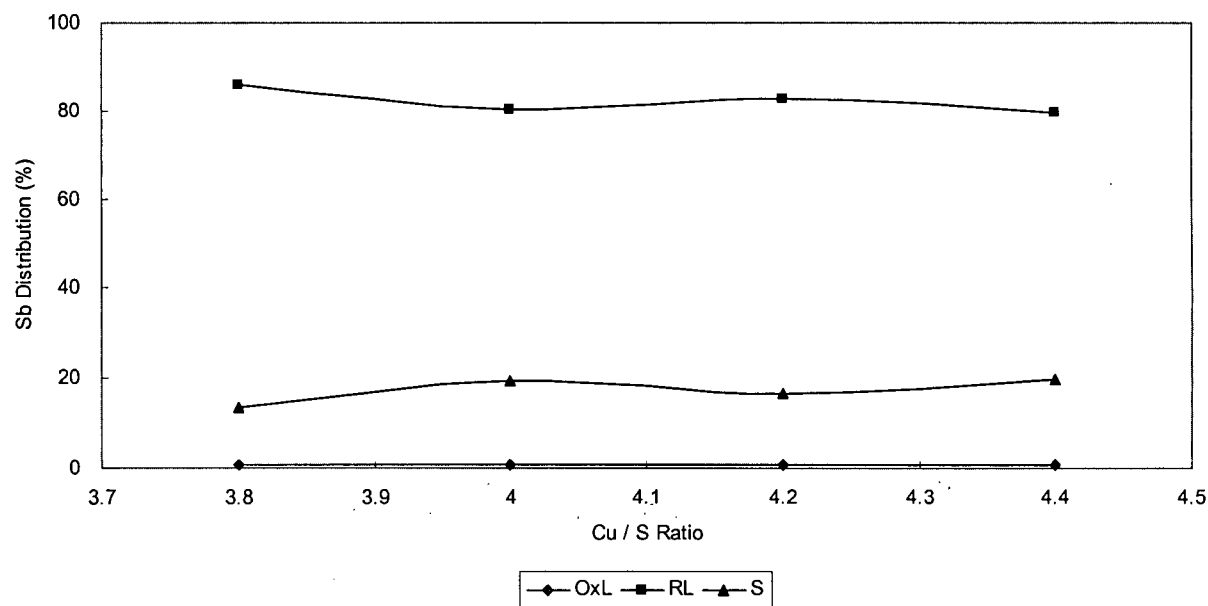


Figure 4.18 Sb distribution as a function of various Cu/S ratios in the batch test feed

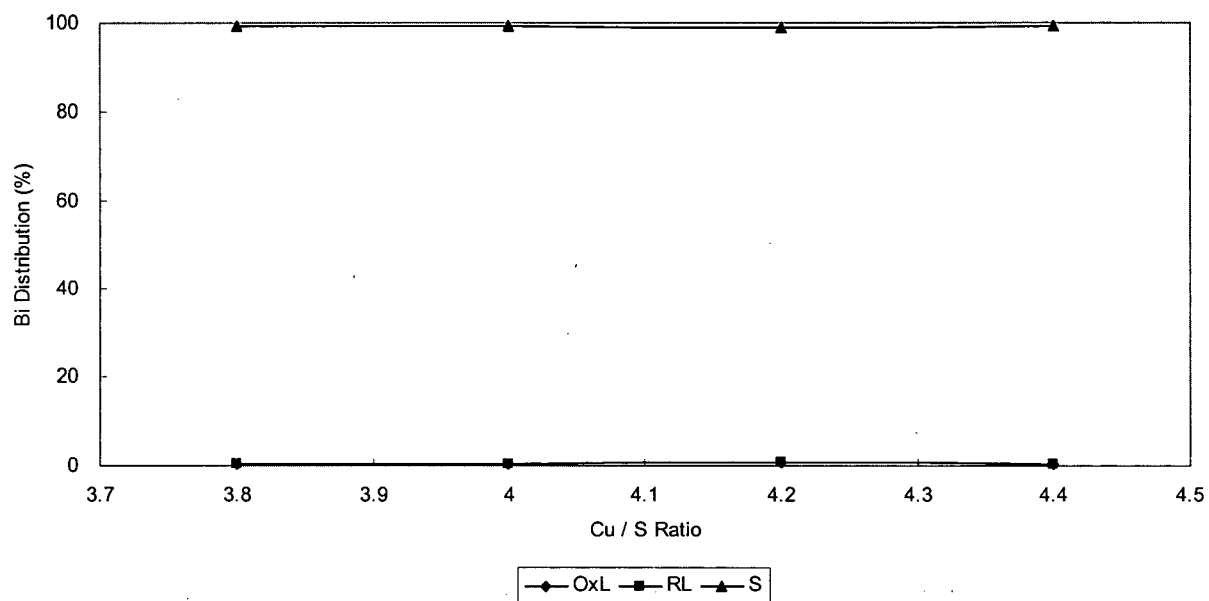


Figure 4.19 Bi distribution as a function of various Cu/S ratios in the batch test feed

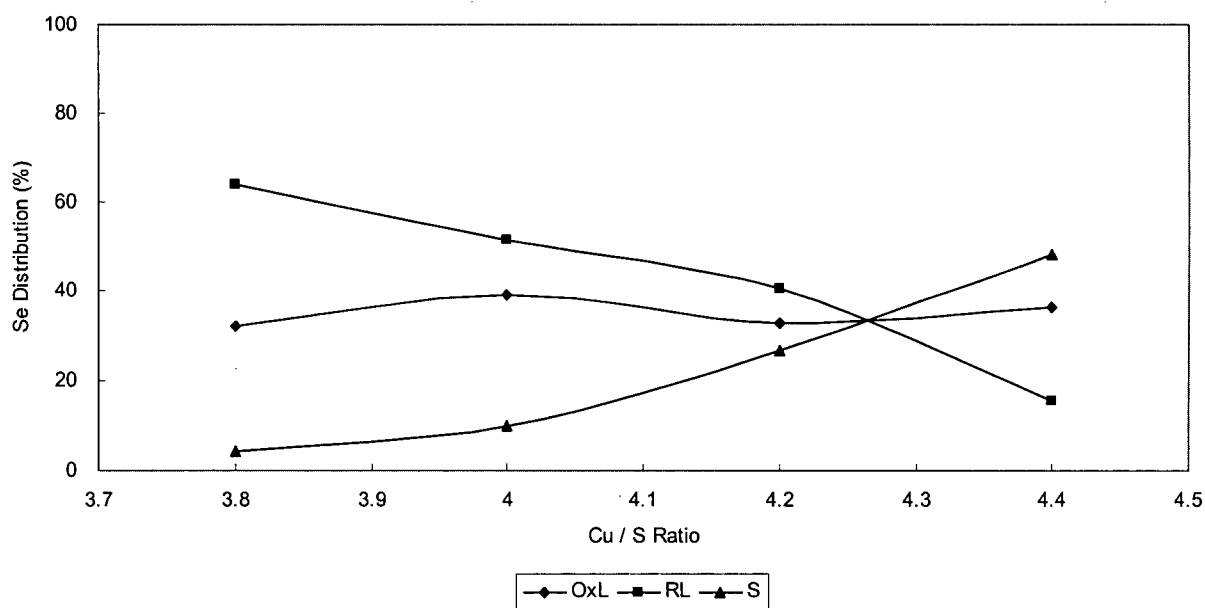


Figure 4.20 Se distribution as a function of various Cu/S ratios in the batch test feed

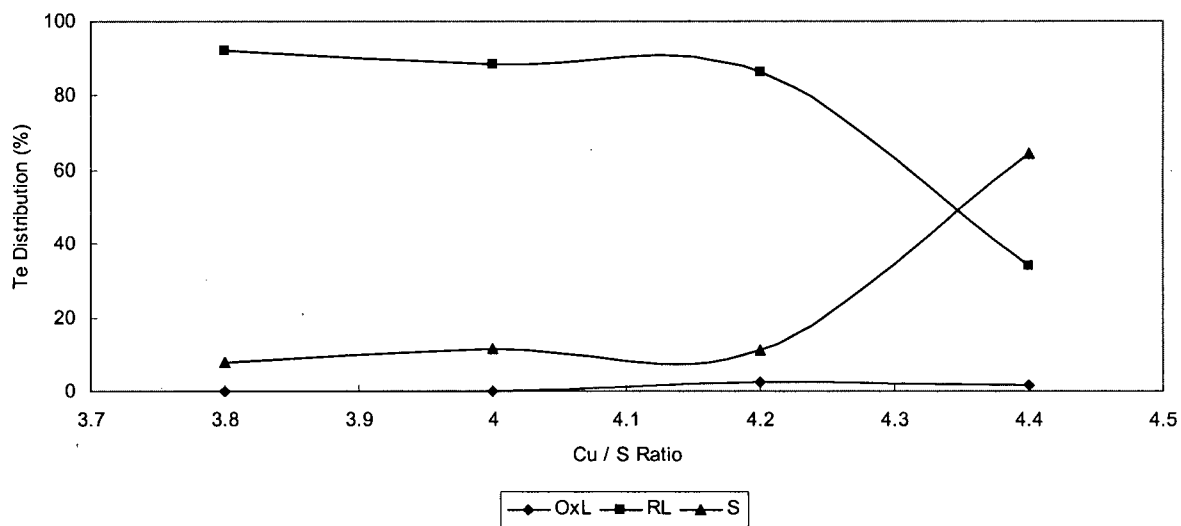


Figure 4.21 Te distribution as a function of various Cu/S ratios in the batch test feed

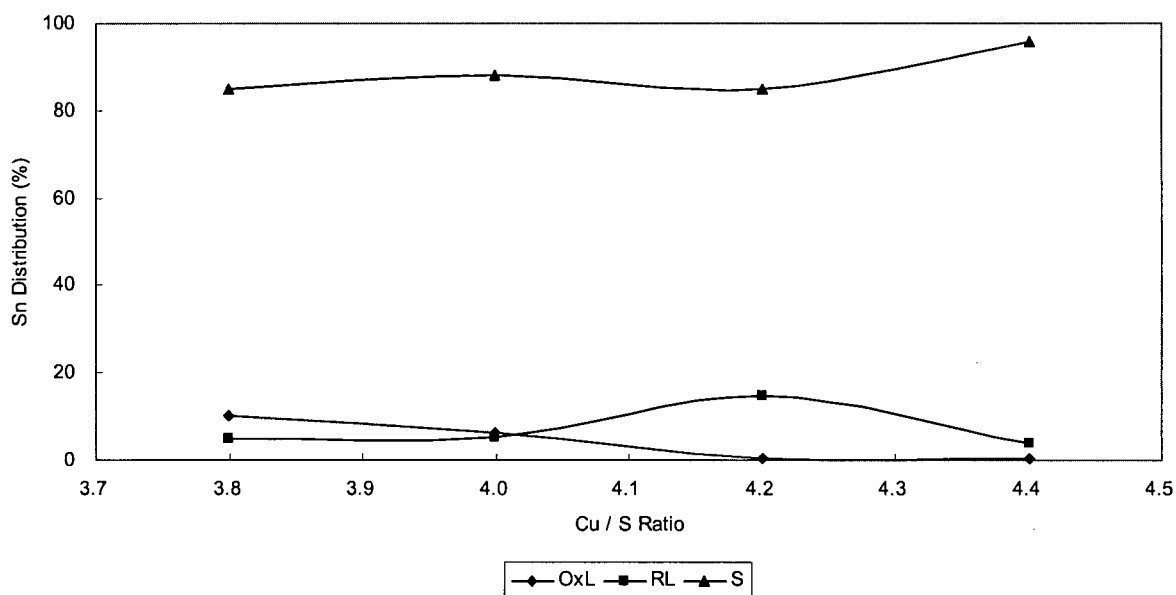


Figure 4.22 Sn distribution as a function of various Cu/S ratios in the batch test feed



## 4.4 Impurity Addition

During the second stage leaching process in CRED, spent electrolyte from electrowinning is recycled and added in the feed of pressure leach, which contains many impurities such as As, Sb, Bi, Pb, Fe and Sn. Some of these impurities may affect the leaching process greatly. In this series of experiments the effect of these impurities on the leaching process was investigated.

A series of contrast experiments were done at low and high concentrations for each impurity, respectively. When one impurity was studied, other concentrations of impurities were kept at the average level. The range of typical composition (low and high) and average level of the spent electrolyte are presented in table 3.3.

The results of the tests are showed in Table 4.2. In this table, only selected elements whose distribution had obvious differences are shown.

For arsenic addition, there was a little effect on the behavior of Se. When the concentration of arsenic in the electrolyte rises from 0.5 g/L to 3.0 g/L, the distribution of selenium in releach solution decreases from 44.94% to 39.90%, leaving more selenium in final unleached solids. This is because the high concentration of arsenic could increase the viscosity of basic copper sulfate slurries, and basic copper arsenate, is believed to be formed [4]. At the same time, unleached copper selenide and some complex precipitates containing selenium were left in the final unleached residues. Therefore, the level of arsenic in the feed of oxidative pressure leaching may have an effect on the viscosity during the leaching process [2,3,4], which may affect the behavior of selenium. Higher concentrations of arsenic in the feed will cause a more viscous slurry of basic copper sulfate, resulting in more selenium left in the final unleached residues.

For bismuth, it also has some effects on the distribution of selenium. When the concentration of bismuth in the electrolyte increased from 100 ppm to 500 ppm, more selenium was left in

the final unleached solids. It is believed bismuth may increase the viscosity of basic copper sulfate slurries and consequently plays the similar role as arsenic.

For iron, on the one hand, it could increase the leaching rates in most studies by acting as a charge carrier between the oxygen and the copper sulfide particles; on the other hand, it is also believed to have an important effect on the precipitation behavior of basic copper sulfate. Grewal [2] studied the iron leaching process and found that most of iron in solution precipitates rapidly with the basic copper sulfate. The experiments with no iron in solution showed that the resulting basic copper sulfate slurry was much more viscous and the agglomerate size of the precipitate was finer. But when more iron was added to the spent electrolyte (10 g/L), copper extraction was affected greatly. Although leach time was extended to 7 hours, the oxidative leaching was incomplete and more than 10 % of copper was left in the final unleached solids. Zhang et al. [12] reported that more elemental sulfur could be formed with the increase of iron concentration. So elemental sulfur may hinder the reactions between solids and liquids, which results in the low extraction of chalcocite during oxidative pressure leaching. Because selenium and tellurium can form some complex phases with copper, they had more than 68% and 33% of total amounts left in the final unleached solids, respectively.

For lead, antimony and tin, in their changing ranges, there were no distinctive effects of these impurities on the behavior of distribution.

Table 4.2 Distribution of Selected Elements with Different Impurity Addition

As	As(%)			Se(%)								
	Ox L	R L	Solids	Ox L	R L	Solids						
[As] 0.5	0.35	82.89	16.76	49.29	44.94	5.77						
[As] 3.0	0.30	88.16	11.54	49.16	39.90	10.94						
Bi	Bi (%)			Se(%)								
	Ox L	R L	Solids	Ox L	R L	Solids						
[Bi] 100	0.06	80.72	19.22	41.57	51.15	7.29						
[Bi] 500	0.05	76.65	23.30	47.37	36.95	15.67						
Fe	Fe(%)			Cu(%)			Se(%)			Te(%)		
	Ox L	R L	Solids	Ox L	R L	Solids	Ox L	R L	Solids	Ox L	R L	Solids
[Fe] 1	3.32	91.89	4.79	48.57	51.18	0.25	53.90	36.16	9.94	0.54	96.08	3.39
[Fe] 10	8.42	90.28	1.30	47.17	42.06	10.77	23.27	7.75	68.98	0.50	66.22	33.29

Pb	Pb(%)			Sb	Sb(%)			Sn	Sn (%)		
	Ox L	R L	Solids		Ox L	R L	Solids		Ox L	R L	Solids
[Pb] 5	0.02	3.05	96.33	[Sb] 20	0.59	86.51	12.89	[Sn] 1	0.30	6.44	93.26
[Pb] 20	0.05	4.00	95.96	[Sb] 80	0.51	86.89	12.60	[Sn] 5	0.28	5.08	94.64

Note: For As and Fe, the unit is g/L; for Bi, Pb, Sb and Sn, the unit is mg/L.

Ox L --- Oxidative Leaching solution

R L --- Releaching of BCS solution

Solids --- Final Residues

## 4.5 Degree of Oxidation

In this series of experiments, the oxidative pressure leaching was stopped at intermediate oxidation level by shutting down oxygen flow to the autoclave and bleeding residual oxygen in the autoclave. Figure 4.23 shows the four levels of oxygen consumed in this series of experiments: 23%, 64%, 80% and 100%. The values represent the four degrees of oxidation in the pressure leaching.

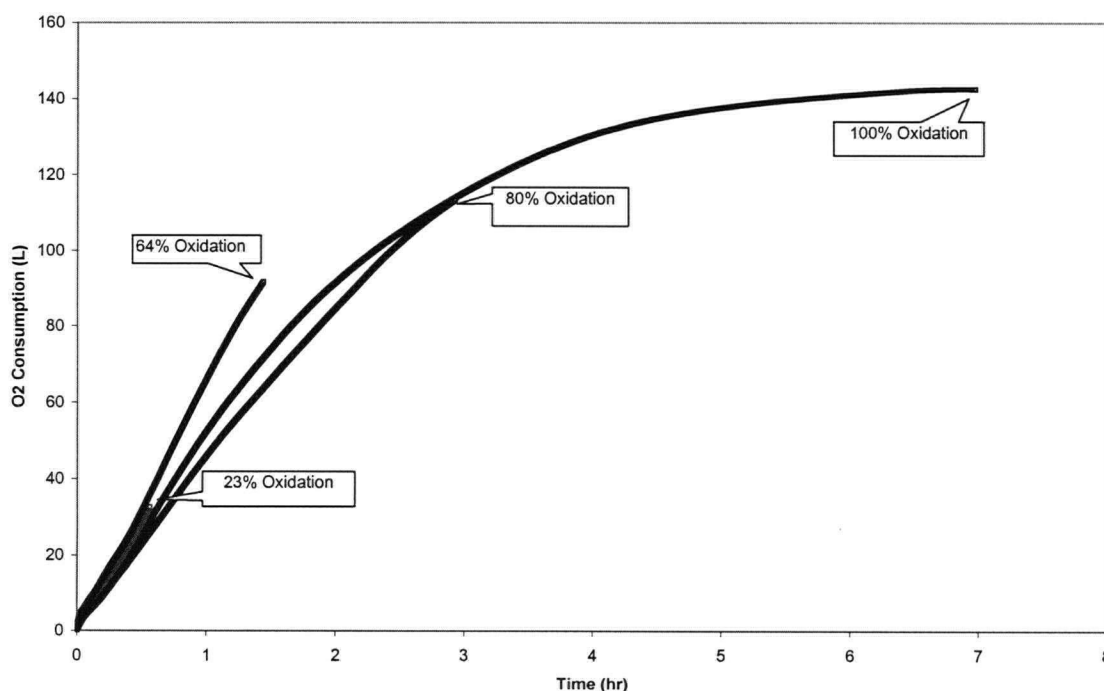


Figure 4.23 The relationship of the oxygen consumption and leach time

In this series of experiments, four experiments were conducted and all feeds were the same for the pressure leaching. The first stage cake weight was 510 g (dry basis) for all experiments. The prepared electrolyte contains Cu, sulfuric acid and other impurities at average level (Table 3.3). Four levels of oxidation were investigated and their effects on the behavior of copper and minor elements were shown in figures below (Figures 4.24 – 4.33).

The degree of oxidation has a great effect on the extraction of copper in the leaching process. As discussed above, reactions occurring in the autoclave are shown below:



Therefore, oxygen is necessary during the oxidative pressure leaching. At the point of 23% oxidation, nearly 50% of copper was left in the final unleached solids. With a higher degree of oxidation, the amount of copper unleached decreased gradually. Finally, at full oxidation, more than 99.8% of copper was extracted from the first stage cake.

For antimony, from Figure 4.29, it can be seen there were obvious changes of distribution in re-leach solution and final unleached solids. This can be deduced from Figure 4.28 which has been discussed in Cu/Acid ratio series of experiments. In general, most of antimony could precipitate with basic copper sulfate and be re-leached by acid in the re-leach stage. With more complete oxidation, more basic copper sulfate would be formed and more antimony also be precipitated resulting in more antimony leached out in re-leach solutions.

For selenium and tellurium, they have an affiliated relationship with copper as discussed above, so Se and Te could form very complex phases with copper and enter the final unleached solids. With the high degree of oxidation, copper extraction rates rise and less copper was left, which results in less selenium and tellurium in the final unleached solids.

For other minor elements, the degree of oxidation had little effect on their behavior during leaching process.

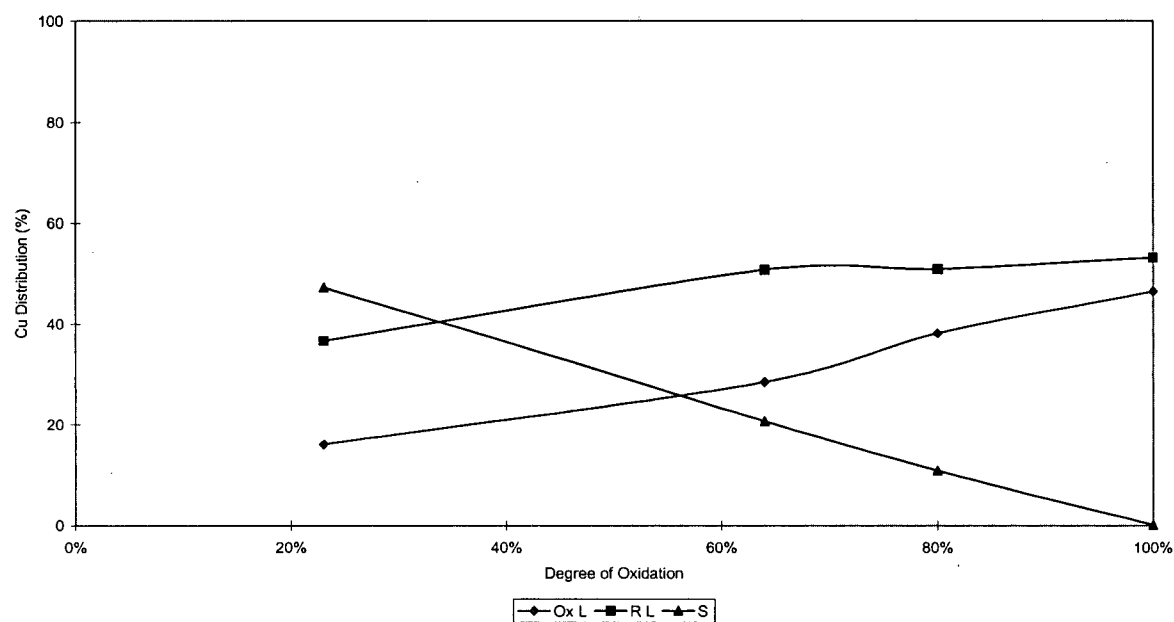


Figure 4.24 Copper distribution at different degrees of oxidation

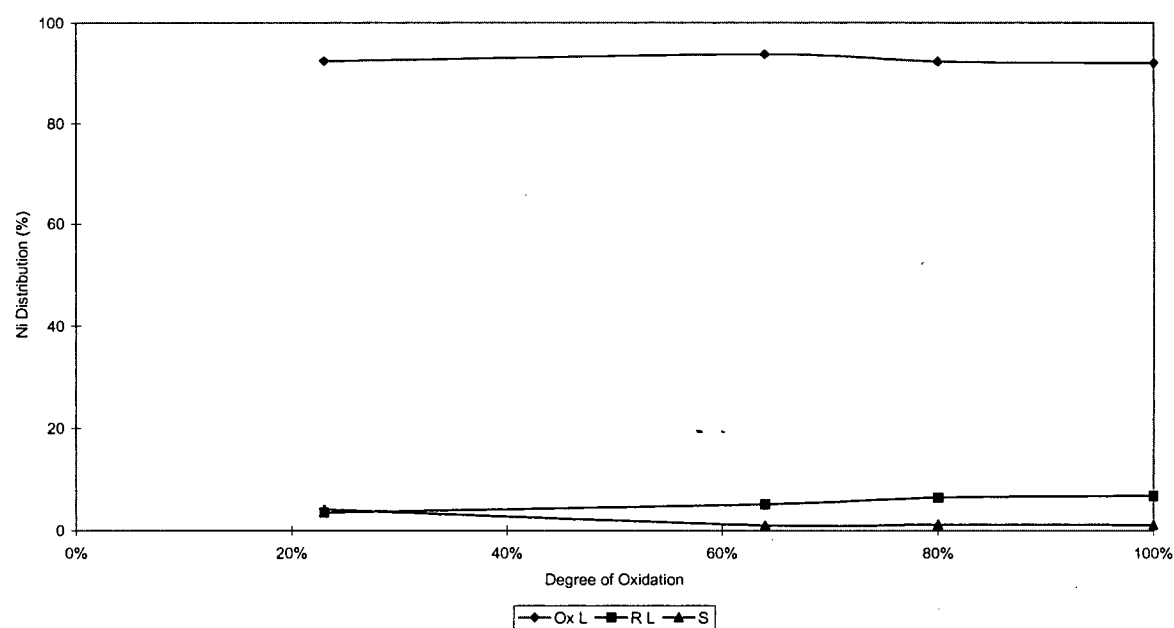


Figure 4.25 Nickel distribution at different degrees of oxidation

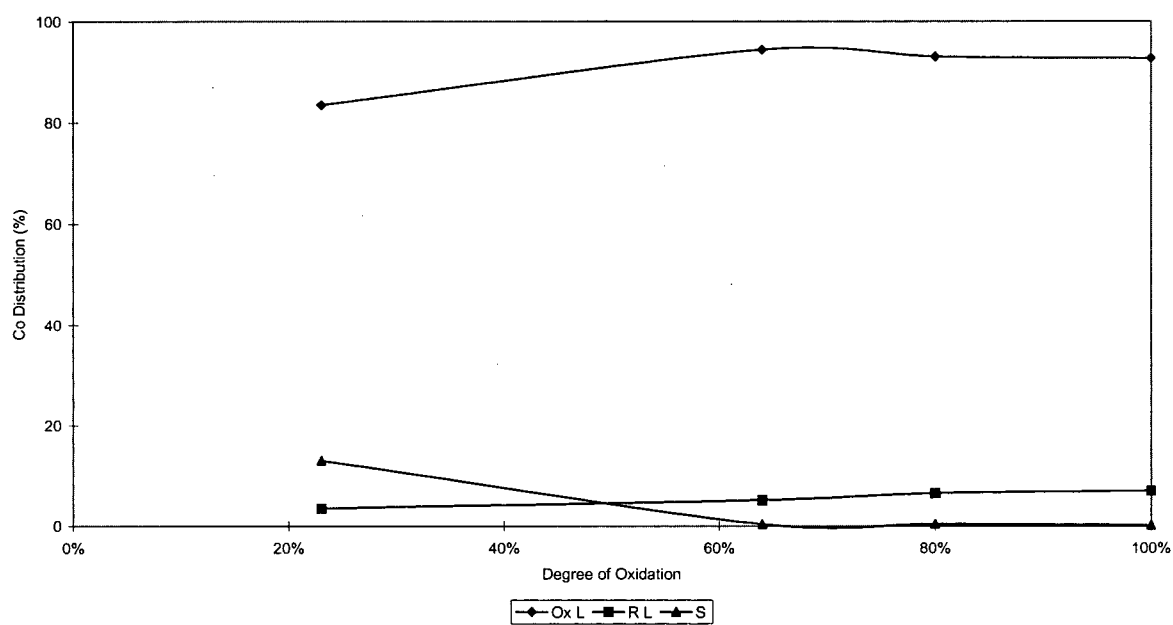


Figure 4.26 Cobalt distribution at different degrees of oxidation

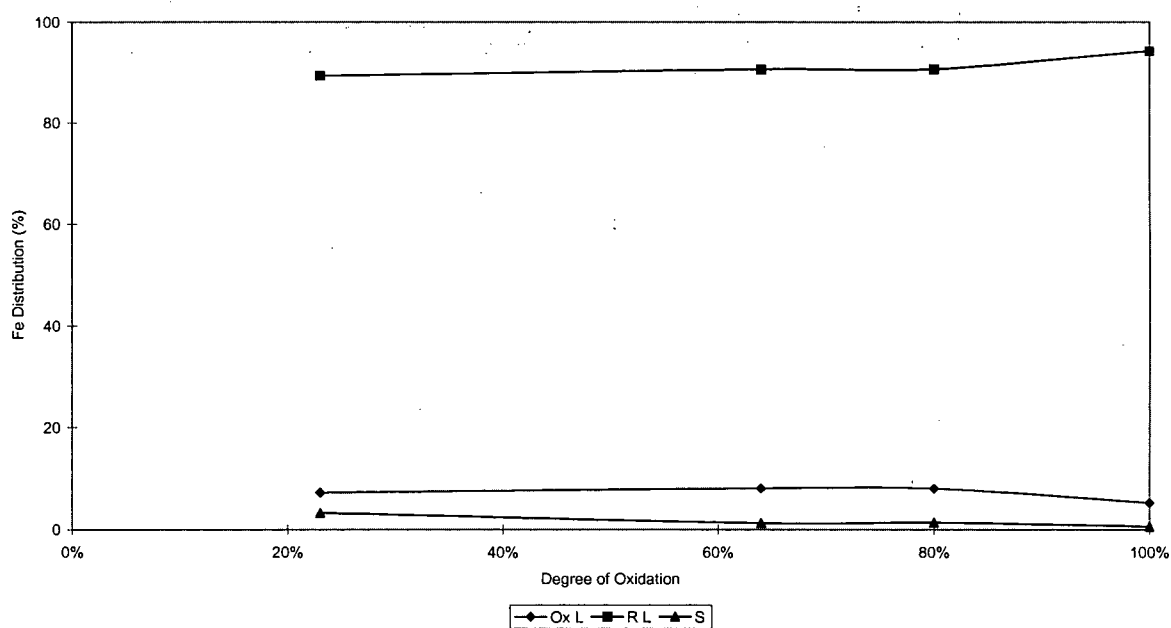


Figure 4.27 Iron distribution at different degrees of oxidation

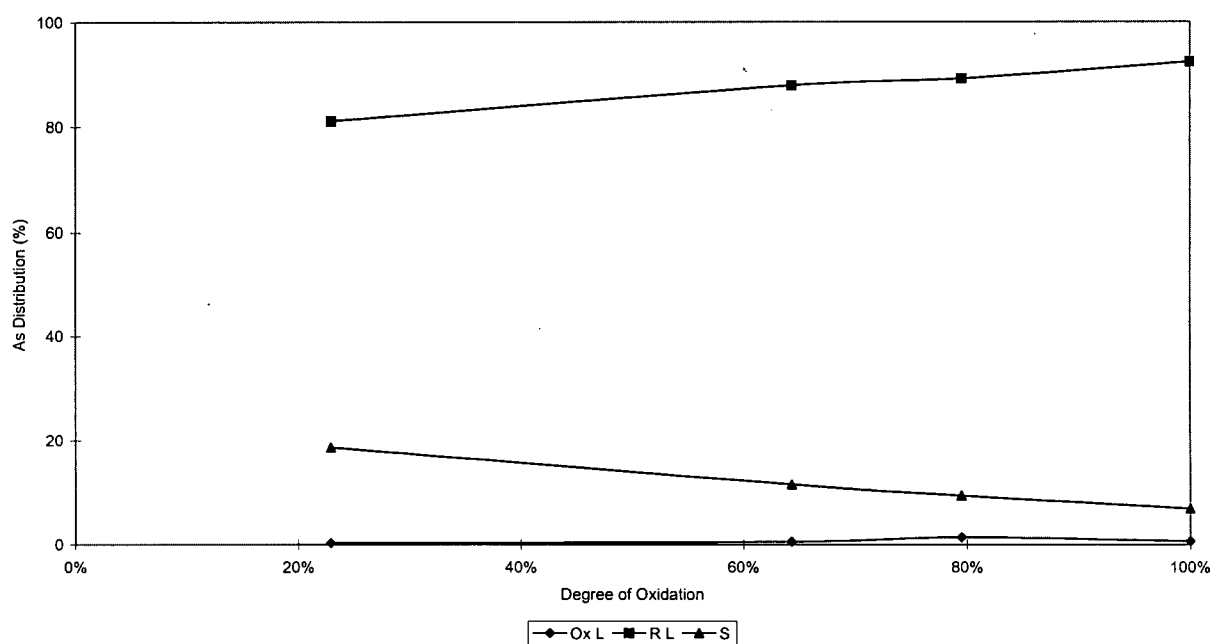


Figure 4.28 Arsenic distribution at different degrees of oxidation

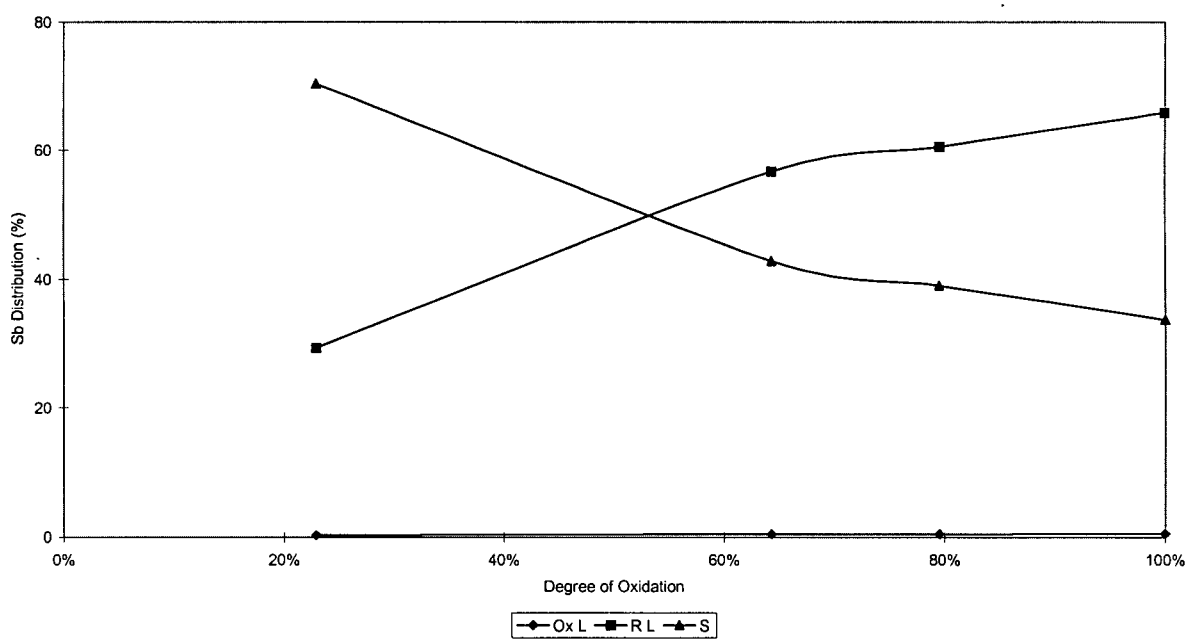


Figure 4.29 Antimony distribution at different degrees of oxidation



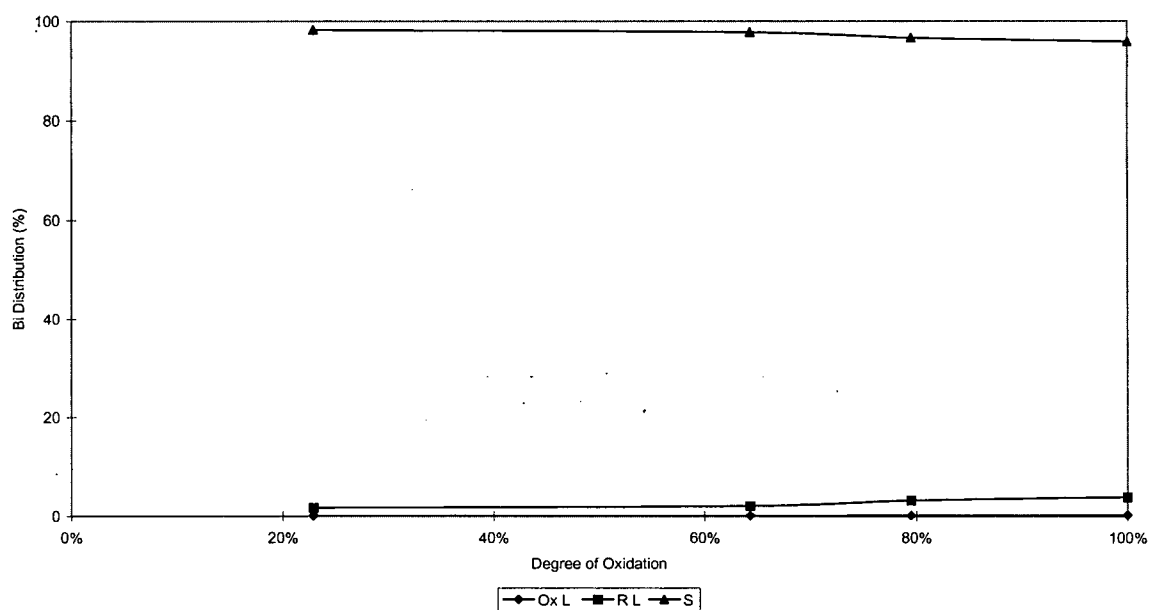


Figure 4.30 Bismuth distribution at different degrees of oxidation

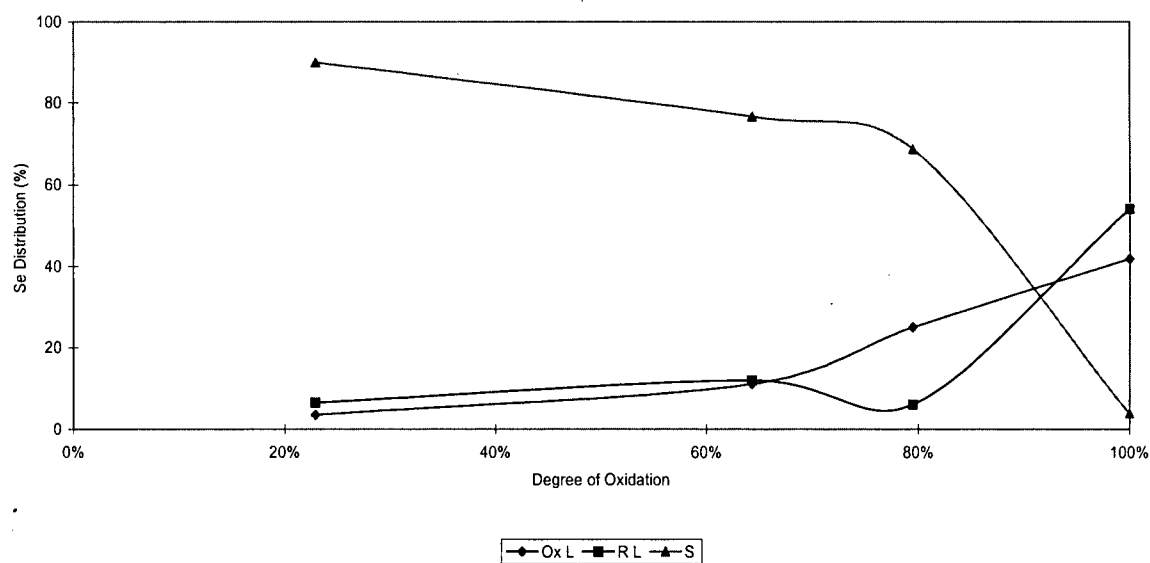


Figure 4.31 Selenium distribution at different degrees of oxidation

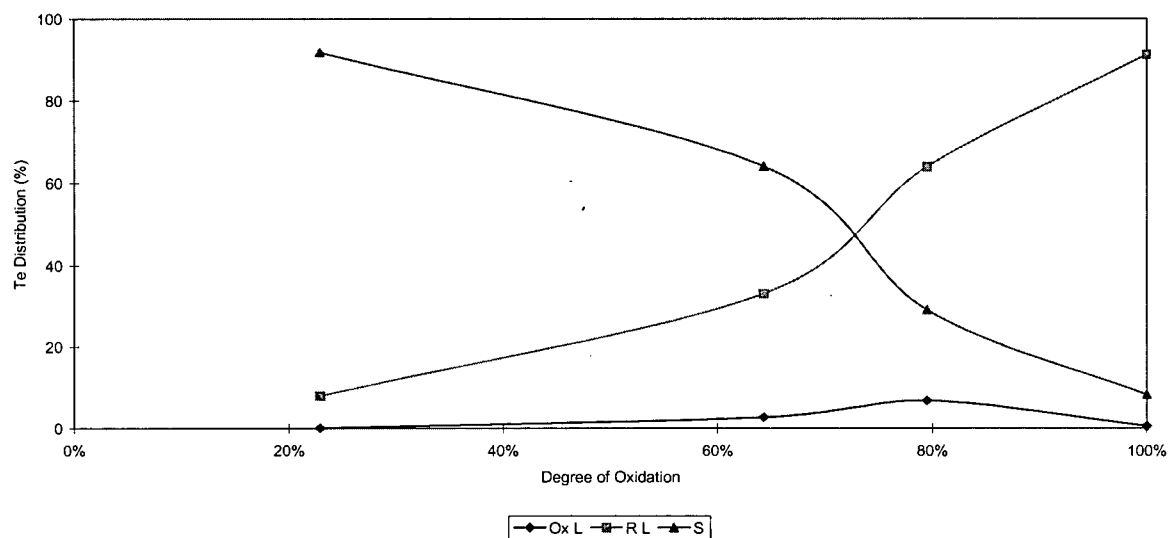


Figure 4.32 Tellurium distribution at different degrees of oxidation

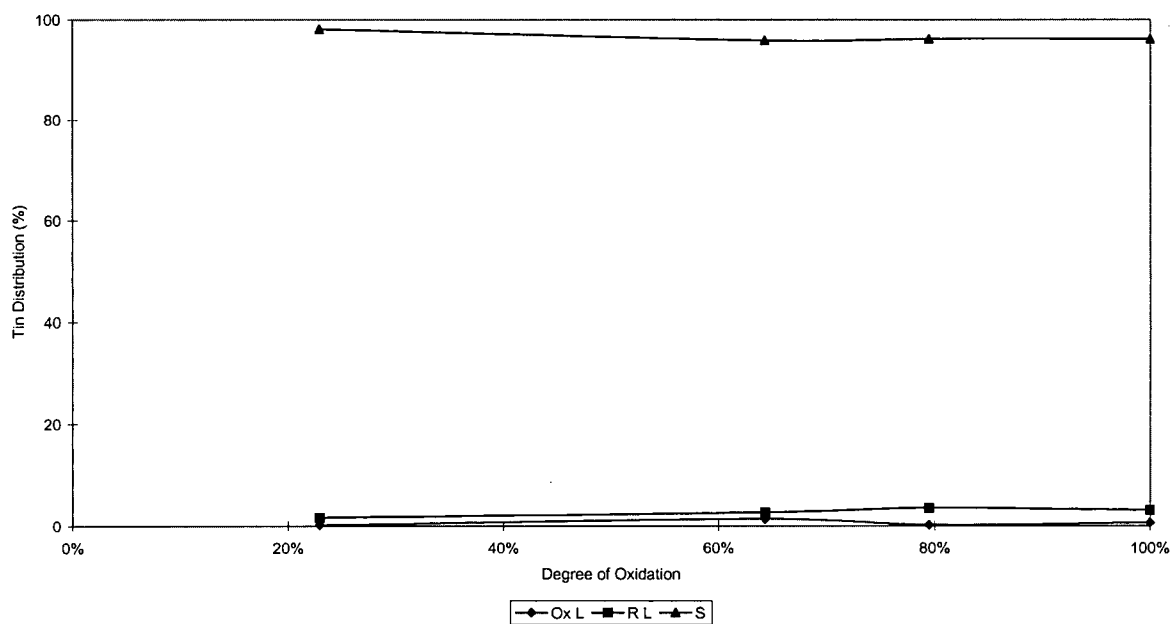


Figure 4.33 Tin distribution at different degrees of oxidation

## 4.6 Analysis of Selenium Species

Selenium is an element of particular interest at INCO CRED. It must be largely removed prior to electrowinning in order to prevent contamination of copper cathodes. In the second stage leaching process at CRED, it is believed that two principal forms of selenium exist (selenite and selenate). In order to understand better the behavior of selenium species, it is imperative to develop a feasible analytical method for selenium speciation.

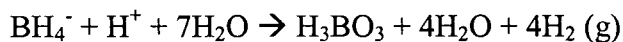
Initially ion chromatography was studied for Se analysis because of its fast and direct character. This method has been widely used in food, medical and environmental protection fields. But for the samples in this study with high concentrations of copper and sulfate, this method was verified as not suitable. The problem was that high concentration of  $\text{SO}_4^{2-}$  may shift and overlap Se peaks while copper and other cations may contaminate and foul the analytical columns used in the chromatograph. Finally, a method based on atomic fluorescence spectrometry with hydride generation (AFS-HG) was developed. This method was verified to be more useful and feasible than ion chromatography. During the course of this program INCO (the sponsor) reported an alternative method for analysis of selenium. These two methods were compared to detect selenium species on a suite of samples. The details of method development and application are presented below.

### 4.6.1 Introduction

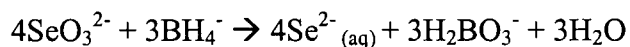
The sample solutions were pretreated with ion exchange resin (Rexyn 101, analytical grade,  $\text{H}^+$  form, Fisher Scientific) to remove metal ions that interfere with the results. After that, the samples were diluted into ~5 M HCl and stored in borosilicate glass bottles at 4 °C [39] for analysis.

Acidified sample solutions are treated with sodium borohydride ( $\text{NaBH}_4$ ) to generate hydrogen gas while Se(IV) is converted to  $\text{H}_2\text{Se}$ . This process includes three reactions:

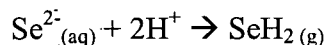
- (1) The decomposition of borohydride on acidification:



- (2) Sodium borohydride reduces selenite to the selenide ion:

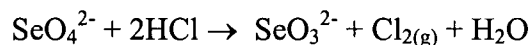


- (3) The volatile selenium hydride is generated:



The gas mixture passes through a hydrogen-air flame where  $\text{H}_2\text{Se}$  is converted into Se atoms. In the flame selenium atoms fluoresce and the signal intensity is proportional to the Se(IV) concentration in the sample. The procedure is automated by means of an Avalon control software.

Only Se(IV) is measured by this method. Se(VI) reacts far too slowly with borohydride at room temperature and hence is not determined. However the method can be adopted for Se(VI) by prereduction to Se(IV). The standard method for reduction of Se(VI) is digestion with high concentration HCl at elevated temperature (near boiling condition). This converts Se(VI) to Se(IV) according to the following reaction:



Total selenium may then be determined as the sum of Se(IV) + Se(VI). It is assumed that no other forms of selenium exist in significant concentrations in solution. In inorganic sulfate systems this is generally valid.

Transition metals, particularly copper, nickel and cobalt, strongly interfere with the analysis of selenium [40]. Several mechanisms have been proposed. It has been suggested that these metals react with borohydride to precipitate very fine solids which act to catalytically decompose  $\text{H}_2\text{Se}$ . Thus it is necessary to take steps to minimize the interference. Again, various methods have been employed by others to counteract this interference. One of these is to use complexing agents. Dr. Yu-Wei Chen at Laurentian University has successfully used 1,10-phenanthroline to complex copper in analysis of Se by AFS-HG in environmental samples. In this work removal of transition metal cations using ion exchange resins was

selected. This was chosen for two reasons. First a wide range of metal ions can be removed while allowing anionic (and neutral) species to pass through the resin. Secondly, the copper concentrations in the samples of interest are typically very high, and complexation might be less practical in such instances.

#### **4.6.2 Verification of the AFS-HG method for Se(IV) and Se(VI) analysis**

##### **4.6.2.1 Sample Treatment**

Samples were first passed through cation exchange resin. Rexyn 101, analytical grade, H<sup>+</sup> form (Fisher Scientific) was used as supplied. The volume of resin required depends in large part on the total concentration of positive charge in the sample. The specified ion exchange capacity is 1.9 meq/mL. The volume of sample used must contain <9.5 meq of positive charge. Five millilitre portions of resin were packed in water in glass columns equipped with Teflon stopcocks. Glass wool was used to support the resin bed. Samples containing metal ions at concentrations similar to those in leach solutions (~40 g/L Cu<sup>+2</sup> + lower concentrations of other transition metal ions) were diluted 10 times and typically 2.00 mL aliquots were used. Larger volumes were used for more dilute samples. The sample was allowed to flow through the resin and the column was then washed with ~30 mL deionized water in three portions. The flow rates were about 0.2 mL/min. The solution exiting the column was collected into a 100 mL volumetric flask containing 20 mL of water and 20 mL of concentrated HCl (Trace metal grade, Fisher Scientific). After the wash a further 20 mL of concentrated HCl was added. The solution was diluted to the mark with deionized water. The total dilution factor then was 500. Samples were stored in borosilicate glass containers that had been cleaned using 1+1 nitric acid. A selenium standard solution initially containing 40 g/L Cu<sup>+2</sup> and lower concentrations of Ni<sup>+2</sup>, Co<sup>+2</sup> and Fe<sup>+2</sup> (pH ~2) was analyzed for copper after the cation exchange treatment. No copper was detected by atomic absorption spectrometry (<0.04 mg/L). Diluted samples were stored in a refrigerator at ~4°C.

##### **4.6.2.2 Se(IV) Analysis**

The AFS-HG instrument measures Se(IV) by peak height. It was calibrated with solutions of Se(IV) using a 1000 mg/L standard (Fisher Scientific) prepared in 4.8 M HCl. Standards

ranged from 0 to 200  $\mu\text{g/L}$ . The calibration was found to be slightly curved and fitted well to a quadratic equation. Comparison with the calibration provides a direct measure of the Se(IV) concentration. The instrument is reportedly capable of quantifying as little as 2 ppt Se. However, to date recoveries of selenium from the cation exchange treatment in this work have been verified down to low ppb levels and not ppt concentrations. The maximum concentration the instrument can analyze is about 200 ppb. A standard was checked periodically to ensure that the instrument was stable. Where standard solutions containing no added metal ions were analyzed the cation exchange pretreatment was omitted.

#### 4.6.2.3 Se(VI) Analysis

Standard solutions of Se(VI) were prepared from  $\text{Na}_2\text{SeO}_4 \cdot 10\text{H}_2\text{O}$  (99.999%, Sigma-Aldrich). The salt was dried in an oven at  $\sim 105^\circ\text{C}$  for 3 hr to drive off excess water. A stock solution containing 1000 mg/L Se(VI) was prepared. The pH was adjusted to  $\sim 2$  with HCl. A 50.00 mL sample of the cation exchange-treated sample was added to a 100 mL round bottom flask equipped with a ground glass joint. A water-cooled Allihn condenser was attached and capped with a rubber stopper. After passage through the resin and dilution the sample contained about 4.8 M of HCl. The flask was heated with a boiling water bath for 45 minutes. While the vessel was heating the stopper atop the condenser was periodically removed for a moment to allow pressure equalization. The vessel was then cooled to room temperature. The interior of the condenser was washed twice with a minimum of deionized water. The solution was then transferred quantitatively to a 100 mL volumetric flask. Enough HCl was added to make up the final solution to about 4.8 M. Samples were analyzed using the calibration obtained with the Se(IV) standards. Where standard solutions containing no added metal ions were analyzed the cation exchange treatment was omitted.

The method submitted by PSA Ltd. (P S Analytical Ltd., Kent, England) describes the procedure of conversion of Se(VI) to Se(IV). It applies an open beaker containing Se(VI) sample with hydrochloride acid ( $\sim 4.8\text{M}$ ), heats the solution to boiling state for 30 minutes. But, this procedure may cause selenium loss (Se-Cl volatile species may be produced). This has been verified by experiments in this work.

#### 4.6.2.4 Testing of the Method

Six tests were done to verify the method.

1. A solution with 20.0 mg/L Se(IV) and 20.0 mg/L Se(VI) was prepared using the stock solutions. The pH adjusted to ~2 using HCl. This solution was diluted by 500 times. The expected final concentrations were 40.0 ppb each of Se(IV) and Se(VI).
2. The stock solution was diluted 200 times and then 20.0 ml of the diluted solution was transferred to a 100 mL round bottom flask. It was treated with 13 mL of concentrated HCl. The solution was digested at 100°C as described above. The solution was transferred to a 100 ml volumetric flask, treated with HCl to obtain a concentration of 4.8 M and diluted with water. The total dilution factor was 1000. The final expected total selenium concentration was 40.0 ppb, all as Se(IV).
3. A 20.0 mg/L Se(VI) solution was prepared using the stock solution with metals added ( $\text{Cu}^{+2}$  50 g/L,  $\text{Ni}^{+2}$  3 g/L,  $\text{Co}^{+2}$  3 g/L and  $\text{Fe}^{+3}$  0.15 g/L), and the pH was adjusted to <2 using HCl. The solution was first diluted by 10 times, and then 2.00 ml of the diluted sample was run through 5 ml of cation exchange resin as outlined above. The final volume was 100.0 mL. The total dilution factor was 500. The Se(VI) concentration was 40.0 ppb. No Se(IV) was expected to be present in the final sample.
4. A 50.00 mL sample of the final solution from 3 above was digested to convert Se(VI) to Se(IV) as outlined previously. The final volume was 100.0 mL (dilution factor:1000). The expected Se(IV) concentration was 20.0 ppb.
5. A solution of 20.0 mg/L Se(VI) and 20.0 mg/L Se(IV) was prepared with metals added as per 3. The pH adjusted to ~2 using HCl. The solution was first diluted by 10 times, and then 2.00 ml of the diluted sample was run through 5ml of cation as above. The effluent was collected in a 100 ml volumetric flask. The total extent of dilution was 500 times. The expected Se(IV) and Se(VI) concentrations were 40.0 ppb each.
6. A 50.00 ml aliquot of the final solution from 5 above was digested as described before. The final volume was 100.0 ml. The total dilution factor was 1000 times. The expected Se(IV) concentration was 40.0 ppb.

The calibration data is shown in Figure 4.34. Expected concentrations of Se(IV) and Se(VI) before and after treatment of samples are shown in Table 4.3. The results of analysis for selenium are shown in Table 4.4.

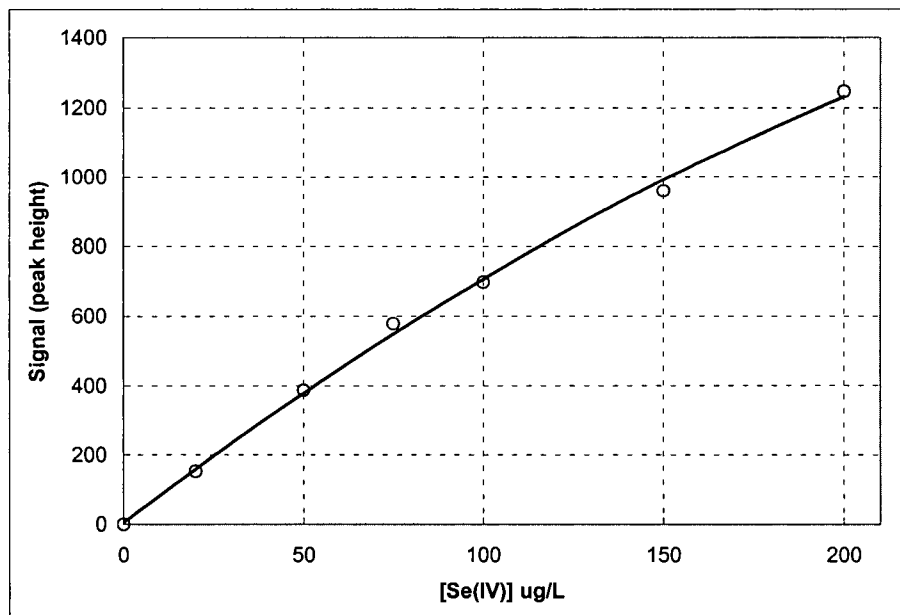


Figure 4.34. Se(IV) calibration curve

Table 4.3 Summary of expected concentrations of standard selenium solutions before and after treatment. (All samples were diluted into 4.8 M HCl.)

No.	Sample Description	Treatment Procedure	Initial Se mg/L		After treatment ppb	
			Se(IV)	Se(VI)	Se(IV)	Se(VI)
1	Se(VI)+Se(IV)	None	20.0	20.0	40.0	40.0
2	Se(VI)+Se(IV)	Digested	20.0	20.0	40.0	0
3	Se(VI)+metals	Ion exchange	0	20.0	0	40.0
4	Se(VI)+metals	Ion exchange + digestion	0	20.0	20.0	0
5	Se(VI)+Se(IV)+metals	Ion exchange	20.0	20.0	40.0	40.0
6	Se(VI)+Se(IV)+metals	Ion exchange + digestion	20.0	20.0	40.0	0



Table 4.4 Analysis of selenium in standard solutions with and without metals.

No.	Diluted sample		Undiluted sample						
	Se(IV) ppb		Se(IV) mg/L		Total Se mg/L Analyzed	Se(VI) mg/L		Deviation %	
	Analyzed	Expected	Analyzed	Expected		Analyzed	Expected	Se(IV)	Se(VI)
1	39.6	40.0	19.8	20.0				-1.1	
2	40.9	40.0			40.9	21.1	20.0		5.5
3	0.54	0	0.27	0				n/a	
4	19.6	20.0			19.6	19.3	20.0		-3.4
5	40.4	40.0	20.2	20.0				0.9	
6	40.5	40.0			40.5	20.4	20.0		1.8

The results generally showed excellent agreement with the anticipated values. The result for test 3 showed a small amount of Se(IV) where none was expected. The signal ( $\sim 8.6$  units) was well above the blank value of  $\sim 0.2$ - $0.4$  units. Whether this was due to contamination, decomposition of Se(VI) or other factors is not known at this time. The value was small and only about 1% of the total selenium originally present. The manufacturer of the instrument indicates that the standard deviation ( $\sigma$ ) for the analysis is  $\pm 5\%$ . The results obtained were well within  $2\sigma$ . The method therefore appears to be quite reliable. Cation exchange effectively mitigates interference from common transition metal cations while allowing for good recovery of selenium, and the digestion method is reliable.

#### 4.6.3 Analysis of INCO-CRED samples

##### 4.6.3.1 Samples of INCO-CRED

On May 31, 2004 seven samples were taken at INCO's CRED plant to follow the selenium concentrations from the second stage leach product hold tank through to electrowinning (Table 4.5).

Table 4.5 Sampling for selenium analysis at INCO's CRED plant on May 31, 2004.

Sample No.	Sample Name	Time Obtained
#1	2nd stage Product Hold Tank	11:10 am
#2	Cu Shot Tower Inlet (Filter Press Filtrate)	11:20 am
#3	Cu Shot Tower Outlet	11:23 am
#4	Spent Electrolyte	11:05 am
#5	Aging Tower No. 1	11:25 - 11:45 am
#6	Aging Tower No. 2	11:25 - 11:45 am
#7	Aging Tower No. 4	11:25 - 11:45 am

The samples were diluted with de-ionized water by a factor of 10/3 using graduated cylinders. This was done to minimize precipitation of solutions which contained high concentrations of copper sulfate. Then the diluted samples were split in two and sent to INCO Technology Services Limited (INCO's ITSL) in Mississauga and by air to University of British Columbia (UBC).

#### 4.6.3.2 Results of analysis

The samples were analyzed by INCO-ITSL and in this work. A sub sample of each CRED sample was also sent out for an ICP analysis using mass spectrometry detection by ALS Environmental (Vancouver, B.C.). The results are shown in Table 4.6.

Table 4.6 Results of compositions of May 31 CRED samples by INCO, UBC and ALS  
(adjusted for dilution)

Sample Name	INCO analyses			UBC analyses			ICP *	INCO analyses						
	Se mg/L	Se(IV) mg/L	Se(VI) mg/L	Se total mg/L <sup>1</sup>	Se(IV) mg/L	Se(VI) mg/L	Se total mg/L	H <sub>2</sub> SO <sub>4</sub> g/L	Cu g/L	Ni g/L	Co g/L	Fe g/L	Fe(II) g/L	S g/L
1. Filtered Product Hold	17.8	13.3	3.3	19.0	11.1	7.9	16.0	72.7	93	30.8	31.7	1.6	<0.6	83
2. Filter Press Filtrate	33.7	33.3	3.3	36.8	33.9	2.9	32.7	137	115	16.5	18.7	13.0	5.0	133
3. Cu Shot Tower	4.0	<3	<3	3.2	0.3	2.9	<7	144	126	17.3	19.3	14.0	13.3	140
4. Spent Electrolyte	1.2	<3	<3	0.6	0.3	0.3	<7	215	53	16.3	18.0	12.6	6.3	129
5. Aging Tower #1	2.4	<3	<3	1.9	0.1	1.8	<7	140	121	17.2	19.2	13.7	13.3	139
6. Aging Tower #2	1.9	<3	<3	1.3	0.1	1.2	<7	146	114	16.8	18.8	13.0	13.3	135
7. Aging Tower #4	1.8	<3	<3	0.5	0.1	0.4	<7	147	114	16.9	18.7	13.1	12.7	135
<sup>1</sup> Se(VI) taken to be total Se - Se(IV) <sup>2</sup> ALS = ALS Environmental, Vancouver, B.C.														
Sample Name	INCO Analyses													
	As g/L	Te mg/L	Ca mg/L	Al mg/L	Mg mg/L	Si mg/L	Pb mg/L	Zn mg/L	Mn mg/L	Cr mg/L	Ag mg/L	Bi mg/L	Sb mg/L	Sn mg/L
1. Filtered Product Hold	0.09	9.9	263	15.9	41.3	41.7	<15	31.0	8.6	<3	0.9	3.6	13.2	3.0
2. Filter Press Filtrate	4.6	142	220	13.4	33.2	29.5	33.7	19.3	5.2	<3	0.8	322	131	47.3
3. Cu Shot Tower	4.8	4.7	226	13.9	33.7	30.1	26.1	20.9	5.5	3.5	<0.03	299	121	7.3
4. Spent Electrolyte	4.6	9.6	250	18.0	37.3	29.0	24.2	18.4	5.2	<3	0.1	264	137	22.7
5. Aging Tower #1	4.8	1.3	225	12.9	33.0	30.3	26.2	21.2	5.4	<3	<0.03	298	119	2.7
6. Aging Tower #2	4.7	1.2	220	14.5	32.4	29.3	25.5	19.6	5.2	<3	<0.03	302	120	2.0
7. Aging Tower #4	4.7	1.0	221	12.1	32.2	28.4	25.6	19.7	5.2	<3	<0.03	287	127	2.7

The agreement for samples where there were substantial concentrations of selenium is quite good between the two methods of INCO and UBC. The AFS-HG (UBC) analyses are more sensitive than INCO or ALS analyses and UBC analyses show that selenite ( $\text{Se}^{4+}$ ) can be reduced and precipitated more rapidly than selenate ( $\text{Se}^{6+}$ ) in the copper shot and aging towers. The concentrations of selenate decrease gradually from aging tower #1 to #4, while selenite concentration reaches 0.1 mg/L in aging tower #1.

Figure 4.35 shows the total Se results by INCO and UBC. Figure 4.36 and Figure 4.37 present Se(IV) and Se(VI) results, respectively.

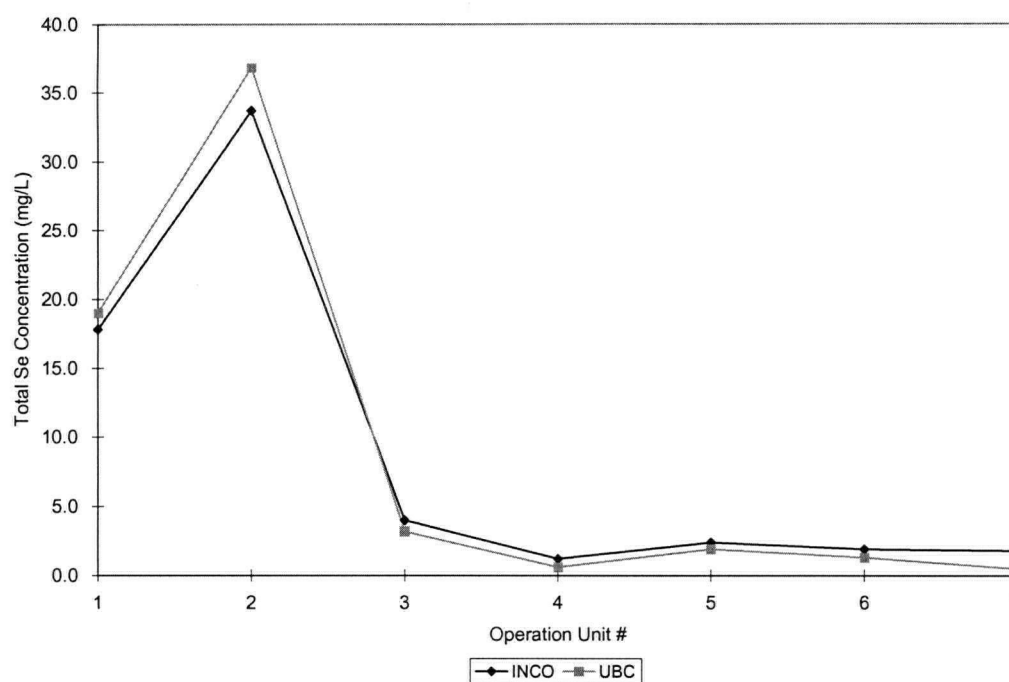


Figure 4.35 Analytical results of Se(total) concentration by INCO and in this work

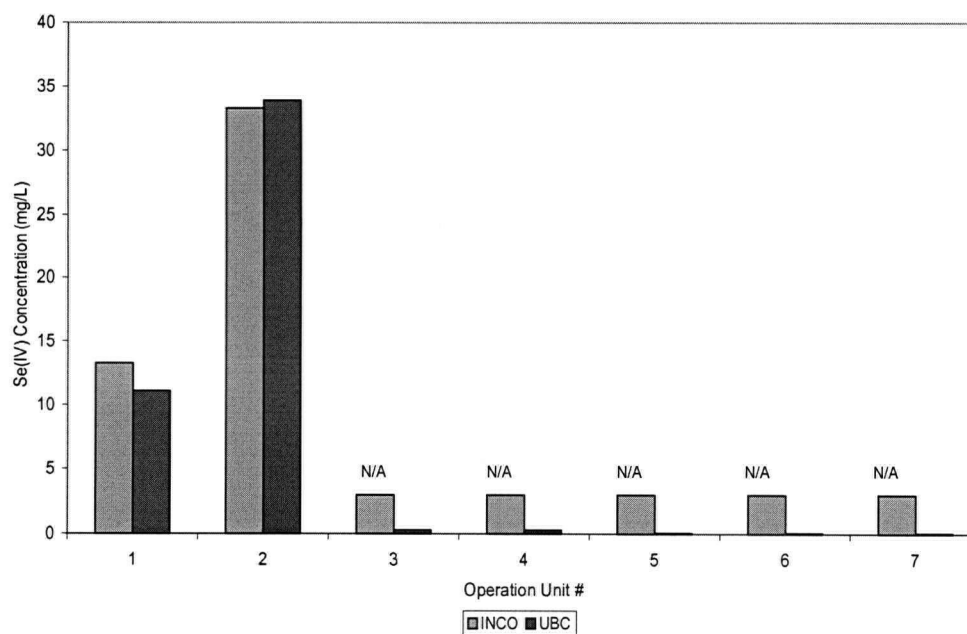


Figure 4.36 Analytical results of Se(IV) by INCO and in this work

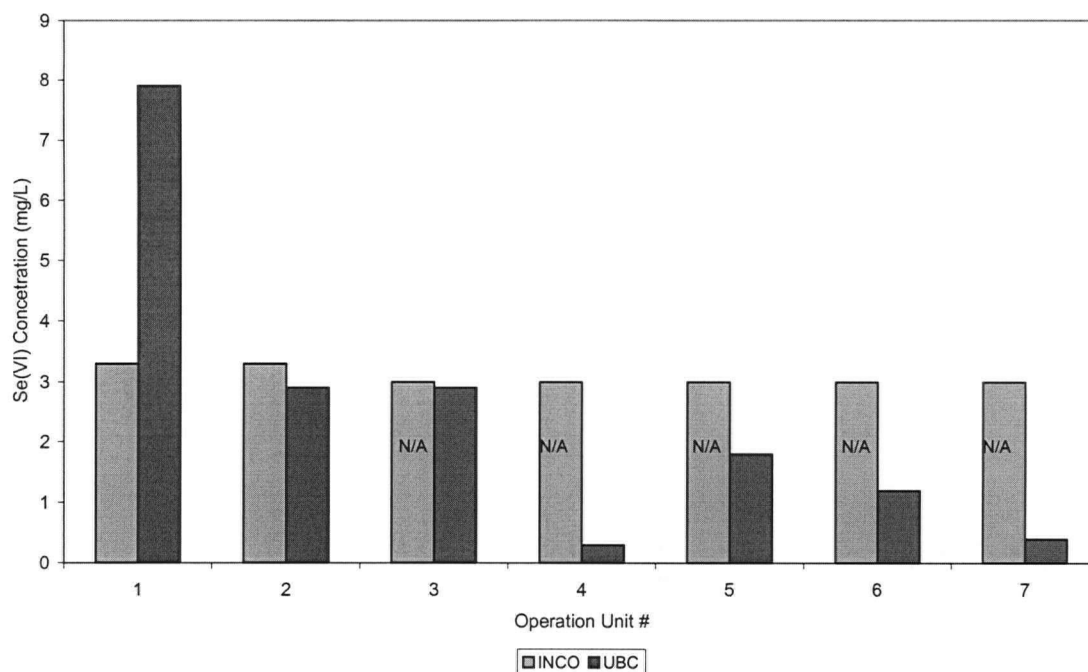


Figure 4.37 Analytical results of Se(VI) by INCO and UBC

In the case of the product hold tank sample (#1) there is a significant difference between the Se(VI) results for the two methods. Our analysis (Table 4.6) indicated 7.9 mg/L, while ITSL's value was 3.3 mg/L. The total selenium numbers, however, were quite similar (ITSL: 17.8 mg/L, UBC 19.0 mg/L). The samples were older by the time we analyzed them, so one might expect a lower Se(VI) value with time. The AFS-HG method may have an advantage of higher sensitivity. The final four samples (from the copper shot tower on) indicated very low levels of selenium by the AFS-HG method ( $<2$  mg/L). The instrument has several gain ranges from 1 to 1000. Analysis of low concentration samples may be readily performed at higher sensitivity settings with suitable standards. However, we have yet to verify quantitative recovery of selenium from the ion exchange treatment step for very low concentrations. In any event, our results corroborate those of ITSL that in the latter four samples selenium concentrations were very low ( $<3$  mg/L).

Analysis of total selenium using ICP-MS by ALS showed that the first two samples in the tables the results accord well with the total selenium analyses by both ITSL and UBC.

Unfortunately the extent of dilution employed by the commercial lab resulted in poor detection limits ( $>7$  mg/L).

#### 4.6.4 Analytical results in the laboratory work

Selenium speciation of the laboratory experiments was also determined. First, Ion Chromatography was applied to analyze Se species in solutions of experiments. But the concentrations of sulfate and copper were so high that selenium peaks were overlapped by the sulfate peak and the column was contaminated by copper and other cations very soon. Therefore, the reference of the sulfate and cations were the main problem in the analysis. Later, the method of Atomic Fluorescence Spectrometry with Hydride Generation (AFS-HG) was developed and resolved the problem of sulfate reference; ion-exchange technique removed copper ion and other cations efficiently. This analytical method for Se species was proved successful for samples at CRED.

For the laboratory study, a representative experiment was analyzed using AFS-HG method. The experimental conditions are shown below:

Oxidative Pressure Leaching (OxL) – 1<sup>st</sup> stage cake: 510 g (dry basis)

Total pressure: 150 psig.

Leaching temperature: 115°C

Spent Electrolyte Composition – 40 g/L  $\text{Cu}^{2+}$ , 200 g/L  $\text{H}_2\text{SO}_4$ , 5 g/L  $\text{Fe}^{2+}$ , 2 g/L As, 300 ppm Bi, 10 ppm Pb, 50 ppm Sb, 3 ppm Sn.

Releaching conditions (RL) -- pH  $\sim 0.5$ , Leach time: 3 hrs

These conditions were similar to practical operation at CRED plant. Figure 4.38 and 4.39 show the results for Se species in the laboratory work.

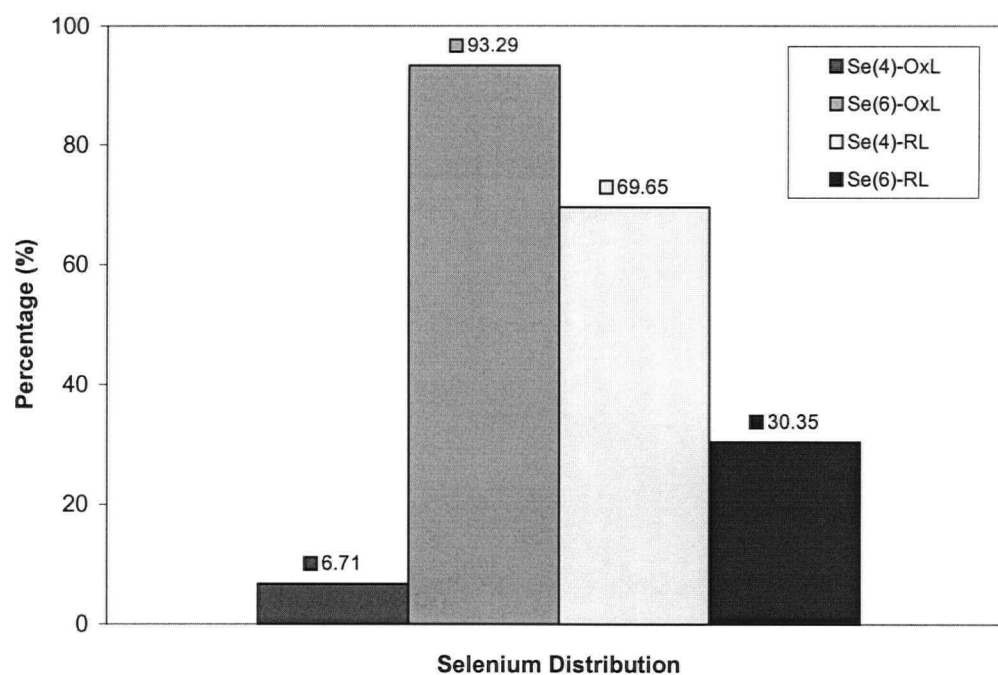


Figure 4.38 Se distribution in oxidative pressure leaching and releaching processes

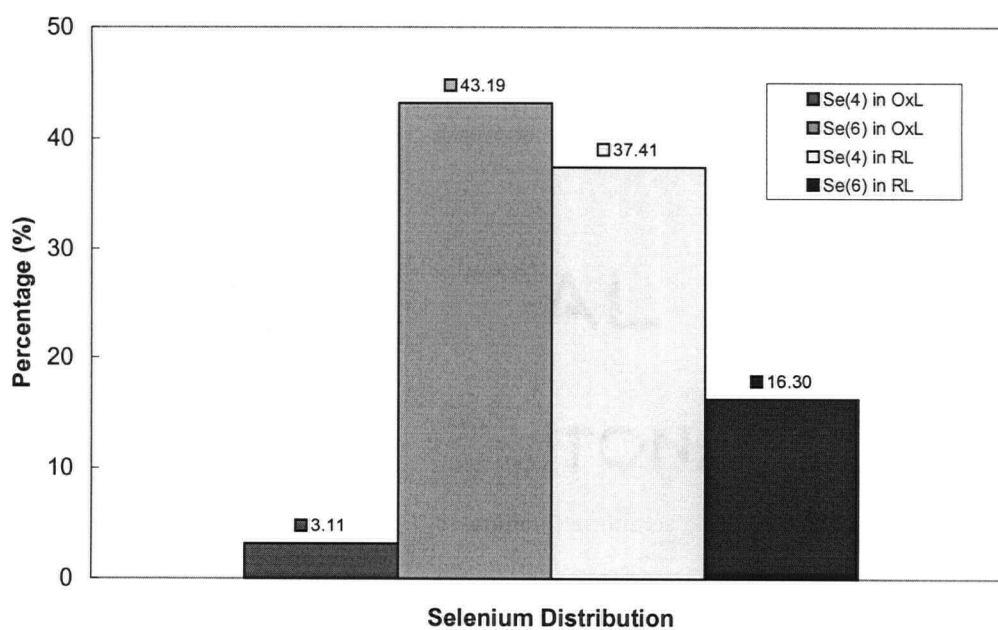


Figure 4.39 Se distribution in the second stage leaching

From Figure 4.38, it can be seen that 93.29 % of selenium occur as the form of selenate ( $\text{Se}^{\text{VI}}$ ) in the filtrate after oxidative pressure leaching, whereas in the leaching filtrate 30.35% of selenium appears as selenate. Considering the distribution of selenium in the leaching process (46.30% of Se in oxidative pressure leaching filtrate and 53.70% of Se retaining in the releaching filtrate), we can have a rough outline about Se species distribution during the second stage leaching process. Selenate ( $\text{Se}^{\text{VI}}$ ) accounts for 43.19% in oxidative pressure leaching filtrate and 16.30% in releaching filtrate, respectively. Selenite ( $\text{Se}^{\text{IV}}$ ) accounts for 3.11% in oxidative pressure leaching filtrate and 37.41% in releaching filtrate, respectively. Detailed analytical results are shown as Appendix B.



## 4.7 Summary

### Part I – The impact of variables on minor element behavior:

1. With the increase in Cu/Acid ratios, there are no distinctive effects on the distribution of minor elements during the leaching process.
2. Cu/S ratios had little effect on the distribution of minor elements except for Se and Te. With increase in the Cu/S ratios, more Se and Te were left in the final unleached solids, while the distribution of Se and Te is fairly stable in the pressure leaching solution.
3. Some impurities (As, Bi and Fe) may exhibit distinct effects on the distribution of some elements; other impurities (Pb, Sb and Sn) have almost no discernable effects on the distribution of minor elements.
4. The degree of oxidation may result in distribution changes of some elements (e.g. Cu, Se and Te).

### Part II - Analysis of selenium species:

1. The AFS-HG method of analysis for Se(IV) and total selenium was verified as reliable and highly sensitive.
2. The AFS-HG method necessarily involves transition metal cations removal where their concentrations are significant. This also results in dilution of the sample.
3. The AFS-HG method with cation exchange pretreatment appears to offer a suitable alternative method for analysis and speciation of selenium in metallurgical process solutions.
4. Results of INCO-ITSL internal analyses and the ion exchange AFS-HG method used in this study were generally in good agreement.

## CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

### 5.1 Conclusions

This study investigated the effects of some important factors on the behavior of minor elements during the second stage leaching process at INCO CRED. A practical, reliable and sensitive analytical method was also developed for Se speciation in strong electrolyte.

#### 1) Minor element behavior

In this study four important variables were investigated, including Cu/Acid ratio, Cu/S ratio, level of impurities and extent of oxidation.

In the Cu/Acid series of experiments, with change of Cu/acid (molar basis) ratios, there was no significant change in the distribution of minor elements in three parts of the second stage leaching process at CRED. However, the "slow cook" was encountered with higher Cu/acid ratios ( $>3$ ), which require extended leach times for full oxidation.

With changes of Cu/S ratios (wt./wt.), the distribution of selenium and tellurium exhibit obvious changes. Other minor element behavior was similar to that in the Cu/Acid ratio series of experiments. During the second stage leaching, it is believed that selenium and tellurium could form copper selenides/tellurides or other complex precipitates with copper. Higher Cu/S ratios will result in more selenium and tellurium retained in the final residues. Therefore, when Cu/S ratios rise from 3.8 to 4.4, especially above 4.2, the distribution of selenium and tellurium in the final unleached residue increase from 26% to 48% and from 11% to 64%, respectively.

In this study effects of six impurities normally existing in the spent electrolyte on the behavior of minor elements were studied. The results show that some impurities, such as As, Bi and Fe, may have distinct effects on the distribution of minor elements within their fluctuating ranges. Other impurities, such as Pb, Sb and Sn, have very low concentrations and little effect on the distribution of minor elements.

Oxygen is crucial during the oxidative pressure leaching process. The most distinct influence of deficient oxidation during pressure leaching is that the copper extraction decreases dramatically, which results in the distribution changes of selenium and tellurium. Since it is possible for selenium and tellurium to form some complex precipitates with Cu, when the distribution of copper changes, selenium and tellurium may change with copper.

## 2) Se analysis

High levels of sulfate limit the application of ion chromatography. When Se was determined by AFS-HG, transition metals such as  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$  and so on, may interfere strongly. Therefore cation exchange resin (Rexyn 101, analytical grade,  $\text{H}^+$  form (Fisher Scientific)) was used to pretreat solution samples to remove cupric and other cations. The analytical results of CRED process solutions by INCO-ITSL and in this work were generally in good agreement.

AFS-HG method has proved to be a successful method for analysis of selenium species.

## 5.2 Recommendations for further work

Further works need to focus on the following aspects:

1. The leaching process should imitate industrial operation thoroughly. For example, at CRED, basic copper sulfate is not separated from copper sulfate solution after pressure leaching. However, in this study, a pressure filter was used to separate basic copper sulfate from copper sulfate solution and crystallization of copper sulfate was unavoidable, which may affect minor element behavior.
2. Alternative methods (besides XRD and SEM) should be applied to identify species formed in the leaching process. These species can give full understanding for minor element behavior.
3. For selenium analysis, laborious steps of sample treatment could be automated. Sample handling and treatment issues for this method should to be properly investigated. Further testing would be required to verify that the method is suitable for very low ppb of Se(IV) in the sample.

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## **Appendix A – P S Analytical Method for Se Species**

### **P S Analytical**

#### **Millennium Excalibur Method for Selenium in Drinking, Surface, Ground, Saline and Industrial & Domestic Waste Waters**

##### **1. Principle**

- 1.1 Acidified sample solutions are treated with sodium terahydroborate to generate the covalent gaseous hydride (selenium hydride). The hydride and excess hydrogen are swept out of the generation vessel using a stream of argon, into a chemical generated hydrogen diffusion flame. The hydrides are atomized and the resulting atoms detected by atomic fluorescence spectrometry [1]. The procedure is automated by means of an autosampler and Avalon windows control software.

##### **2. Performance Characteristics**

- 2.1 The linear dynamic range of this method is approximately 2 ppb to 100 ppb when using the continuous flow approach. Samples containing selenium at concentrations higher than the dynamic range may be analysed following appropriate dilution of the sample. The linear dynamic range may be extended to 10 mg/L when a discrete sample injection approach is used.
- 2.2 The method detection limit (MDL) may be dependant on the selected operating conditions and calibration range. With high purity reagents a MDL of less than 2 ppb is obtainable.
- 2.3 The sensitivity of this method is dependant on the selected operating conditions. On maximum amplification each fluorescence arbitrary unit is equivalent to approximately 0.2 ng/L.
- 2.4 It is important to use high purity reagents in all cases. The concentration blank value should be less than 0.2 µg/L selenium.



- 2.5 The relative standard deviation is typically less than 5% for concentrations greater than twenty times the method detection limit (MDL).

### **3 Interferences**

- 3.1 The hydride generation technique is prone to interferences by transition metals. For the majority of natural samples, this type of interference should not be significant. The user should carry out recovery tests on typical waters and also determine the maximum concentrations of transition metals.
- 3.2 Inorganic selenium normally occurs in two oxidation states: Se(IV) and Se(VI). It is essential to convert all selenium species to the Se(IV) state prior to generating the hydrides. Selenium(VI) does not form the hydride.
- 3.3 Naturally occurring selenium compounds do not react with sodium tetrahydroborate. The organic forms of selenium are unlikely to be present in significant amounts in portable waters and most rivers.

### **4 Hazards**

- 4.1 Each chemical reagent used in this method should be regarded as a potential health hazard and exposure to these reagents should be as low as possible. Each laboratory is responsible for maintaining a current awareness file regarding the safe handling of the chemicals specified in this method. A reference file of material data handling sheets should also be available to all personnel involved in the analysis.
- 4.2 Sodium tetrahydroborate is very toxic. NEVER handle the solid material.
- 4.3 ALWAYS dispose of any excess sodium tetrahydroborate by carefully pouring the diluted solution into a copious stream of running water in a clean sink in a fume cupboard.
- 4.4 Keep sodium tetrahydroborate (solid or solution) away from all other chemicals. It reacts violently with acid, liberating hydrogen and also reacts with many substances to form highly toxic gases.
- 4.5 ALWAYS use argon in the hydride generation apparatus. If air is used then a violent explosion will occur.

- 4.6 The acidification or processing of samples containing reactive materials may result in the release of toxic gases such as cyanides or sulphides. Processing of all samples should be carried out in a fume hood.
- 4.7 NEVER directly view the boosted discharge hollow cathode lamp – this lamp emits intense UV radiation.

## 5 **Reagents and Standards**

Reagents may contain selenium as an impurity. Ultra-pure reagents must be used at all times.

### R5.1 Water

For all sample preparations and dilutions distilled or de-ionised water is required.

### R5.2 Hydrochloric acid (35 – 37 %) HCl

High purity hydrochloric acid should be used. Selenium is sometimes found in hydrochloric acid and can be up to 10 µg/L even in high purity acids.

### R5.3 0.7 % m/v sodium tetrahydroborate (NaBH<sub>4</sub>) in 0.1 mol/L sodium hydroxide (NaOH)

Dissolve 7.0 g sodium tetrahydroborate (NaBH<sub>4</sub>) in 500 ml water and add 4.0 g sodium hydroxide. Dilute to 1000 ml with water. Filter the solution through a 0.45 µm membrane before use. Prepare freshly each day and do not keep in a closed container because of pressure build-up due to hydrogen evolution.

### R5.4 Reagent Blank

For each 1000 ml, prepare a solution containing 400 ml concentrated hydrochloric acid (R5.2). Dilute to volume with water.

**Note:** On the continuous flow system, the reagent blank solution is run as background for automatic blank subtraction. This solution may contain trace levels of detectable amounts of selenium. It is important that the same reagents are used for sample and standard preparation and for preparation of the reagent blank.

### R5.5 Standard Selenium Solutions

#### R5.5.1 Solution A – 1000 mg/L Se(IV)

A commercial quantitative standard solution is suitable. This solution is stable for at least six months.

#### R5.5.2 Solution B – 10 mg/L Se(IV)

Dilute 1 ml of solution A with approximately 20 ml of water. Add 40 ml concentrated hydrochloric acid (R5.2). Dilute to 100 ml with water. Prepare weekly.

#### R5.5.3 Calibration Standards

Prepare a minimum of four selenium (IV) calibration standards spanning the concentration range of interest by serial dilution of stock solution B. Each calibration standard should contain 40 ml concentrated hydrochloric acid (R5.2) per 100 ml in borosilicate volumetric flasks. Prepare daily.

**Note:** The reagent blank solution is identical to the standard blank solution.

#### R5.5.4 Selenium (VI) Standard Solution 1000 mg/L

Dissolve 1.197 g of sodium selenate dried at 105°C for 2 hours in 200 ml of water containing 150 ml concentrated hydrochloric acid (R5.2). Dilute to 500 ml in a volumetric flask with water. This standard should be used to prepare a suitable selenium (VI) standard (as per section R5.5.3) to check quantitative recovery of selenium (VI). This solution is stable for at least six months.

### 6. Apparatus and Instrumentation

#### 6.1 Atomic Fluorescence System – Millennium Excalibur PSA 10.055.

A schematic diagram of the automated selenium analysis system is shown in figure 1. This consists of an autosampler, an integrated continuous flow vapour generator and atomic fluorescence spectrometer and a control computer.

#### 6.2 An argon gas supply (high purity grade 99.99%, with two stage regulator).

#### 6.3 Labware.

For the determination of selenium at very low concentrations, contamination and loss are of critical consideration. Potential contamination sources include improperly cleaned

laboratory apparatus and general contamination within the laboratory environment. A clean laboratory work area, designed for trace element sample handling must be used. All re-usable labware in contact with the sample should be cleaned prior to use. Labware should be soaked in (1+1) nitric acid for at least twenty four hours and rinsed three times with water. Following this, refill labware with 5% hydrochloric acid and leave for twenty four hours. Disposable (single-use) plastic labware does not require special cleaning provided that negligible selenium contamination in that material is demonstrated.

- 6.3.1 Storage/sample processing bottles – Narrow mouth bottles, PTFE. Borosilicate glass should be avoided for storage of samples since some glass can contain appreciable amounts of selenium.
- 6.3.2 Instrument reagent reservoir – 2 litre capacity and PTFE tubing for transfer of contents via peristaltic pump.
- 6.3.3 Autosampler vials- Polystyrene.
- 6.4 Sample Processing Equipment.
  - 6.4.1 Air displacement pipette – Micro-pipette system capable of delivering volumes from 10 to 1000µl with an assortment of metal-free, disposable pipette tips.
  - 6.4.2 Balances – Analytical balance, capable of accurately weighing to  $\pm 0.1$  mg; top-pan balance, accurate to  $\pm 0.1$  g.

## 7. **Sample Collection, Preservation and Storage**

- 7.1 For the determination of selenium in aqueous samples, acidify with high-purity hydrochloric acid at the time of collection. Normally, 2ml of (1+1) acid per 100 ml of sample is sufficient for most samples.

**Note:** The sample may also be preserved in 1% nitric acid, although hydrochloric acid is preferred.

## 8. **Sample Preparation Procedure**

- 8.1 Accurately transfer an aliquot of the sample (40-50 ml) to a 100 ml tared container. The sample may also be dispensed by weight. In this case calculate the volume from the density and the weight and record the volume.

**Note:** A 250 ml tall form beaker with watch glass is suitable.

- 8.2 Add 40 ml of concentrated hydrochloric acid (R5.2).
- 8.3 Boil the acidified sample solution gently for 30 minutes at 120°C. Allow to cool and dilute to 100 ml with water. This hydrochloric acid digestion ensures that selenium (VI) is quantitatively converted to selenium (IV).



**Note:** This digestion should be carried out in an open container to prevent chlorine back oxidation of selenium (IV) to selenium (VI).

## 9. Instrumental Set Up

- 9.1 The instrumentation should be configured as shown in figure 1 and described in the Millennium Excalibur user manual [2].
- 9.2 The continuous flow vapour generator consists of a peristaltic pump to deliver reductant, reagent blank and sample. A switching valve is used to alternate between the reagent blank and sample solutions. The analysis cycle has three stages.

**Delay Time** – Primes sample tubing for analysis. The sample is diverted to waste, whilst the blank goes to gas/liquid separator with sodium tetrahydroborate to establish baseline. Typical setting is 10 seconds.

**Analysis Time** – The switching valve is activated so that the sample is introduced to the gas/liquid separator with sodium tetrahydroborate. Meanwhile the blank is diverted back to the reagent bottle. The signal reaches steady state in approximately 20 secs and is held for a further 10 secs so that the peak height can be established (Total time = 30 secs).

**Memory Time** – Sample is diverted to waste and blank is diverted to separator to allow system to return to baseline. Typical setting is 40 seconds.

- 9.3 Replace tubing for reagents on a weekly basis or when changing the analyte to be determined. All tube distances between the autosampler, vapour generator and detector should be kept to minimum length.
- 9.4 Fill the reagent reservoirs with reagent blank (R5.4) and sodium tetrahydroborate solution (R5.3).

- 9.5 Turn on pump and ensure that all three lines (reductant, blank and sample) are pumping properly. Ratio of flow rates of reductant lines to blank/sample lines should be approximately 1:2. Typical flows are 4-5 ml min<sup>-1</sup> for sodium tetrahydroborate and 8-10 ml min<sup>-1</sup> for sample and blank solutions.
- 9.6 Turn on the argon carrier gas and air dryer gas. These are preset to flow rates of 300 ml min<sup>-1</sup> and 2.5 l min<sup>-1</sup> respectively.
- 9.7 Select the required amplification range for the atomic fluorescence detector. Four sensitivity ranges (1, 10, 100, 1000) may be selected using the Avalon software. The analyst must ensure that the selected detector range is appropriate to the sample concentration being determined. Typical conditions for each amplification range are given below.

For samples which are off scale for a given range setting, either re-analyse at a lower sensitivity or dilute a fresh undigested sample into the calibration range. If a digested sample is diluted then the diluent should be the reagent blank solution (R5.4)

Typical Performance Data for Selenium

Range	Concentration Range	Delay Time	Analysis Time	Memory Time
1	0 – 200 ppb	10	5	40
10	0 – 20 ppb	10	15	40
100	0 – 2 ppb	10	30	40
1000	0 – 100 ppt	10	30	40

**10. Standardization and Sample Analysis**

- 10.1 Establish instrument software run procedures for quantitative analysis.
- 10.2 Switch on the boosted discharge hollow cathode lamp. For selenium the primary and boost current settings are 20.0 and 25.0 mA respectively. Lamp warm up time is approximately 20 mins.

- 10.3 With the reagent blank and sodium tetrahydroborate flowing to the gas/liquid separator, ensure that the system is equilibrated and a steady stream of hydrogen is produced. Ignite the flame and allow 5 mins to stabilise.
- 10.4 Load the autosampler tray with standards, samples and blanks and start the autosampler programme. A minimum of two replicate data measurements should be taken for each sample and averaged for the data calculations.

## 11. Data Analysis and Calculations

- 11.1 The weight dilution factor of each sample should be applied. If additional dilutions were made to any samples, the appropriate factor should be applied to the calculated sample concentrations. Concentrations of samples where additional reagents were added to complete digestion or to preserve the sample should be corrected with the corresponding blank subtraction.
- 11.2 Quality control data obtained during the analysis provides an indication of the quality of the sample data. These should be provided with the sample results. Selenium (IV).

**Note:** Use concentration units of  $\text{ng l}^{-1}$  or  $\mu\text{g l}^{-1}$ . Choose units which will be appropriate for the calibration range.

## References

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## Appendix B – Analytical results in the laboratory work

Analytical results:

Section	Assay Value	Dilution Factor	[Se(IV)]	Total [Se]	[Se(VI)]	Soln. Vol.	Se Wt.	Se(IV)%	Se(VI)%
	ppb	X	ppm	ppm	ppm	L	mg	%	%
Filtrate	15.940	200	3.188	43.2	40.012	0.896	136.82	6.71	93.29
Wash Water	3.474	100	0.347	6.8	6.453	5.890			
Releaching	65.610	500	32.805	47.1	14.295	3.370	158.73	69.65	30.35

Total Se distribution in 2nd stage leaching:

Filtrate	Se in OxL 46.30%
Wash Water	
Releaching	Se in RL 53.70%

Se species distribution in 2nd stage leaching:

Se(IV) in OxL	3.11 %
Se(VI) in OxL	43.19 %
Se(IV) in RL	37.41 %
Se(VI) in RL	16.30 %

Note: OxL -- Oxidative Pressure Leaching  
 RL -- Releaching of basic copper sulfate