ANALYSIS OF THE FIRST-STAGE LEACH PROCESS

AT INCO LTD.'S COPPER REFINERY

by

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ABSTRACT

The INCO Ltd. Copper Refinery Electrowinning Department (CRED) in Copper Cliff, Ontario, processes a Cu, Ni, Co, Fe, As, S and precious metals containing residue produced by the INCO Pressure Carbonyl (IPC) plant. This residue is treated batchwise in two successive leaching stages. The non-oxidative First-Stage Leach (FSL) process extracts the vast majority of the Ni, Co, Fe and As values. The Second-Stage Leach (SSL) process comprises the aqueous pressure oxidation of a predominantly Cu_2S feed under acid-deficient conditions. The basic copper sulfate (BCS) precipitated in this stage is subsequently redissolved with spent electrolyte to separate the copper values from the final residue rich in precious and platinum group metals.

The present study is part of a joint INCO-UBC research effort aiming at the optimization of both leaching stages. The purpose of this project is to provide a better understanding of the first-stage chemistry in general and of the behavior of arsenic in particular, since elevated concentrations of this element are detrimental to the efficiency of the second-stage system.

The test work shows that the FSL process is insensitive to physicomechanical parameters such as agitation rate and pulp density, as long as the "solids off-bottom condition" is satisfied. In contrast, the effect of temperature and reactor residence time on impurity extraction is pronounced, especially in the case of arsenic. On the basis of thermodynamics and experimental observations made in the course of the investigations, a tentative reaction model is proposed to explain reprecipitation of this element (and nickel) under copper-depleted first-stage conditions.

The presence of organic electrowinning additives in solution does not influence the Ni, Co, Fe and As recoveries achieved in the first stage. The iron and, to a lesser extent, nickel extraction depend on the availability of acid in solution, whereas cobalt is leached principally by metathesis reactions. Two scenarios for the leaching of arsenic are postulated, yet neither one can be confirmed; the concentration of arsenic is either below the detection limit of the equipment (XRD) or is obscured by the presence of other elements (SEM).

Arsenic redissolution from a copper-depleted FSL batch cannot be accomplished by the introduction of pregnant copper electrolyte to the first-stage flash tank under the conditions of the laboratory simulation. In order to mitigate arsenic related second-stage leaching difficulties it is recommended that a potential probe be installed between the pressure let-down vessel and the filter feed tank. The on-line potential readings would allow timely changes in the make-up to avoid copper depletion of subsequent batches.

Simplified calculations have shown that the use of compressed air instead of "push steam" for discharging of first-stage reactors leads to an unacceptable increase in the copper level in solution.

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LIST OF ABBREVIATIONS

AAS   Ammoniacal Ammonium Sulfate
AMAX   American Metals ClimAX

BCL   Bamangwato Concession Limited
BCS   Basic Copper Sulfate
BNC   Basic Nickel Carbonate
B(Ni,Co)C   mixture of Basic NIckel and CObalt Carbonates

CCCR   Copper Cliff Copper Refinery
CCNR   Copper Cliff Nickel Refinery
CRED   Copper Refinery Electrowinning Department

D2EHPA   Di-2-Ethyl-Hexyl Phosphoric Acid
DSA   Dimensionally Stable Anode

EDX   Energy-Dispersive X-ray
EW   ElectroWinning

FCL   Falconbridge Chlorine Leach
FML   Falconbridge Matte Leach
FSL   First-Stage Leach

ICP   Inductively Coupled Plasma
INCO   The International Nickel COmpany of Canada
IPC   INCO Pressure Carbonyl
IPL   International Plasma Laboratory
IUPAC   International Union of Pure and Applied Chemistry
IX   Ion eXchange

JRGRL   J. Roy Gordon Research Laboratory

MPP   Matte Processing Plant

NBS	National Bureau of Standards
NRC	Nickel Refinery Convertor
O/F	OverFlow
ORP	Oxidation-Reduction Potential
PGM's	Platinum Group Metals
P(G)M's	mixture of Precious and Platinum Group Metals
PHT	Product Holding Tank
PM's	Precious Metals
RBMR	Rustenburg Base Metal Refiners
SCE	Saturated Calomel Electrode
SEM	Scanning Electron Microscopy
SHE	Standard Hydrogen Electrode
SLN	Société Le Nickel
SS	Stainless Steel
SSL	Second-Stage Leach
SX	Solvent eXtraction
TBP	Tri-Butyl Phosphate
TIOA	Tri-Iso-Octyl Amine
TOL	Total Oxidative Leach
UBC	The University of British Columbia
U/F	UnderFlow
UN	United Nations
USGS	United States Geological Survey
XRD	X-Ray Diffraction

ACKNOWLEDGMENTS

MOTTO

"Engineers are the pride of the nation"

DEDICATION

To my lovely wife Laurence

To my parents and my sister

CHAPTER 1

INTRODUCTION

The title of this thesis clearly shows both the company- and process-specific nature of its topic. In order to place the present investigations within the context of previous joint INCO-UBC research efforts, it is necessary to first review the metallurgical difficulties encountered in the two-stage leaching operation of INCO's Copper Refinery Electrowinning Department (CRED).

In the oxidative Second-Stage Leach (SSL) process practiced at the CRED plant of INCO's Copper Refinery at Copper Cliff, Ontario, the intermediate chalcocite (Cu_2S) residue from the metathetic First-Stage Leach (FSL) process is batch pressure leached under acid-deficient conditions to produce a high-strength copper electrolyte for electrowinning and a residue rich in precious and platinum group metals for further upgrading. The Cu_2S-containing residue is converted to covellite (CuS), $CuSO_4$, and the basic copper sulfate antlerite ($CuSO_4 \cdot 2Cu(OH)_2$) within 1 hour. Subsequently, CuS is oxidized to $CuSO_4$ in the presence of the basic copper sulfate (BCS) precipitate. This takes 4-5 hours for completion under normal circumstances, but may take as long as 20 hours under so-called "slow cook" conditions. Plant experience shows that 10-20% of the SSL batches require those throughput-limiting extended reactor residence times.

In recent years, several collaborative studies carried out by CRED personnel, research staff at INCO's J. Roy Gordon Research Laboratory (JRGRL), and faculty and students of UBC's Department of Metals and Materials Engineering, have focused on specific chemical and physicomechanical SSL process parameters in order to identify and mitigate the "slow cook" phenomena.

The earliest laboratory work [1,2] concentrated on the verification of a mathematical screening model for the prediction of the SSL reaction sequence under various operating conditions. The results indicated that chemically controlled kinetics cannot be responsible for the periodic upsets experienced in the CRED operation. A gas-liquid mass transfer rate controlling mechanism was proposed instead.

Subsequent research [3] established a link between the feed composition, the apparent slurry viscosity and the copper extraction rate. It became evident that long second-stage leaching conditions are chiefly associated with two types of troublesome feeds: the high-(Cu : S) feed and the high-arsenic feed.

The most recent investigations [4,5] elaborated on copper extractions achieved from BCS precipitated at different leaching temperatures and with different levels of arsenic in the batch. They have shown that careful temperature control is critical to the SSL process, especially when high-arsenic feeds are being leached.

High-(Cu : S) feeds to the CRED plant are caused by excessive sulfur removal prior to INCO's carbonylation process at the Nickel Refinery.

The *concentration of BCS* in the second-stage autoclave depends mainly on the feed solids content and on the (Cu : S)$_{total}$ ratio in second-stage batch make-up. The latter is obviously affected by both the feed Cu : S ratio and the quantity of sulfuric acid - as spent copper electrolyte - utilized.

Batches of high-(Cu : S) feeds can be leached more rapidly in the plant by increasing the acid content during second-stage batch make-up. This lowers the (Cu : S)$_{total}$ ratio, postpones the onset of BCS formation and reduces the final concentration of antlerite. Injection of acid into the autoclave at the beginning of CuS leaching has a similar effect: it lowers the pulp density by partially redissolving the BCS already present. Regardless of the mode of acid addition, the concentrations and viscosities of the BCS slurries decrease and the covellite leaching rates improve.

Unfortunately, the introduction of greater quantities of spent electrolyte to the batch by either method also promotes the undesirable formation of elemental sulfur. In addition, it increases the risk of crystallization of copper sulfate hydrates upon cooling of the SSL slurry during discharge. Furthermore, the addition of extra arsenic-containing spent copper electrolyte increases the amount of this unwanted element in the SSL system. Therefore, the only acceptable way to overcome the problems related to high-(Cu : S) feeds is to operate the SSL process at a lower pulp density, which ultimately limits the capacity of the leaching plant.

Sources of high-arsenic feeds are either residues produced under copper-deficient FSL conditions, or incompletely leached FSL residues. Copper depletion, of course, results in a change in the redox potential of the FSL system, causing reprecipitation of any dissolved arsenic, presumably as a base metal arsenide or arsenic sulfide.

The *morphology of BCS* precipitated from high-arsenic feeds and common feeds is markedly dissimilar. Relatively large, compact, well-defined platelets are formed under normal circumstances. Clusters of small, irregularly shaped or submicron acicular (needle-like) particulates occur in the presence of high levels of arsenic in the SSL system. The formation of such aggregates is accompanied by an increase in slurry viscosity and simultaneous drop in copper extraction.

Interestingly, a higher degree of acicularity is noticed for the copper-depleted source than for the incompletely leached source. Furthermore, arsenic contained in the spent copper electrolyte has the same negative impact on the SSL process as arsenic present in FSL residues of the copper-depleted type. It is believed that the modification of antlerite crystal shapes results from a heterogeneous nucleation effect with some arsenic species acting as a BCS nucleation-catalyzing substrate during the early stages of second-stage leaching. Such a substrate, likely composed of the basic copper arsenate olivenite ($Cu_2AsO_4(OH)$), decreases the critical supersaturation requirements for nucleation and increases heterogeneous nucleation rates at the expense of crystal growth rates. Hence, it is crucial the total arsenic level of the SSL batch be minimized.

SSL temperatures higher than 115°C enhance problematic BCS characteristics via higher supersaturation levels from increased initial rates of copper sulfide leaching, by decreased nucleation activation energies and through decreased precipitate solubility. The combined effect of high feed arsenic content and higher leach temperature is particularly detrimental to copper extraction kinetics.

Methods to alleviate the SSL process difficulties related to high-arsenic feeds are (1) to reduce the target FSL solids concentration in batch make-up, (2) to improve temperature control, and (3) to increase the agitation efficiency in order to improve gas-liquid mass transfer. Most of all, however, the extraction of arsenic achieved during first-stage leaching should be maximized to mitigate the deleterious role of the element in second-stage leaching. It is this insight that has instigated the current INCO-UBC investigations.

Thus, the principal aim of the present project is to provide a better understanding of the chemistry and kinetics of the FSL process, particularly with respect to arsenic, in order to enhance the metallurgical performance in the SSL process. In addition, it is hoped that the experimental results will aid in the development of a superior control strategy for the CRED leaching operation.

This thesis supersedes any views expressed and results reported previously [6,7]. It is organized in six chapters. Chapter 2 is an inventory of contemporary industrial nickel-copper matte leaching technology. The chapter includes a general overview of INCO's operations in the Sudbury Basin as well as a more detailed description of the CRED plant. In Chapter 3 selected potential-pH diagrams for the systems arsenic-sulfur-water and nickel-sulfur-water are developed. Chapter 4 describes the experimental program, the results of which are summarized and discussed in Chapter 5. Finally, conclusions and recommendations for future research follow in Chapter 6.

CHAPTER 2

INDUSTRIAL NICKEL-COPPER MATTE LEACHING PRACTICE

2.1   Introduction

In this chapter, matte is defined as a generally sulfur-deficient pyrometallurgical product, essentially consisting of various nickel, copper and iron sulfides, a metallic phase with native metals and alloys, and both "simple" and spinel-type oxides. The actual concentrations of nickel, copper, cobalt, iron, sulfur, precious metals (PM's), platinum group metals (PGM's) and other elements can greatly vary, although the mineralogical composition of most mattes is quite similar.

The alloys are important to the metallurgical industry since (1) during smelting they often act as scavengers for P(G)M's, and (2) they are magnetic, allowing relatively easy magnetic separation, and hence, concentration of the P(G)M values, after slow cooling of the matte. At present INCO and Rustenburg Platinum Mines are the only two companies in the western world to process iron-nickel-copper alloys separately; whole matte oxidative pressure leaching and, to a lesser extent, matte electrolysis, are practiced by the majority of modern integrated hydrometallurgical matte treatment plants in the world. The traditional, mainly pyrometallurgical route of matte smelting, slow cooling and separation, followed by roasting and reduction melting of the nickel sulfides and fire refining of the copper sulfides to produce crude metallic anodes for conventional electrorefining circuits of both metals, is presumably still employed at the Russian Monchegorsk and Norilsk plants [8].

Considering its limited bearing on the present leaching studies, matte electrorefining is not discussed in detail here. In such an electrolysis process matte is anodically dissolved, leaving a voluminous layer of elemental sulfur which acts as an effective collector for P(G)M's as well as selenium and tellurium. Depending on the composition of the anode, either copper or nickel may be electrodeposited at the cathode. The production of copper powder from corroding bagged matte anodes in a all-sulfate medium was formerly practiced by Engelhard Industries in New Jersey [9]. A similar process for a mixed sulfate-chloride electrolyte was patented in the Soviet Union [10]. Nickel cathodes were previously produced by Shimura Kako in Japan [11]. Currently, the production of nickel cathodes from electrodissolving matte anodes in a sulfate-chloride(-borate) electrolyte with divided cells is carried out at INCO's Thompson Refinery [12], the Jinchuan Non-ferrous Metals Complex in China [13] and Sumitomo's Niihama Refinery in Japan [14].

In view of the heterogeneous composition of matte, it is not surprising that hydrometallurgical process flowsheets for the treatment of nickel-copper mattes are among the most complex and diverse in the metallurgical industry. Only in South Africa, and likely soon in Zimbabwe, are PGM's the primary matte products and base metals and other elements by-products. Eramet of France is the only company in the western world to solely process a virtually copper-free nickel matte produced from laterite ore. The economic distinction between "nickel-copper mattes", "precious metals mattes" and "nickel mattes" is not valid in this chapter, since all of the mattes are subjected to the same kind of leaching processes.

Nickel and cobalt may be marketed as sheared cathode slabs or special cathode shapes, as mixed precipitates or crystalline salts, or as powders, pellets and briquettes. Copper is usually sold as cathodes. Few refineries in the world produce separate P(G)M products, so that PM's and PGM's are often traded as concentrates. Sulfur is either recovered as $S°$, Na_2SO_4 or $(NH_4)_2SO_4$ for sale to the chemical industry, or rejected as $CaSO_4$. Most leaching and electrorefining plants also make selenium and tellurium products.

To satisfy changing market demands, matte processing has been a field of continuous hydrometallurgical innovation. This chapter, therefore, describes the evolution of commercial nickel-copper matte leaching processes as part of an inventory of available technology. It is meant to complement and update parts of the established works [8,15]. Emphasis is put on the leaching chemistry in chloride, sulfate and nitrate media; the individual metal recovery processes further downstream are not addressed in great depth. Since accurate information about plant practice in the former Soviet Union is generally unavailable, the following review focuses on the industrial "know-how" in the western world.

2.2   Chloride Lixiviants

Chloride solutions are highly suitable media for matte processing. By virtue of a lower electrolyte resistivity, they offer the advantages of a lower cell voltage and a higher current density in nickel electrowinning when compared to predominantly sulfate media. Copper can exist in two valency states in acidic chloride solutions and thus serve as an "electron carrier" for the electrochemical matte leaching reactions. Finally, the economically important removal of cobalt from solution is greatly facilitated when the substantial chloride concentrations introduced through oxidative hydrolysis of this metal with Cl_2-$NiCO_3$ can be tolerated and accommodated by the nickel electrolyte.

Unfortunately, the aggressive nature of chloride lixiviants and fear of process control difficulties have limited the use of hydrochloric acid and chlorine gas in the metallurgical industry. To date there are only two companies that successfully operate all-chloride nickel and cobalt flowsheets: Falconbridge of Norway and Eramet of France.

2.2.1   Falconbridge technology

2.2.1.1 Matte Leach Process

The Falconbridge Matte Leach (FML) process was engineered for and piloted at the Falconbridge Nikkelverk in Kristiansand, Norway. It was implemented by the late 1960's to bridge the transition of the refinery's old modified Hybinette flowsheet to the chlorine leach process practiced today. At the time the refinery processed nickel-copper convertor matte from the Falconbridge smelter in Sudbury, with typically 48% nickel, 27% copper, 22% sulfur, about 1% each of cobalt and iron, as well as impurities such as arsenic, lead and selenium.
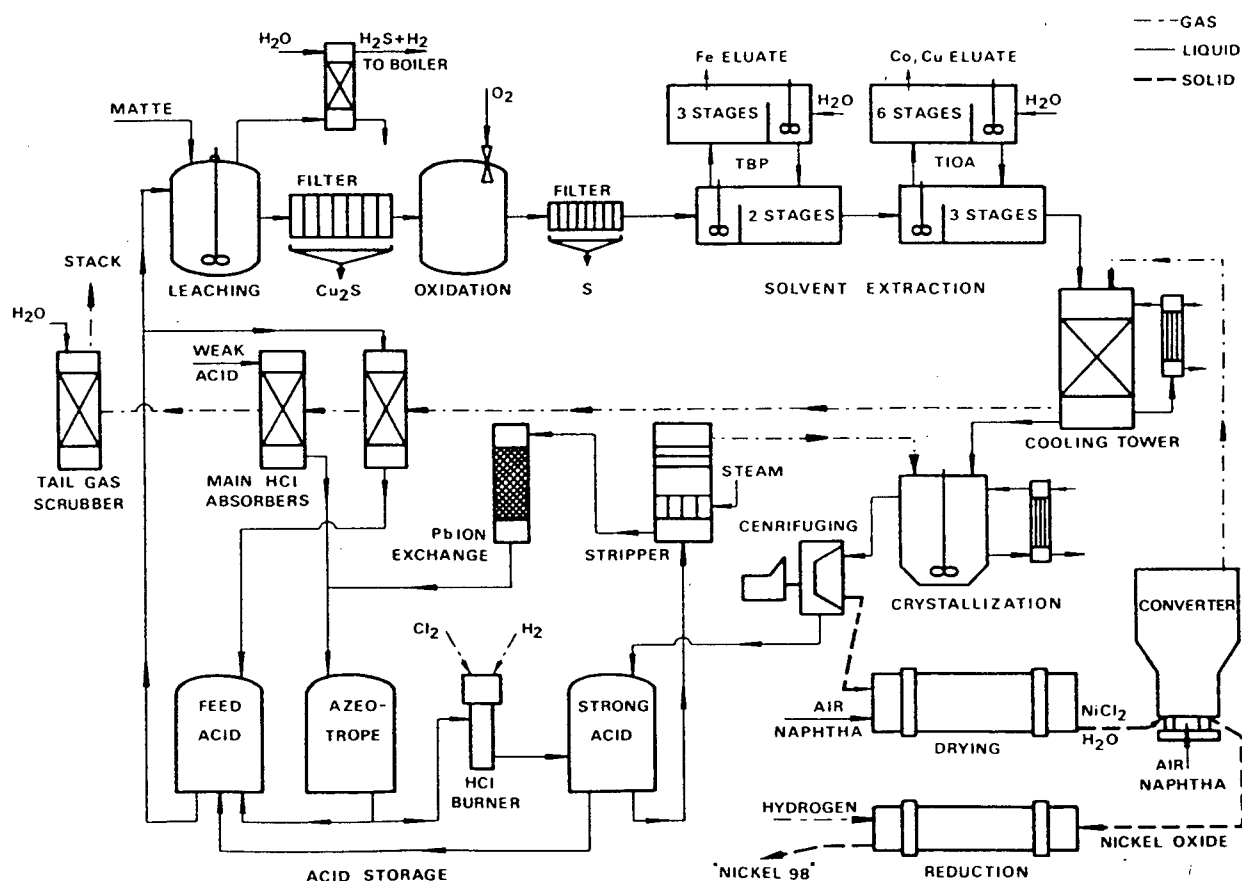
Figure 2-1.   Schematic flowsheet of the Falconbridge Matte Leach (FML) process [16].

Figure 2-1 is a schematic flowsheet of the FML process [16]. The requirements of the pilot plant were drawn as a 98% minus 325 mesh fraction. Non-oxidative leaching of the matte with strong hydrochloric acid at 70°C in a four-stage co-current cascade of mechanically agitated rubber-lined tanks selectively dissolved 98% of the nickel, leaving copper and P(G)M's as an insoluble sulfide residue. The total residence time in the leaching circuit was about 12 hours.

The Cu_2S residue obtained after filtration of the leach slurry served as the feed material to the copper section of the refinery's older modified Hybinette flowsheet [17]. In this way the P(G)M's were more directly concentrated as solids, resulting from the copper leach, instead of as nickel anode slimes.

Gas formed during the nickel leach consisted of a mixture of H_2 and H_2S. It was cooled, scrubbed free of HCl and combusted in a waste heat boiler. The combustion gases were combined with the roaster off gases and treated for recovery of liquid SO_2.

The pregnant nickel solution, containing approximately 120 g/L nickel and 160 g/L HCl as well as about 2 g/L each of iron, cobalt and copper, was purified in three stages. First, oxygen was passed through the solution to oxidize dissolved H_2S to $S°$ and ferrous iron to its ferric state. After filtration for removal of the sulfur, the solution was cooled to room temperature in preparation for solvent extraction. Iron(III) was then removed with the solvating extractant tri-butyl phosphate (TBP). Finally, treatment of the iron-free raffinate with solvating tri-iso-octyl amine (TIOA), followed by selective stripping, removed cobalt and copper. All stripping was carried out with water.

Lead was the only remaining impurity after solvent extraction treatment. Since it was highly soluble under the crystallizer conditions - through complexation as chloride anions - and caused no serious contamination of the crystallizer product, it was removed from the acid regeneration system in a small ion exchange column.

In the continuous crystallizer HCl gas was injected into the purified pregnant nickel solution to "salt out" crystals of $NiCl_2 \cdot 4H_2O$. Following centrifuging, mother liquor with roughly 28 g/L nickel and 330 g/L HCl flowed into strong acid storage tanks, whereas the crystals discharged into a bin feeding a direct-fired rotary dryer.

In the dryer about 3 of the 4 moles of water of crystallization were removed from the crystals. Partly dehydrated nickel chloride was then fed to a high-temperature fluidized-bed hydrolysis reactor ("converter"), in which rounded high-density particles of nickel oxide were formed according to the reaction:

$$NiCl_2 + H_2O \rightarrow NiO + 2\,HCl \qquad\qquad (2\text{-}1)$$
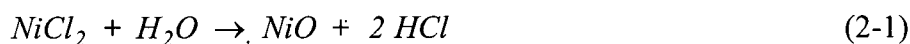
The NiO granules were continuously discharged from the bottom of the pyrohydrolyzer, cooled, and screened for recovery of minus 35 mesh material, which was recycled to serve as seed material for the vapor deposition hydrolysis reactions.

The converter off gases, before passing through HCl absorbers, passed directly through a cooling tower fed with purified pregnant solution.   The latter underwent considerable concentration in nickel in this operation, emerging as crystallizer feed. This enrichment resulted partly from evaporation and partly from dissolution of NiO fines which were carried over with the converter off gases. Unfortunately, it also led to the presence of some nickel oxide in the crystalline product.

The cooled gases entered the HCl adsorption system for recovery of the regenerated acid. Reduction of NiO to a high-purity granular nickel metal product, designated NICKEL 98, was done in a rotary hydrogen reduction furnace.

2.2.1.2 Chlorine Leach Process

The modified Hybinette process was in use at the Kristiansand Nikkelverk until the late 1970's, when conversion to the Falconbridge Chlorine Leach (FCL) process was initiated.   Nickel electrowinning from all-chloride electrolyte [18] has since replaced electrorefining of the metal in a chloride-sulfate electrolyte. A blend of convertor mattes, mainly from the Falconbridge smelter in Sudbury and the BCL smelter in Botswana, is currently being processed. The feed to the refinery typically contains 40-45% nickel, 25-30% copper, 20-22% sulfur, 1-1.5% cobalt and 2-3% iron.

Figure 2-2 is a schematic flowsheet of the FCL process [19]. The matte consists principally of heazlewoodite (Ni_3S_2), chalcocite (Cu_2S) and an alloy with Ni : Cu = 7 : 3. It is wet-ground to a particle size wholly finer than 80 mesh and advanced to the atmospheric leaching tanks. Chlorine from the nickel tankhouse is fed under the impeller and the temperature is held at the boiling point of the slurry. The main leaching reactions [20] are:

$$2\ CuCl\ +\ Cl_2\ \rightarrow\ 2\ CuCl_2 \tag{2-2}$$

$$Ni_3S_2\ +\ 2\ CuCl_2\ \rightarrow\ NiCl_2\ +\ 2\ NiS\ +\ 2\ CuCl \tag{2-3}$$

$$NiS\ +\ 2\ CuCl_2\ \rightarrow\ NiCl_2\ +\ 2\ CuCl\ +\ S^\circ \tag{2-4}$$

$$Cu_2S\ +\ S^\circ\ \rightarrow\ 2\ CuS \tag{2-5}$$
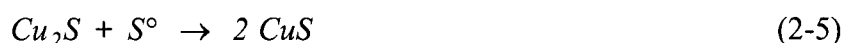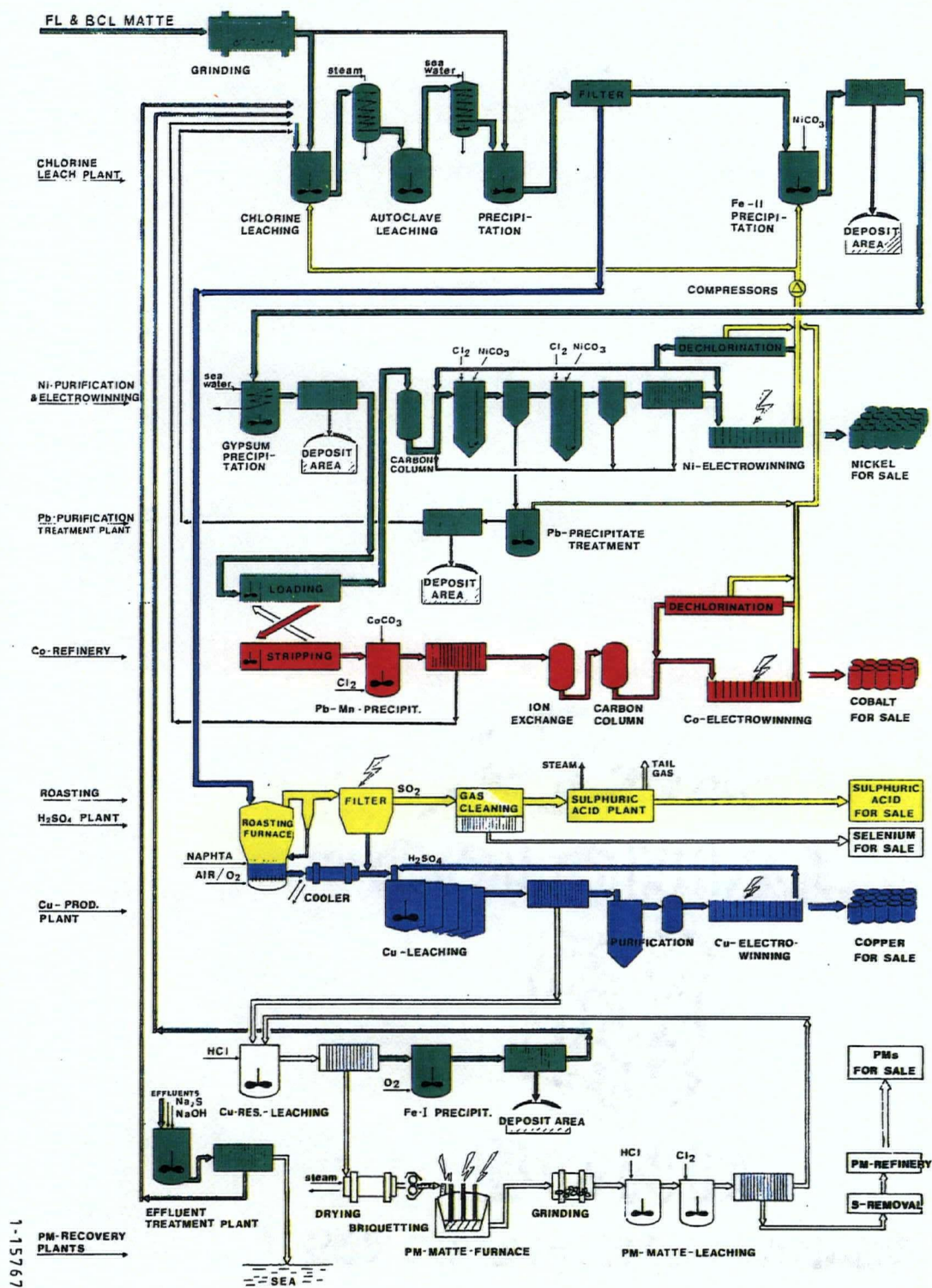
Figure 2-2. Schematic flowsheet of the Falconbridge Chlorine Leach (FCL) process [19].

The leaching process is based on control of the oxidation-reduction potential (ORP) to maintain a desired ratio of cupric to cuprous ion; at all times sufficient CuCl must be available to ensure immediate absorption of the chlorine as the nickel leaching intermediary $CuCl_2$.

Leach slurry at 110°C is pumped from the leach tanks through a steam preheater where its temperature is raised to about 130°C, and then to the first of two autoclaves in which the exchange reactions are sufficiently exothermic to raise the temperature to 140-145°C. Although in the autoclaves the principal reactions take place between the solution and unleached millerite (NiS) in the chlorine leach residue, any tendency for the ORP and dissolved copper to vary beyond set limits is automatically adjusted by the introduction of minor amounts of fresh matte. The slurry flows continuously into the second autoclave and is discharged via a cooling system to the first of two "cementation" tanks in tandem. The leaching chemistry of the autoclave train [19] is best described by:

$$NiS + 2\,CuCl \rightarrow NiCl_2 + Cu_2S \qquad (2\text{-}6)$$

The reactions [19] between the leached slurry and the fresh matte introduced in the copper precipitation tanks are:

$$Ni_3S_2 + S° + 2\,CuCl \rightarrow NiCl_2 + NiS + Cu_2S \qquad (2\text{-}7)$$

$$Ni + S° + 2\,CuCl \rightarrow NiCl_2 + Cu_2S \qquad (2\text{-}8)$$

$$S° + 2\,CuCl \rightarrow CuCl_2 + CuS \qquad (2\text{-}9)$$
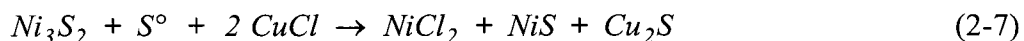
The formation of covellite (CuS) through reaction (2-5) occurs throughout the above circuit. The overall nickel extraction of the leaching-copper precipitation system is 90%. The copper concentration decreases from 50-70 g/L in the leach tanks to 0.5 g/L in the second copper precipitation vessel. After filtration, the resulting strong nickel chloride solution is purified and sent to the nickel tankhouse. Various nickel products are produced by electrowinning, including cathodes and "crowns". Anodes (DSA's) are fitted with a hood, a diaphragm bag, and a duct connecting the top of the hood to a manifold running alongside the cell for withdrawal of chlorine and anolyte by suction.

Purification of the pregnant nickel solution involves (1) precipitation of iron and arsenic with Cl_2 and $NiCO_3$, (2) precipitation of gypsum through cooling, (3) solvent extraction of cobalt with TIOA, and (4) precipitation of lead, manganese and other trace impurities with Cl_2 and $NiCO_3$,

after dilution of the nickel stream with anolyte. The all-chloride pregnant cobalt solution contains 80-90 g/L cobalt and is pumped to the cobalt tankhouse.

The copper sulfide chlorine leach residue acts as a scavenger for P(G)M's. It is dead roasted in fluidized-bed roasters. Sulfur dioxide is recovered from the roaster off gases and marketed as H_2SO_4. The calcine is leached in spent copper electrolyte and copper is electrodeposited from the pregnant solution. Using some of the idle FML equipment, the copper leach residue is subjected to lixiviation with HCl-Cl_2 [21] to solubilize residual nickel and copper while leaving the P(G)M's intact. This step also releases residual iron, which is precipitated and filtered off before the nickel-copper solution is sent back to leaching. The final crude P(G)M concentrate is further treated in the precious metals refinery.

2.2.2   Eramet technology

Eramet (formerly SLN) in Le Havre-Sandouville, France, developed and still operates the only other commercial all-chloride process for the integrated recovery of nickel and cobalt from matte. The matte, shipped from the company's Doniambo smelter in New Caledonia, contains virtually no copper. Since it has proven difficult to find detailed information about the present refinery practice, this section chiefly discusses the original pilot-plant campaign carried out at Minemet Recherche in the mid 1970's for the development of a hydrometallurgical flowsheet for the SLN Refinery [22].

Figure 2-3 is a simplified flowsheet of the originally piloted process. Matte was crushed, ground and fed to a fluidized-bed roaster. After roasting, the NiO calcine, with minor metallic nickel and nickel sulfide, was leached with strong (8N) HCl in a two-stage countercurrent leaching circuit, kept at the boiling point of the slurry:

$$NiO + 2\,HCl \rightarrow NiCl_2 + H_2O \qquad\qquad (2\text{-}10)$$

$$Ni + 2\,HCl \rightarrow NiCl_2 + H_2 \qquad\qquad (2\text{-}11)$$

$$NiS + 2\,HCl \rightarrow NiCl_2 + H_2S \qquad\qquad (2\text{-}12)$$
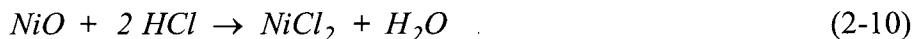
The residence time was 4 hours in each tank.

Figure 2-3. Simplified flowsheet of the proposed and piloted SLN Refinery process (after [22]).

Following liquid-solid separation, the leach solution was advanced to an iron oxidation step, where at 75°C an upward flow of chlorine gas was bubbled through a packed column to ensure the formation of the extractable Fe(III) species $FeCl_4^-$ in the descending leach solution. Traces of elemental sulfur, formed by the oxidation of residual dissolved H_2S, were then filtered off the $NiCl_2$ stream prior to further purification stages.

In two ion exchange columns in series chloride complexed cobalt, copper, iron and zinc were removed using the strong basic anion exchanger IRA 400. Evidently, the ORP of the chlorine-treated leach solution had to be carefully controlled to prevent degradation of the resin.

The chloride level of the eluate was adjusted to $5N$ by the addition of some $NiCl_2$. The solution was then concentrated to approximately 160-170 g/L nickel, 30 g/L iron and 20 g/L cobalt by evaporation, before solvent extraction of iron with Amberlite LA 2 and cobalt with TIOA. Cobalt was subsequently recovered by electrodeposition. The raffinate was mixed with the nickel solution from ion exchange.

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The chloride level of the eluate was adjusted to $5N$ by the addition of some $NiCl_2$. The solution was then concentrated to approximately 160-170 g/L nickel, 30 g/L iron and 20 g/L cobalt by evaporation, before solvent extraction of iron with Amberlite LA 2 and cobalt with TIOA. Cobalt was subsequently recovered by electrodeposition. The raffinate was mixed with the nickel solution from ion exchange.

The pH of the pregnant $NiCl_2$ solution was gradually increased with $NiCO_3$ for purification. First, lead was removed through selective electrowinning at pH 2. Secondly, mixed hydroxides of lead, chromium and aluminum were precipitated at pH 3.5. The third purification step comprised ion exchange with a small column to remove the last traces of base metals. Build-up of the remaining impurities - sodium, calcium, magnesium and sulfate - was prevented by thorough washing of the $NiCO_3$ cake produced through addition of Na_2CO_3 to a small stream of catholyte. All impurity residues required further processing for re-extraction of entrained nickel.

Nickel was electrowon in diaphragm cells with air-mixing of the catholyte for improved mass transfer, and hence, deposition rates. Chlorine was recovered at the anodes for production of HCl for the leaching circuit.

The major drawbacks of this rather cumbersome flowsheet were the necessity of production units for both hydrochloric and sulfuric acid. In particular, the use of H_2 rendered the process economics unfavorable.

The finally adapted flowsheet [23] at the Eramet Refinery in 1978 is remarkably similar to the FCL process. In view of the low copper content of the Doniambo matte, chlorine leaching with $FeCl_3$ as the leaching intermediary is employed instead. Sulfur remains in its elemental state in the leach residue. Iron(III) chloride is removed by solvent extraction with TBP. Part of it is recycled to the leaching stage, whereas the other portion is concentrated through evaporation and sold. Cobalt is extracted from the impure nickel chloride solution with TIOA and sold as solution for cobalt metal recovery elsewhere. After a similar deleading electrolysis stage as devised for the process described above, the $NiCl_2$ solution is passed through columns of activated carbon to remove residual impurities. Nickel is electrowon onto titanium cathodes in electrolysis cells with graphite anodes.

2.3   Sulfate Lixiviants

Sulfuric acid is the most frequently used mineral acid in the hydrometallurgical processing of matte. Its lack of selectivity and corrosive nature are largely offset by its low cost and wide availability. This section discusses the sulfuric acid based processes developed by AMAX, INCO, Outokumpu, Sherritt and the Mansfeld Kombinat.

2.3.1   AMAX technology

The AMAX Port Nickel Refinery in Louisiana was in production from 1974 to 1986. It was the only producer of pure nickel in the USA during that period.
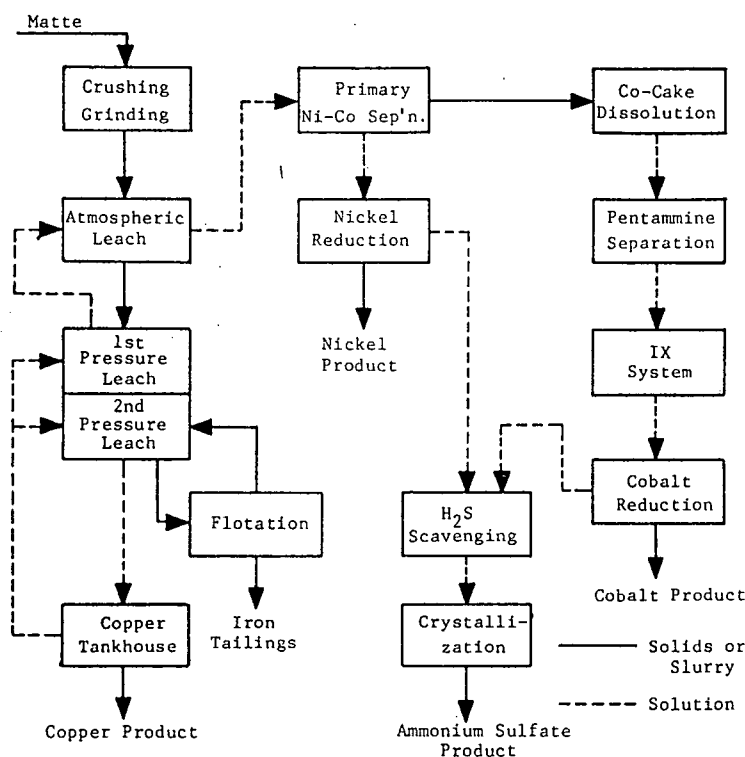
Figure 2-4.   Simplified flowsheet of AMAX's Port Nickel Refinery [24].

Figure 2-4 is a simplified flowsheet of the Port Nickel plant [24]. The feed to the plant was matte from Africa (BCL) and Australia, which was crushed, ground to 95% passing 200 mesh and blended. The average composition of the matte was 47% nickel, 30% copper, 20% sulfur, 1% iron and 0.5% cobalt.

The nickel-copper matte was leached in a multi-stage countercurrent circuit of atmospheric and pressure leaching. The leaching chemistry of such a circuit is covered in sections 2.3.3 and 2.3.4. The residue, consisting almost entirely of iron oxide, was cleaned of unleached sulfides in flotation banks operating in closed circuit with the leaching plant. No reagents were needed to float the sulfide minerals due to the presence of the naturally hydrophobic layer of elemental sulfur that encapsulated them.

Copper was electrowon as cathodes. Cobalt was precipitated from the impure $NiSO_4$ solution with ammoniacal ammonium peroxydisulfate:

$$2\ CoSO_4\ +\ 6\ NH_3\ +\ (NH_4)_2S_2O_8\ +\ 6\ H_2O\ \rightarrow\ 2\ Co(OH)_3\ +\ 4\ (NH_4)_2SO_4 \qquad (2\text{-}13)$$
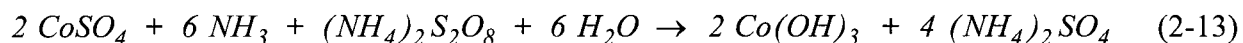
Following liquid-solid separation, nickel powder was produced from the cobalt-free ammoniacal ammonium sulfate (AAS) solution in an adapted Sherritt hydrogen reduction process. The powder was the basis for various sintered nickel products. Cobalt metal was produced in a modified Sherritt "pentammine" process, which involved (1) redissolution of the cobaltic hydroxide cake in a reducing H_2SO_4-CH_3OH lixiviant, (2) ammoniation, (3) ion exchange with TP 207 resin to remove trace nickel and other divalent ions, and (4) hydrogen reduction of cobalt. Cobalt was sold as powder and as "cubes".

The nickel and cobalt reduction end solutions were combined and subjected to a H_2S scavenging treatment in a pipe reactor at neutral pH and ambient temperature. After pressure filtration, fertilizer-grade $(NH_4)_2SO_4$ was crystallized from the base metal depleted solution by evaporation.

2.3.2   INCO technology

INCO's matte processing facilities in Canada comprise (1) the aforementioned electrolytic Thompson Refinery, operated by the Manitoba Division, and (2) a vast metallurgical complex centered around the township of Copper Cliff in the Sudbury Basin, operated by the Ontario Division. Since the present thesis is an analysis of one of the intermediary leaching processes practiced at the Copper Refinery, a brief general overview of INCO's operations in the Sudbury Basin is first given.

Five underground INCO mines currently produce the nickel-copper ores from the Canadian Shield. All run-of-mine ore is crushed, ground in a semi-autogenous grinding circuit, and floated in large Outokumpu flotation cells at the Clarabelle Mill to reject pyrrhotite and other gangue minerals. The mill has a capacity of 40,000 tons per day of ore and produces a bulk nickel-copper concentrate that proceeds to the smelter.

At the smelter, a recent five-year, $600 million (Cdn.) SO_2 abatement program has replaced multi-hearth roasters, reverberatory furnaces and the majority of the convertors with two INCO designed flash furnaces. In addition, a new sulfuric acid plant and a liquid sulfur dioxide facility have been erected.

The flash furnaces produce a matte assaying roughly 35% nickel and 35% copper, the balance being sulfur. In the separation section of the Matte Processing Plant (MPP), the matte is cast into molds and allowed to cool over a four-day period to promote the formation of large

Ni_3S_2 and Cu_2S crystals. Since the matte is deficient in sulfur, a metallic phase containing a magnetic iron-nickel-copper alloy is also formed.

In the MPP the matte is crushed, rod-milled and passed over magnetic separators to remove the metallics, which report to the Copper Cliff Nickel Refinery (CCNR). The non-magnetic fraction is ball-milled and pumped to flotation columns for Cu_2S-Ni_3S_2 separation. Chalcocite reports to the froth phase, whereas heazlewoodite is collected at the bottom of the columns. After filtration, the copper sulfide (MK) filter cake is converted to blister copper and transported in hot metal rail cars to the Copper Cliff Copper Refinery (CCCR), where it is fire-refined to anode quality, cast and finally electrorefined. Heazlewoodite is oxidized in fluidized-bed roasters. The resulting NiO calcine is either sold or further treated at the CCNR or the Clydach Refinery in Wales.

The CCNR is the western world's largest producer of nickel. It operates a high-pressure variation of Mond's carbonylation process that extracts the majority of the nickel and about a third of the iron, as gaseous $Ni(CO)_4$ and $Fe(CO)_5$, respectively, from the metallic fraction mentioned earlier. Carbonylation is carried out batchwise in three horizontal, cylindrical rotating reactors. The volatile nickel tetra- and iron pentacarbonyls are condensed and separated through distillation. The presence of $Fe(CO)_5$ necessitates the production of a ferronickel product along with the highly pure nickel.

The CCNR consists of two individual plants, namely (1) the Nickel Refinery Convertor (NRC) plant, where the alloy phase is melted in top-blown rotary convertors together with secondaries of various sources, and granulated in preparation of carbonylation, and (2) the INCO Pressure Carbonyl (IPC) plant, where nickel is extracted and decomposed into pellets and powders of extreme purity.

The IPC process leaves a porous, granular residue, which, after depressurizing and purging with inert gas, is discharged from the reactor, slurried with water and milled to typically 80% passing 325 mesh before pumping to the Copper Refinery Electrowinning Department (CRED) of the CCCR as a dilute (5% solids) slurry.

The CRED plant was commissioned in the early 1970's. Figure 2-5 is a simplified flowsheet of the current process [25,26].

The incoming IPC slurry is thickened to approximately 55% solids, at which pulp density the material is stored in three holding tanks. In this way, daily fluctuations in the composition of the residue are smoothed out and a fairly uniform composition of the feed over several batches is achieved. Some 50 tons of residue are processed daily.
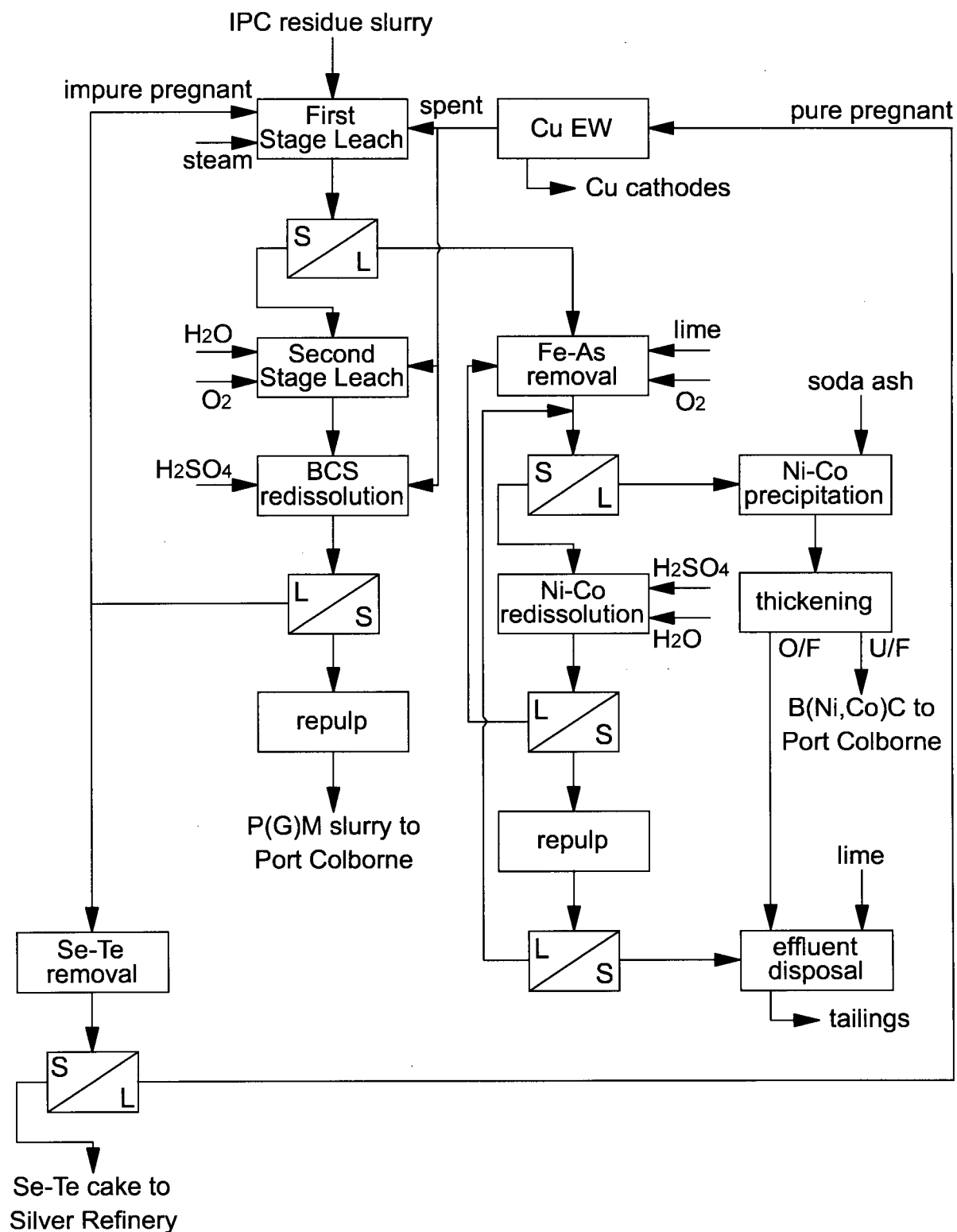
Figure 2-5.   Simplified flowsheet of INCO's CRED plant (after [25,26]).

A constant volume tank suspended on load cells allows known quantities of thickened slurry to be advanced from the holding tanks into the first-stage batch make-up tank. Here, desired mixtures of spent and pregnant copper electrolytes are added to the thickened slurry, and steam is used to preheat the batch to 80°C. The preheated batch is then gravity fed to one of three mechanically agitated brick-lined first-stage autoclaves.

In the first-stage autoclaves the 20% solids slurry of IPC residue, electrolytes and steam condensate together is maintained at 160°C and 80 psig "steam" pressure for one hour. The purpose of the First-Stage Leach (FSL) process is to dissolve nickel, cobalt, iron and arsenic, in order to separate these elements from selenium, tellurium and the P(G)M's, all of which remain in a substantially Cu_2S-containing residue. The total FSL cycle time including batch make-up, heating, leaching and discharging is typically 3-3.5 hours.

The mineralogical composition of the highly reduced IPC residue is mainly Cu_xS ($1.76 < x < 2$), pentlandite (M_9S_8 with M = Ni, Fe, Co), Ni_3S_2, metallics (Cu, Ni), spinel-type oxides (MFe_2O_4), and oxidation products formed during transport and storage, such as cuprite (Cu_2O), tenorite (CuO) and bunsenite (NiO). It is black in appearance and has a density of about 5500 kg/m^3.

The first-stage leaching chemistry involves the dissolution of the oxide minerals:

$$MO + H_2SO_4 \rightarrow MSO_4 + H_2O \tag{2-14}$$

$$MFe_2O_4 + 4\,H_2SO_4 \rightarrow MSO_4 + Fe_2(SO_4)_3 + 4\,H_2O \tag{2-15}$$
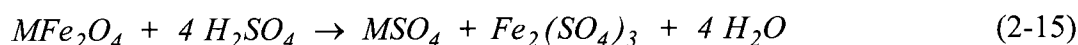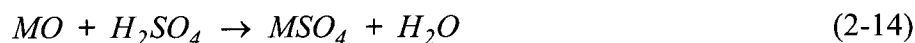
cementation reactions:

$$M + CuSO_4 \rightarrow MSO_4 + Cu \tag{2-16}$$

and metathesis (or "double decomposition") reactions in which reductants such as cuprous ion are attributed an important role [27]:

$$Cu + CuSO_4 \rightarrow Cu_2SO_4 \tag{2-17}$$

$$M_9S_8 + 7\,Cu_2SO_4 + 2\,CuSO_4 \rightarrow 9\,MSO_4 + 8\,Cu_2S \tag{2-18}$$
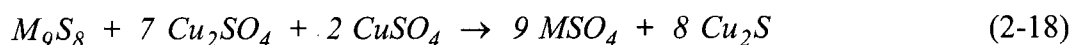
In order to obtain optimum extractions of impurities, the FSL process is conducted with excesses of both cupric ion and sulfuric acid, typically 1-5 g/L and 20-60 g/L more, respectively, than

required. Excess acid, of course, is needed to prevent hydrolysis of the extracted metal values. A copper clean-up step with NaHS was abandoned in 1988 because of operating difficulties, and any residual copper is now either lost to the tailings or reports to the nickel-cobalt product as an unwanted contaminant.

Indeed, the residual copper concentration must be carefully controlled. Insufficient copper in solution at the end of the FSL produces low potentials causing "reprecipitation" of dissolved arsenic and enhanced corrosion rates due to the action of H_2S. During discharge, too high a level risks clogging of chokes and adjacent piping on the low-pressure side with elemental copper, formed through the disproportionation reaction:

$$Cu_2SO_4 \rightarrow Cu + CuSO_4 \qquad (2-19)$$

The FSL filtrate is subjected to a two-stage hot lime treatment. At a temperature of 100°C at 50 psig oxygen pressure and a pH increasing from about 3.2 in the first autoclave to 4.1 in the second one, a mixture of ferric hydroxide, copper and iron arsenates and gypsum is precipitated. After filtration the iron-arsenic cake is repulped with water and H_2SO_4 (pH 2-2.2) to redissolve co-precipitated nickel and cobalt. Another liquid-solid separation step then separates the nickel-cobalt solution from the ferric arsenate residue, which is once more repulped and filtered before it is discarded. At this point the pregnant solution contains approximately 15 g/L each of nickel and cobalt.

In two precipitation tanks in series kept at 75°C, the pH of the nickel-cobalt solution is adjusted to 7.7 and 8.8, respectively, by the addition of soda ash. The resulting mixture of basic nickel and cobalt carbonates (B(Ni,Co)C) is trucked to the Port Colborne Cobalt Refinery as thickener underflow slurry. At Port Colborne it is refined into electrolytic cobalt "rounds" and $NiCO_3$, which is trucked back to CRED for drying and packaging.

The FSL cake is recovered from the rotary vacuum filter and slurried to 25-30% solids with water and some spent copper electrolyte in the second-stage batch make-up tank. The batch is then charged into one of two mechanically agitated second-stage autoclaves.

The Second-Stage Leach (SSL) process is a total oxidative leach (TOL) in an acid-deficient environment at 115°C and a total pressure of 150 psig . It yields a slurry of $CuSO_4$ and a residue of essentially di-basic copper sulfate (antlerite) and P(G)M's. The equilibrium between dissolved copper and antlerite buffers the solution pH between 2 and 3. Simplifying the chemistry for a chalcocite feed, the sequential reactions are:

$$Cu_2S + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow CuSO_4 + CuS + H_2O \qquad (2-20)$$

$$Cu_2S + \tfrac{1}{2} CuSO_4 + H_2O + \tfrac{1}{2} O_2 \rightarrow CuS + \tfrac{1}{2} CuSO_4 \cdot 2Cu(OH)_2 \qquad (2\text{-}21)$$

$$CuS + 2 O_2 \rightarrow CuSO_4 \qquad (2\text{-}22)$$
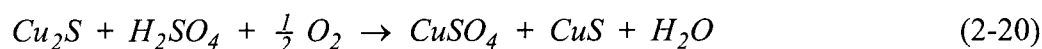
Any metallic copper present in the FSL residue reacts according to:

$$Cu + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow CuSO_4 + H_2O \qquad (2\text{-}23)$$
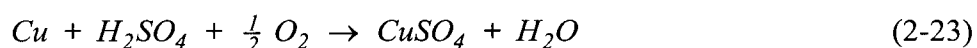
while the formation of elemental sulfur is considered to be a minor side reaction under normal operating conditions:

$$CuS + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow CuSO_4 + S^\circ + H_2O \qquad (2\text{-}24)$$
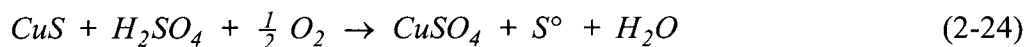
The brick-lined second-stage autoclaves are equipped with cooling coils which abstract the heat generated by the above exothermic reactions and serve as baffles at the same time. The retention time of a batch in the second-stage reactor is typically 4-6 hours, but may be as long as 20 hours under the "slow cook" conditions explained in Chapter 1. The second-stage slurry is mixed with spent electrolyte from the copper tank house to redissolve antlerite according to:

$$CuSO_4 \cdot 2Cu(OH)_2 + 2 H_2SO_4 \rightarrow 3 CuSO_4 + 4 H_2O \qquad (2\text{-}25)$$
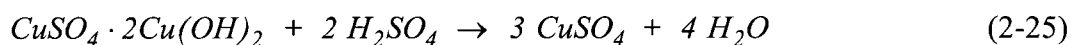
Perlite filter-aid assisted pressure filtration then separates the impure pregnant copper electrolyte from a high-grade P(G)M residue which, after repulping, is sent for further concentration at Port Colborne.

After heating of the pregnant electrolyte to 95°C in a heat exchanger, it is pumped upward through a bed of copper wire choppings in a cementation reactor to remove selenium and tellurium from solution. Unfavorable kinetics necessitate a retention time of 12-14 hours in four consecutive plug-flow aging towers to drive the copper selenide and telluride formation reactions to completion.

The purified $CuSO_4$ solution is advanced to a conventional electrowinning process with antimonial lead anodes and titanium blank sheets. The crude selenium-tellurium concentrate is routed to the CCCR "Silver Refinery" and integrated with the treatment of anode mud from the copper electrorefining process. The "Silver Refinery" produces metallic silver and gold, separate impure selenium and tellurium cakes and a PGM-rich residue for further upgrading at Port Colborne. The PGM's are finally separated at the Acton Refinery in England.

2.3.3   Outokumpu technology

2.3.3.1 Finnish operations

Outokumpu's Harjavalta Works in Finland process a high-grade matte largely produced from concentrates and secondaries from the company's own mills and refineries. The matte is blown to a very low sulfur content ($\approx$8%) prior to entering the leaching plant.

Historically, Outokumpu has employed atmospheric pressure leaching of the matte to extract and separate its nickel and copper values [8]. Apart from the obvious physicomechanical process parameters, the maximum degree of dissolution of nickel and copper attainable in such a leaching process depends on the Ni : Cu ratio and sulfur content of the matte [28]. With ever decreasing Ni : Cu ratios in the ore and matte, the nickel extraction achieved with the original three-stage atmospheric leaching system became insufficient and resulted in unacceptably high circulating loads of nickel-copper residue to the smelter. The addition of a selective oxygen pressure leaching stage became therefore necessary. A 70 m³ five-compartment autoclave was added to the Harjavalta operations in 1981 [28], followed by a seven-compartment reactor in 1986 [29].

Figure 2-6.   Schematic flowsheet of Outokumpu's Harjavalta Works [29].

Figure 2-6 is a schematic flowsheet of the Harjavalta Works [29]. Granulated matte is wet-ground to 90% minus 270 mesh and proceeds to the countercurrent leaching circuit.

Until recently, 130 m^3 atmospheric leaching vessels were used in the atmospheric section. Agitation was carried out by blowing air into the reactors through their conical bottoms, while oxygen at the same time acted as an oxidizer. Apparently, new in-house developed oxygen-blown atmospheric reactors are now being utilized, which has improved the tolerance to iron and arsenic in the Outokumpu process. The new reactors were installed as part of the latest expansion at Harjavalta [30].

In the first-stage atmospheric leach, metallic nickel, present in the freshly introduced matte, cements copper from solution:

$$Ni + CuSO_4 \rightarrow NiSO_4 + Cu \tag{2-26}$$

leaving an impure $NiSO_4$ solution which is pumped to the purification section.

Only when excess metallic nickel is depleted through oxidation:

$$Ni + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow NiSO_4 + H_2O \tag{2-27}$$
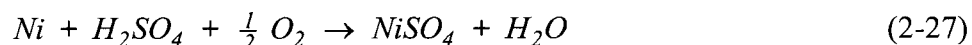
the release of nickel into solution in the successive atmospheric leaching stages becomes dictated by the - kinetically also fast - solid state transformation of heazlewoodite to millerite:

$$Ni_3S_2 + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow NiSO_4 + 2 NiS + H_2O \tag{2-28}$$

Insufficient atmospheric oxidation leaves unreacted heazlewoodite in the leach residue, whereas excessive oxidation leads to the unwanted formation of polydymite (Ni_3S_4):

$$4 NiS + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow NiSO_4 + Ni_3S_4 + H_2O \tag{2-29}$$
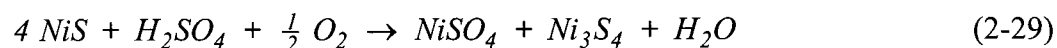
A millerite residue is preferred, since the metathetic leaching of NiS with $CuSO_4$ to $NiSO_4$ and digenite (Cu_9S_5) according to:

$$6 NiS + 9 CuSO_4 + 4 H_2O \rightarrow 6 NiSO_4 + Cu_9S_5 + 4 H_2SO_4 \tag{2-30}$$
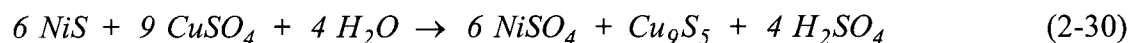
is kinetically much faster than the reactions of Ni_3S_2 and Ni_3S_4 with copper sulfate at the prevailing autoclave conditions:

$$8\ Ni_3S_2\ +\ 27\ CuSO_4\ +\ 4\ H_2O\ \rightarrow\ 24\ NiSO_4\ +\ 3\ Cu_9S_5\ +\ 4\ H_2SO_4 \tag{2-31}$$

$$8\ Ni_3S_4\ +\ 45\ CuSO_4\ +\ 28\ H_2O\ \rightarrow\ 24\ NiSO_4\ +\ 5\ Cu_9S_5\ +\ 28\ H_2SO_4 \tag{2-32}$$

To enhance the conversion of any residual heazlewoodite to millerite while leaving the copper sulfides intact, and to promote the reaction [28]:

$$NiS\ +\ CuS\ +\ Cu_2S\ +\ H_2SO_4\ +\ \tfrac{1}{2}O_2\ \rightarrow\ NiSO_4\ +\ 3\ CuS\ +\ H_2O \tag{2-33}$$
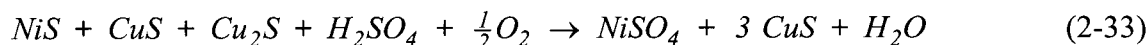
autoclave leaching is carried out with only a slight oxygen overpressure.

Depending on the ORP and pH, metallic copper reacts to form either cuprite or antlerite:

$$2\ Cu\ +\ \tfrac{1}{2}\ O_2\ \rightarrow\ Cu_2O \tag{2-34}$$

$$3\ Cu\ +\ H_2O\ +\ H_2SO_4\ +\ \tfrac{3}{2}\ O_2\ \rightarrow\ CuSO_4\cdot 2Cu(OH)_2 \tag{2-35}$$

The only sources of soluble copper are cuprite:

$$Cu_2O\ +\ 2\ H_2SO_4\ +\ \tfrac{1}{2}\ O_2\ \rightarrow\ 2\ CuSO_4\ +\ 2\ H_2O \tag{2-36}$$

and chalcocite, which may react in several steps to covellite under the mildly oxidizing conditions in the autoclaves:

$$Cu_2S\ +\ x\ H_2SO_4\ +\ \tfrac{x}{2}\ O_2\ \rightarrow\ x\ CuSO_4\ +\ Cu_{2-x}S\ +\ H_2O \tag{2-37}$$
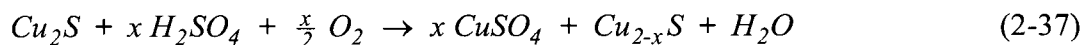
In the Outokumpu process lead is scavenged from solution through the addition of $Ba(OH)_2$, which isomorphously co-precipitates $PbSO_4$ with $BaSO_4$. Cobalt and a host of other impurity elements are removed from the pregnant $NiSO_4$ solution by "group" precipitation with a slurry of the powerful oxidizing agent "nickelic" hydroxide ($NiO_{3-4}\cdot nH_2O$) at near neutral pH and elevated temperature. No detailed information is available yet about the separate iron removal step added recently to the Harjavalta flowsheet [30].

Nickelic hydroxide is produced electrolytically from a $NiSO_4$ catholyte side stream. Taking the formula of nickelic hydroxide as $Ni(OH)_3$ for simplicity reasons, the reactions are:

$$NiSO_4\ +\ 2\ NaOH\ \rightarrow\ Ni(OH)_2\ +\ Na_2SO_4 \tag{2-38}$$

$$Ni(OH)_2 + H_2O \rightarrow Ni(OH)_3 + H^+ + e^- \tag{2-39}$$

$$CoSO_4 + Ni(OH)_3 \rightarrow Co(OH)_3 + NiSO_4 \tag{2-40}$$
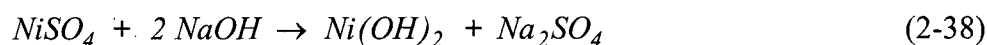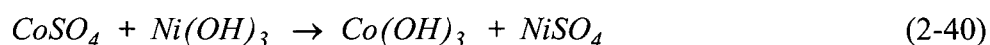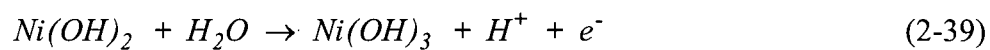
The cobalt cake is routed to the Kokkola Works, where cobalt and nickel powders are produced according to Sherritt's ammoniacal pressure leaching and hydrogen reduction technology. Nickel is electrodeposited from the all-sulfate electrolyte in divided cells with lead anodes. Excess sodium and sulfuric acid are bled from the anolyte as crystalline "Glauber's salt" $(Na_2SO_4 \cdot 10H_2O)$. The concentration of Na_2SO_4 is kept at 150 g/L.

After start-up of the second autoclave, the expensive electrolytic removal of copper (as a powder) between the atmospheric leaching stages was abandoned. Instead, the copper sulfide-iron oxide autoclave residue can now be fed directly to the copper smelter. The P(G)M values of the copper anode slimes are ultimately refined at the Pori Works.

2.3.3.2 Zimbabwean operations

Outokumpu has become a process licenser with a record of successful technology transfer. Variants of the Harjavalta process are practiced by the Empress Refinery and Bindura Refinery in Zimbabwe [31]. A third Zimbabwean refinery, the BHP-Delta Gold Hartley Platinum Complex [30], is scheduled to reach full production by early 1997.

2.3.4   Sherritt technology

2.3.4.1 Introduction

The original Sherritt autoclave process was developed in the early 1950's. It was designed to process the nickel-cobalt sulfide concentrates produced from an ore deposit at Lynn Lake, Manitoba, in an ammoniacal ammonium sulfate (AAS) medium. The process, invented by Professor Forward of UBC, and pioneered and perfected at the company's refinery in Fort Saskatchewan, Alberta, is well documented in literature and therefore not reviewed here.

Ammonia has been employed extensively in the metallurgical industry, because (1) it is a strong and selective ligand for nickel, cobalt and copper, (2) it is readily recovered, and (3) it is compatible with carbon steel equipment. In contrast, the use of pressure metallurgy has been extended to acidic sulfate lixiviants only a few decades ago.

Today there are six matte leaching plants alone which utilize Sherritt's aqueous pressure oxidation technology. The company's own facility now operates as a toll refinery treating a variety of feed materials, such as matte, concentrates and precipitates, in an AAS medium to produce nickel and cobalt powder and briquettes, and ammonium sulfate. Although designed for a nickel concentrate feed, the Western Mining Kwinana Refinery in Australia [32] currently treats matte from the Kambalda smelter using a similar process. The Impala, Rustenburg, Western and Northam operations, all located within the Bushveld Igneous Complex in South Africa, employ acidic pressure leaching processes to separate the primary product, a P(G)M concentrate, from by-products nickel, copper and cobalt. Another South African acidic pressure leaching plant, the small-scale nickel-copper refinery of Barplats Platinum, was in operation only from 1989 to 1991.

The complexity of the South African installations differs greatly with the production scale and the relative value of P(G)M's and base metals in the matte. In this section the flowsheets of the Impala and Rustenburg base metal refineries are described in detail. The smaller Western Platinum, Barplats Platinum and Northam Platinum operations are discussed briefly with the aid of a general, conceptual flowsheet.

2.3.4.2 Impala Platinum

Acid pressure oxidation of matte was first put into production by Impala Platinum in 1969 at its nickel-copper refinery in Springs, Transvaal. Figure 2-7 is a simplified flowsheet of the plant.

Ore from the Merensky Reef is mined, concentrated and smelted into a matte containing about 50% nickel, 28% copper, 0.5-1% iron and minor quantities of cobalt and P(G)M's. The main matte minerals are cobaltiferous heazlewoodite (Ni_3S_2), nickeliferous chalcocite (Cu_2S) and djurleite ($Cu_{1.93}S$), an alloy phase, and "refractory" oxide mineralization, including the spinels chromite ($FeCr_2O_4$), trevorite ($NiFe_2O_4$) and magnetite ($FeFe_2O_4$), as well as bunsenite (NiO) dendrites in Ni_3S_2 [33]. The matte is granulated, wet-ground in ball mills, filtered, repulped with spent electrolyte from the copper tankhouse and fed to a three-stage pressure leaching circuit.

The major portion of the nickel values (80-85%) is preferentially extracted at 280°F and 135 psig in the four-compartment first-stage autoclave . Initially, leaching is carried out under oxidizing conditions in the presence of air or O_2. Later, the admission of oxygen is discontinued to enable dissolved copper to exchange with unleached nickel sulfide. The total retention time in the first-stage autoclave is 3 hours.
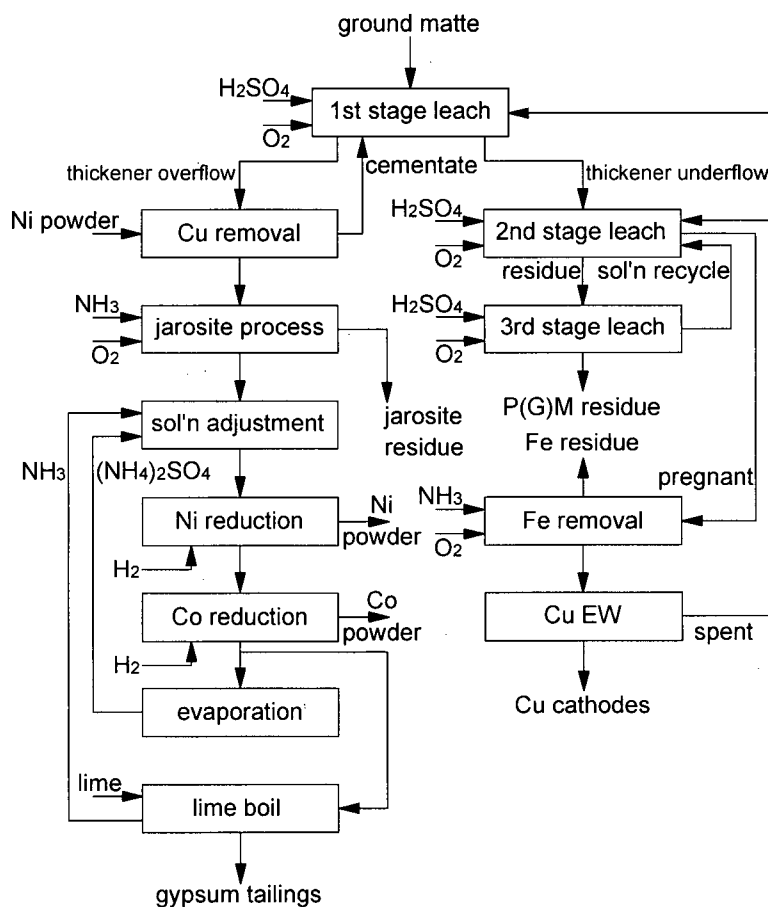
Figure 2-7. Simplified flowsheet of the Impala Platinum nickel-copper refinery (after [34,35]).

The alloy phase and cementate react rapidly in the feed tanks to the first-stage leach:

$$M + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow MSO_4 + H_2O \qquad (2\text{-}41)$$
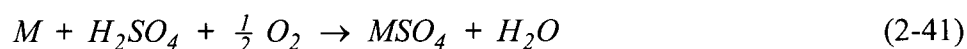
In essence, first-stage leaching can be described by the following reaction chemistry [33,34]:
- oxidative leaching:

$$Ni_3S_2 + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow NiSO_4 + 2\, NiS + H_2O \qquad (2\text{-}28)$$

$$2\, Ni_3S_2 + 3\, H_2SO_4 + \tfrac{3}{2} O_2 \rightarrow 3\, NiSO_4 + Ni_3S_4 + 3\, H_2O \qquad (2\text{-}42)$$

$$3\, Ni_3S_2 + 2\, CuSO_4 + 4\, H_2SO_4 + 2\, O_2 \rightarrow 6\, NiSO_4 + Ni_3S_4 + 2\, CuS + 4\, H_2O \qquad (2\text{-}43)$$

$$5\ Cu_2S\ +\ H_2SO_4\ +\ \tfrac{1}{2}\ O_2\ \rightarrow\ CuSO_4\ +\ Cu_9S_5\ +\ H_2O \tag{2-44}$$

$$Cu_9S_5\ +\ 4\ H_2SO_4\ +\ 2\ O_2\ \rightarrow\ 4\ CuSO_4\ +\ 5\ CuS\ +\ 4\ H_2O \tag{2-45}$$

- non-oxidative leaching:

$$NiS\ +\ CuSO_4\ \rightarrow\ NiSO_4\ +\ CuS \tag{2-46}$$
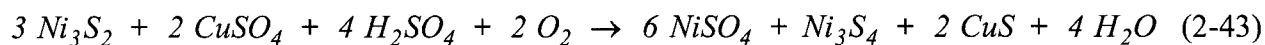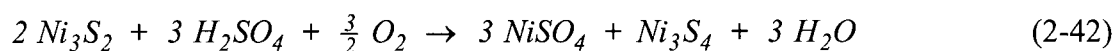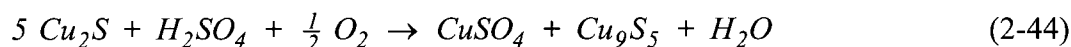
For simplicity of stoichiometry, the formula of digenite, $Cu_{1.76}S$, is represented as Cu_9S_5 in the above reactions.

Leach liquor overflow from the first-stage leach thickener is subjected to two impurity removal processes. First, copper is cemented from solution at pH 2-3 using nickel powder. The cementate is recycled to the first-stage leach. Secondly, the copper-free solution, now containing 100 g/L nickel, is treated in an iron removal stage, which has long been the major bottleneck in the Impala process [35].

Originally, the pH was adjusted with ammonia to 5.5 under aeration to precipitate iron as ferric hydroxide and arsenic as ferric arsenate. The iron-arsenic residue so obtained, unfortunately, also contained copious quantities of co-precipitated nickel and cobalt, and was returned to the smelter to reject iron and recover the sought-after base metals. Arsenic, due to accumulation in the integrated metallurgical flowsheet, reached intolerable levels in the nickel and cobalt recovery circuits. Hence, a separate leach circuit for the residue was developed, which involved a sequence of leaching in sulfuric acid of increasing strength and filtration for recovery of nickel and cobalt, and "bleeding off" of iron and arsenic in a goethite residue. The great number of disadvantages inherent to this leaching process finally led to the implementation of a jarosite process by the late 1980's. Most of the iron, arsenic and lead now leave the hydrometallurgical circuit in a mixed alkali jarosite-ferric arsenate residue.

Filtered solution from the jarosite precipitation stage is prepared for hydrogen reduction by the addition of recycled $(NH_4)_2SO_4$ and NH_3. Nickel powder is precipitated from the resulting ammoniacal nickel "diammine" sulfate solution and either sold as such or briquetted. Cobalt was previously sold in the form of a mixed nickel-cobalt sulfide obtained from the nickel reduction end solution with NaHS, but since 1982 is recovered separately using an altered version of the cobaltic aquopentammine route.

Regeneration of the barren AAS stream regenerates $(NH_4)_2SO_4$ (evaporator) and NH_3 (lime boil) for recycle to the solution adjustment step:

$$Ca(OH)_2 \ + \ (NH_4)_2SO_4 \ \rightarrow \ CaSO_4 \cdot 2H_2O \ + \ 2\,NH_3 \qquad\qquad (2\text{-}47)$$
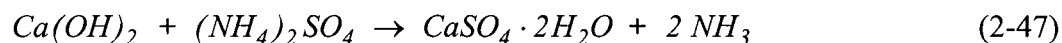
The gypsum formed in reaction (2-47) is pumped to a tailings pond.

The first-stage leach residue is subjected to a second TOL to extract as much of the nickel, copper, cobalt and iron values as possible. The leaching conditions are 275°F, 20 psig partial pressure of oxygen and 4 hours residence time. The main second-stage leaching reactions are (2-45) and:

$$MS \ + \ O_2 \ \rightarrow \ MSO_4 \qquad\qquad (2\text{-}48)$$

$$Ni_3S_4 \ + \ H_2O \ + \ \tfrac{15}{2}\,O_2 \ \rightarrow \ 3\,NiSO_4 \ + \ H_2SO_4 \qquad\qquad (2\text{-}49)$$
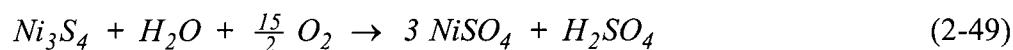
with M = Cu or Ni. Prior to becoming the feed to the copper tankhouse, iron is removed from the second-stage filtrate by oxidation-hydrolysis at pH 2.8 and 180°F. Due to the presence of some co-precipitated copper and nickel, the iron residue is returned to the smelter. Spent copper electrolyte is recycled to the first-stage leach.

The second-stage residue is further treated in a similar third acidic oxidative leaching process to provide a final residue rich in P(G)M's. This residue constitutes the feed to the Impala PGM Refinery. The third stage leach liquor is returned to the second-stage autoclave.

2.3.4.3 Rustenburg Base Metal Refiners

The Rustenburg Base Metal Refiners (RBMR) plant [36,37,38] consists of a PGM enrichment facility and a base metal refinery serving various mines, concentrators and smelters in the Rustenburg district of Transvaal. Hydrometallurgical operations at the integrated Rustenburg Platinum Mines complex, the world's largest producer of PGM's, commenced in 1966. A new refinery with a Sherritt designed leaching circuit was built and commissioned by the end of 1981.

Convertor matte, containing about 43% nickel, 29% copper, 23% sulfur, 1.5% iron and 0.5% cobalt, is cast into ingots at an adjacent smelter and slow-cooled for a period of three days. Following crushing and fine milling, matte is transported to RBMR where it is subjected to magnetic separation. The magnetic alloy fraction then undergoes hydrometallurgical treatment, in order to produce an enriched P(G)M concentrate as a feedstock for the Precious Metals Refinery. The resulting leach solution is pumped to the primary pressure leach, whereas the non-magnetic sulfide fraction of the matte is advanced to the atmospheric leaching stage.

Figure 2-8. Simplified flowsheet of the Rustenburg Base Metal Refiners (RBMR) process [36].

Figure 2-8 is a simplified flowsheet of the RBMR process [36,37]. Fresh matte is contacted with a mixture of primary pressure leach discharge solution and "sulfur removal" solution in a series of four aerated continuous stirred tank reactors. The reactors have a volume of 170 m³ each and the total residence time is 12 hours. The atmospheric copper removal process produces a virtually acid-, copper- and iron-free solution, while stoichiometrically equivalent amounts of nickel pass into solution.

Contrary to the Outokumpu process, copper is precipitated by the *alloy-free* matte either via metathesis with Ni_3S_2 at a solution pH below 2.5:

$$Ni_3S_2 + 2\ CuSO_4 \rightarrow 2\ NiSO_4 + NiS + Cu_2S \qquad (2\text{-}50)$$

or through hydrolysis at a solution pH higher than 2.5. Excess acid is simultaneously removed by the oxidation of heazlewoodite (reaction (2-28)), which really proceeds stepwise through the initial formation of godlevskite, Ni_7S_6:

$$3\ Ni_3S_2\ +\ 2\ H_2SO_4\ +\ O_2\ \rightarrow\ 2\ NiSO_4\ +\ Ni_7S_6\ +\ 2\ H_2O \qquad (2\text{-}51)$$

$$3\ Ni_7S_6\ +\ H_2SO_4\ +\ \tfrac{1}{2}\ O_2\ \rightarrow\ NiSO_4\ +\ 6\ NiS\ +\ H_2O \qquad (2\text{-}52)$$

Reactions (2-51) and (2-52) lower the solution acidity, causing precipitation of antlerite in the pH range 2.5-4.5:

$$3\ CuSO_4\ +\ 4\ H_2O\ \rightarrow\ CuSO_4\cdot 2Cu(OH)_2\ +\ 2\ H_2SO_4 \qquad (2\text{-}53)$$
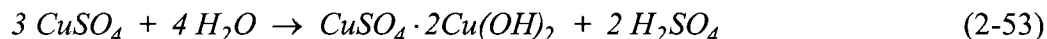
and of ferric hydroxide or parabutlerite in the range 4.5-6:

$$Fe_2(SO_4)_3\ +\ 6\ H_2O\ \rightarrow\ 2\ Fe(OH)_3\ +\ 3\ H_2SO_4 \qquad (2\text{-}54)$$

$$Fe_2(SO_4)_3\ +\ 2\ H_2O\ \rightarrow\ 2\ FeSO_4(OH)\ +\ H_2SO_4 \qquad (2\text{-}55)$$
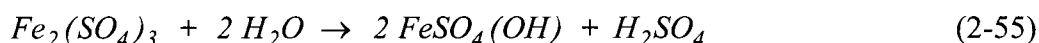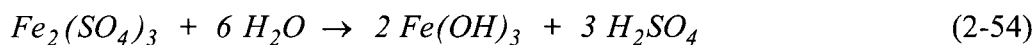
The acid released in the above hydrolysis reactions is consumed by unreacted heazlewoodite and godlevskite. Good aeration is required to promote hydrogen ion removal by reaction (2-51) and (2-52) and shift the equilibrium of reaction (2-53) in favor of antlerite precipitation. Hydrolysis is completed at pH 6, when the atmospheric leaching discharge solution contains less than 10 mg/L each of copper and iron.

Iron rejection is the rate limiting process of the atmospheric leach. Hence, the operating temperature is chosen at 75-80°C where the iron removal rate reaches an optimum. The presence of cupric ion in the feed solution is essential for efficient iron removal.

Although the kinetics of copper rejection through metathesis (reaction (2-50)) are much faster, this mode of operation seems to be unsuitable for mattes with a high iron content. The reason for this is an unacceptably long iron hydrolysis in such instances. Therefore, RBMR operate the copper removal stage at low acidity, necessitating preneutralization of the primary leach liquor to pH 2.5-3 with caustic soda. In this way the kinetics of copper hydrolysis alone determine the outcome of the whole operation, that is, final pH, copper and iron concentrations.

The atmospheric leach slurry is discharged into a large thickener with buffering capacity in the case of process upsets. The impure $NiSO_4$ overflow solution is purified in three steps prior to nickel electrowinning. First, lead is removed with $Ba(OH)_2$. Secondly, cobalt is precipitated using the Outokumpu nickelic hydroxide process. After fine filtration, pregnant nickel electrolyte then enters the tankhouse.

While the lead cake is recycled to the smelter, the cobalt cake is further treated for cobalt recovery. It is first leached with spent nickel electrolyte to redissolve co-precipitated nickel hydroxides. After filtration the enriched cake is then subjected to a reducing leach in a sulfuric acid-formaldehyde solution. Following solution purification, cobalt is extracted using D2EHPA. Finally, the cobalt sulfate strip solution is crystallized to $CoSO_4 \cdot 7H_2O$ for sale. The nickel-containing raffinate is mixed with spent nickel electrolyte and pumped to the "sulfur removal" stage.

In the "sulfur removal" stage the nickel stream is split into two stoichiometric proportions. One part is neutralized to pH 9 with NaOH. The precipitated $Ni(OH)_2$ is filtered on drum filters and redissolved in the remaining volume of spent electrolyte. Since the redissolved cake contains some lead (from anodes) and copper (from busbars) generated during nickel electrowinning, it is recycled to the copper removal stage. The neutralization filtrate is processed in the Na_2SO_4 plant into salable anhydrous crystals.

Thickener underflow slurry is pumped to the primary pressure leach at 135°C and 1050 kPa in a four-compartment horizontal Sherritt autoclave with a working volume of 80 m^3. Spent copper electrolyte is used as the source of acid. Only the leading two compartments are aerated to ensure maximum nickel solubilization; the last two compartments are operated without air to reprecipitate part of the copper in solution. The total residence time in the primary leach amounts to 4 hours. Following liquid-solid separation, the primary leach residue is advanced to the secondary leach. About 80-85% nickel extraction is achieved in the combined copper removal and primary leach stages.

After feed preparation and preheating, the atmospheric solids are essentially a mixture of djurleite ($Cu_{1.93}S$), taken as Cu_2S for simplicity reasons, and millerite. The major reactions taking place during the oxidizing period are dissolution of nickel from millerite:

$$4 \, NiS + H_2SO_4 + \tfrac{1}{2} \, O_2 \rightarrow NiSO_4 + Ni_3S_4 + H_2O \qquad (2\text{-}29)$$
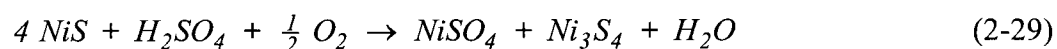
and copper from djurleite:

$$Cu_2S + H_2SO_4 + \tfrac{1}{2} \, O_2 \rightarrow CuSO_4 + CuS + H_2O \qquad (2\text{-}56)$$
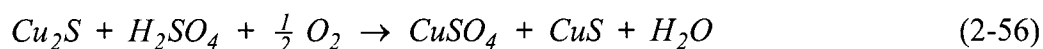
Furthermore, a substantial part of the nickel passes into solution by direct oxidation of millerite:

$$NiS + 2 \, O_2 \rightarrow NiSO_4 \qquad (2\text{-}57)$$

During the non-oxidizing period a large quantity of copper is precipitated through metathesis:

$$NiS + CuSO_4 \rightarrow NiSO_4 + CuS \qquad (2\text{-}46)$$

The drop in pH observed in this stage is believed to be due to a reaction between polydymite and cupric ion. Although the actual mechanism likely involves the formation of a range of non-stoichiometric metal sulfides prior to the formation of a discrete digenite (Cu_9S_5) phase, the overall reaction can be conveniently represented by:

$$4 Ni_3S_4 + 9 CuSO_4 + 8 H_2O \rightarrow 3 NiSO_4 + 9 NiS + Cu_9S_5 + 8 H_2SO_4 \qquad (2\text{-}58)$$
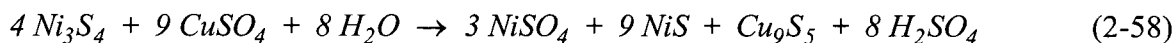
In addition, digenite may be formed in-situ by a solid phase interaction between the covellite surface layer and the residual djurleite core:

$$4 Cu_2S + CuS \rightarrow Cu_9S_5 \qquad (2\text{-}59)$$

Clearly, it is important the nickel extraction be limited during the oxidizing period to leave a sufficient quantity of nickel sulfides for copper precipitation.

Secondary pressure leaching is carried out at 145°C and 1050 kPa in autoclaves similar in construction to the primary ones. Again, spent copper electrolyte is used as the source of acid. Aeration with oxygen-enriched air [38] ensures complete dissolution of copper (98%) and nickel (99%). The overall retention time is normally 8 hours. The major reaction in the initial phases of oxidation is the decomposition of digenite:

$$Cu_9S_5 + 4 H_2SO_4 + 2 O_2 \rightarrow 4 CuSO_4 + 5 CuS + 4 H_2O \qquad (2\text{-}45)$$
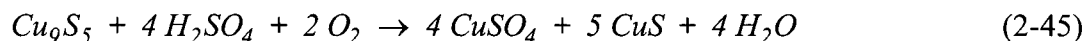
The generated covellite is either directly oxidized to copper sulfate:

$$CuS + 2 O_2 \rightarrow CuSO_4 \qquad (2\text{-}22)$$

or can be decomposed to elemental sulfur:

$$CuS + H_2SO_4 + \frac{1}{2} O_2 \rightarrow CuSO_4 + S° + H_2O \qquad (2\text{-}60)$$
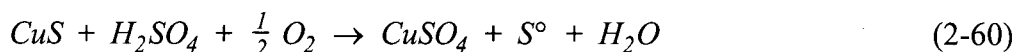
Reactions (2-45) and (2-22) occur simultaneously, oxidized covellite being substituted by covellite generated from digenite, so initially no change occurs in the CuS content of the solids. As the dissolution of copper subsulfides (reaction (2-36)) is kinetically very rapid, the overall leaching time is determined by the oxidation of covellite (reaction (2-22)). The decomposition of CuS according to reaction (2-22) is catalyzed by iron.

Residual polydymite dissolves according to the overall stoichiometry:

$$Ni_3S_4 + H_2O + \frac{15}{2}O_2 \rightarrow 3\,NiSO_4 + H_2SO_4 \tag{2-49}$$
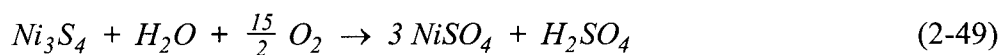
However, the reaction sequence for the decomposition of (copper-bearing) polydymite remains obscure. Millerite is partially converted to polydymite (reaction (2-29)) and partially directly oxidized to $NiSO_4$ (reaction (2-57)).

Iron is precipitated in the form of hematite and sodium jarosite ($NaFe_3(SO_4)_2(OH)_6$). After filtration and washing, the final iron-rich leach residue, the only outlet for iron entering the RBMR process, is treated pyrometallurgically to separate it into a copper bullion containing residual P(G)M's and gold, and a copper matte with silver and other, mostly non-metallic impurities. The bullion is recycled to the convertors, whereas the matte is sold to an overseas refiner.

The copper-rich filtrate is diluted with spent electrolyte to avoid crystallization of $CuSO_4$ and treated with SO_2 in Sherritt's patented selenium removal process. Selenium cake, due to its PGM content, is combined with the secondary leach residue for further treatment.

No further purification other than solution clarification is required in the copper circuit, and the solution, now containing 75 g/L copper, 30 g/L nickel and 60 g/L acid, enters the copper tankhouse. As mentioned, spent copper electrolyte is recycled to both pressure leach stages to supply acid for the dissolution of the base metals.

2.3.4.4 Western, Barplats and Northam Platinum

The Sherritt nickel-copper matte acid leach process in its most recent state of development employs two-stage rather than three-stage leaching. Furthermore, the use of autoclaves has been minimized to just one stage. Figure 2-9 is a conceptual flowsheet of the process practiced at the Western Platinum [39] and Northam Platinum [40] base metal refineries. Barplats Platinum only shortly operated a similar process [40,41].
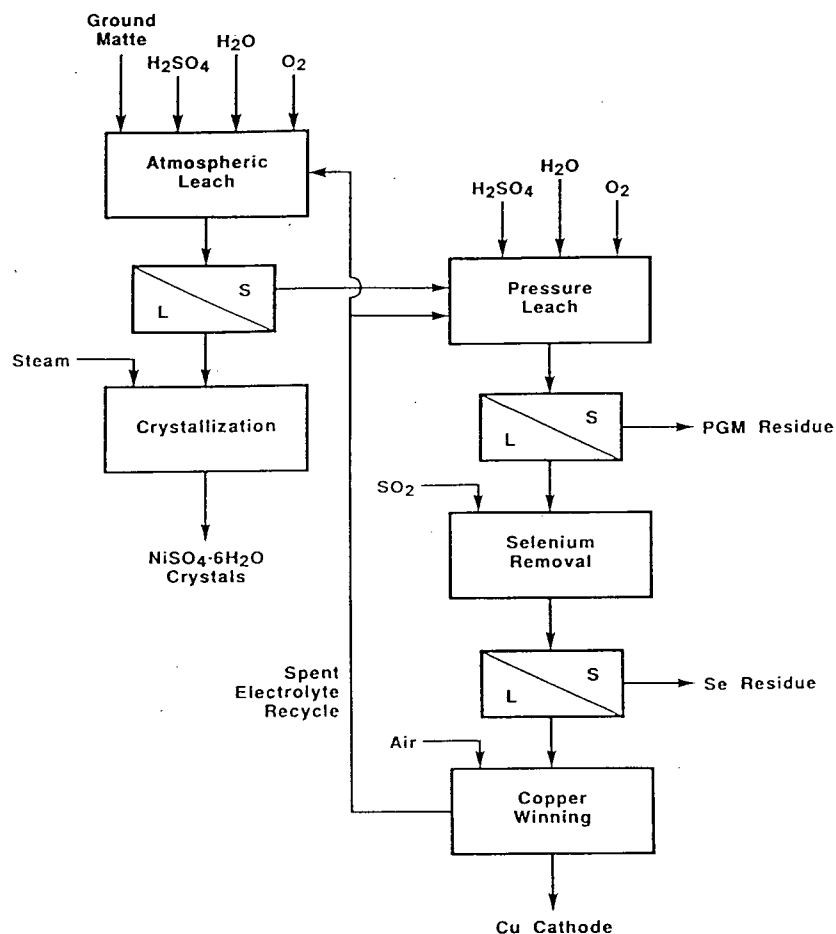
Figure 2-9.   Conceptual flowsheet of the Western, Barplats and Northam Platinum
nickel-copper refineries [41].

Although a first-stage pressure leach provides an improved separation of nickel from copper and thus permits the production of higher grade copper cathode, atmospheric leaching at 85-90°C in a cascade of agitated tanks is preferred for the small-scale operations discussed in this section. In the interests of simplicity and low capital costs, relatively pure $NiSO_4 \cdot 6H_2O$ for upgrading elsewhere is crystallized from the atmospheric leach solution.

The second-stage leach, which is designed to yield maximum extraction of nickel, copper and sulfur while leaving the P(G)M's intact, is a pressure leach operating at 150-160°C under 150-350 kPa partial oxygen pressure. After pressure filtration, the second-stage leachate is treated with SO_2 to eliminate selenium prior to copper electrowinning. Due to the higher nickel content of the copper electrolyte, copper electrodeposition is typically carried out at a somewhat lower current density. Spent copper electrolyte is recycled to provide the acid required in the two leaching stages. The P(G)M's are recovered as a high-grade concentrate in the second-stage residue and in the copper selenide precipitate emanating from the selenium removal process.

2.3.5   Mansfeld Kombinat technology

All of the previous sections deal with the hydrometallurgical processing of *primary* nickel-copper matte. The Nickelhütte Aue of the VEB Mansfeld Kombinat in former East Germany operates a leaching process for the treatment of a *secondary* matte produced from several secondary and internally generated revert materials. The final products are cathode nickel or $NiSO_4$, cathode copper and cobalt oxide. The following paragraph compiles the limited information available about the leaching practice [42,43].

The matte is ground to 100% minus 100 μm, and subjected to batch pressure leaching at 130°C and 0.5-1 MPa partial oxygen pressure in one of three 20 m^3 autoclaves. The working volume of each autoclave is 10 m^3, and the total duration of the heating-leaching-cooling cycle is 12 hours. Oxygen is introduced through the hollow shaft of the gas pumping impeller. The leach filtrate typically contains 50-80 g/L nickel, ≤ 15 g/L copper, ≤ 3 g/L cobalt, 2-5 g/L iron and 20-30 g/L H_2SO_4. To avoid pressure filtration problems, low matte iron contents are preferred.

2.4   Nitrate Lixiviants

Matte leaching in nitrate lixiviants has never been commercialized, however, it was investigated extensively by SLN in France in the mid 1970's. Before the company finally adopted the all-chloride route described in section 2.2.2, various hydrometallurgical processes for nickel production were evaluated, including two process variants which utilized nitric acid in the leaching stage [44].

The common first step of both piloted processes comprised the oxidative leaching of matte from New Caledonia, containing 75% nickel, 0.04% copper, 20% sulfur, 2.5% iron and 1.9% cobalt, in a nitric acid solution at atmospheric pressure and 90°C. Nitrous gases generated during leaching were reconverted to HNO_3. The principal leaching reactions were:

$$Ni + 2\,HNO_3 \rightarrow Ni(NO_3)_2 + H_2 \tag{2-61}$$

$$Ni_3S_2 + 2\,HNO_3 + 4\,O_2 \rightarrow 2\,NiSO_4 + Ni(NO_3)_2 + H_2 \tag{2-62}$$
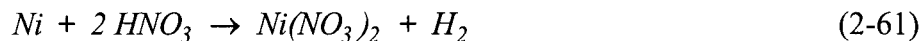
Since nitrate had to be removed from the leach solution prior to subsequent process steps, leaching was followed by a sulfation step. Here, sulfuric acid was added to the slurry in order to displace nitrate ion and satisfy the stoichiometry:

$$"Ni_2S" + H_2SO_4 + 2 O_2 \rightarrow 2 NiSO_4 + H_2 \qquad (2\text{-}63)$$

wherein "Ni_2S" represents the average overall composition of the matte.

The crude nickel sulfate-nitrate solution was purified by simultaneous hydrolysis of iron and precipitation of copper and zinc with H_2S at pH 4. Cobalt was precipitated using either nickelic hydroxide or NaClO. The pure $NiSO_4$-$Ni(NO_3)_2$ solution was then subjected to a denitrification step. Nitrate separation was carried out either "directly" through selective crystallization of $NiSO_4$ or "indirectly" by precipitation of a basic nickel carbonate (BNC). Electrolyte was prepared from the nitrate-free nickel feed by redissolution of the nickel sulfate crystals in water or by the dissolution of BNC in sulfuric acid:

$$NiCO_3 \cdot 3Ni(OH)_2 + 4 H_2SO_4 \rightarrow 4 NiSO_4 + CO_2 + 7 H_2O \qquad (2\text{-}64)$$
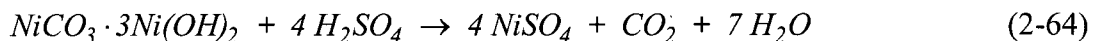
Finally, nickel was recovered through electrowinning.

Both process variants were abandoned because of high operating costs due to severe operating difficulties, including high nickel losses in the purification stage, insufficient cathode impurity and unacceptably high anode corrosion rates.

CHAPTER 3

DEVELOPMENT OF POURBAIX DIAGRAMS FOR THE SYSTEMS ARSENIC-SULFUR-WATER AND NICKEL-SULFUR-WATER

3.1   Introduction

Pourbaix diagrams, despite their limitations, are excellent tools for the study of the thermochemistry of metal-ligand-water systems. In this chapter, therefore, an attempt is made to develop potential-pH diagrams for the system arsenic-sulfur-water at 25 and 160°C, the latter being the temperature at which the First-Stage Leach (FSL) process at INCO's Copper Refinery currently operates. For reasons that will become clear in Chapter 5, an E_h-pH diagram for the system nickel-sulfur-water at room temperature is also computed. Species sets, thermodynamic data and the framework of the the spreadsheet calculations pertaining to the high-temperature arsenic diagram are included in Appendix A.

The diagrams are generated with the aid of the powerful CSIRO Thermochemistry System (Version V) software. For aqueous species, the recent IUPAC thermochemical data compiled by Bard *et al.* [45] are preferred over the older NBS values by Wagman *et al.* [46]. Additional free energy data for aqueous arsenic and nickel species are taken from Robins [47] and Pourbaix [48], respectively. Heat capacity data for hydrogen, oxygen, arsenic and sulfur - in the form of polynomial equations relating C_p^o to temperature - are taken from Rao [49]. Barin's volumes [50] are utilized as a source of standard entropy values of pure compounds at 25°C. Likewise, the Gibbs free energies of formation of all mineral phases, gases and water are obtained from Barin's tables either directly or by linear interpolation.

3.2   Sulfur-Water Diagrams

Although a complete review of the theory of Pourbaix diagrams is beyond the scope of this thesis, the system sulfur-water warrants special attention.

For thermodynamic analysis of many hydrometallurgical systems involving sulfur as a ligand, the great number of aqueous sulfur species can conveniently be reduced to hydrogen sulfide and its ionization products, rhombic sulfur, and bisulfate and sulfate ions. Figure 3-1 is the "standard" S-H_2O diagram at 25°C and unit activity of those species. The host of - mostly metastable - ions

not considered here includes thiosulfate, polythionates, polysulfides, peroxydisulfate as well as dissociation products of sulfurous and "Caro's acid".
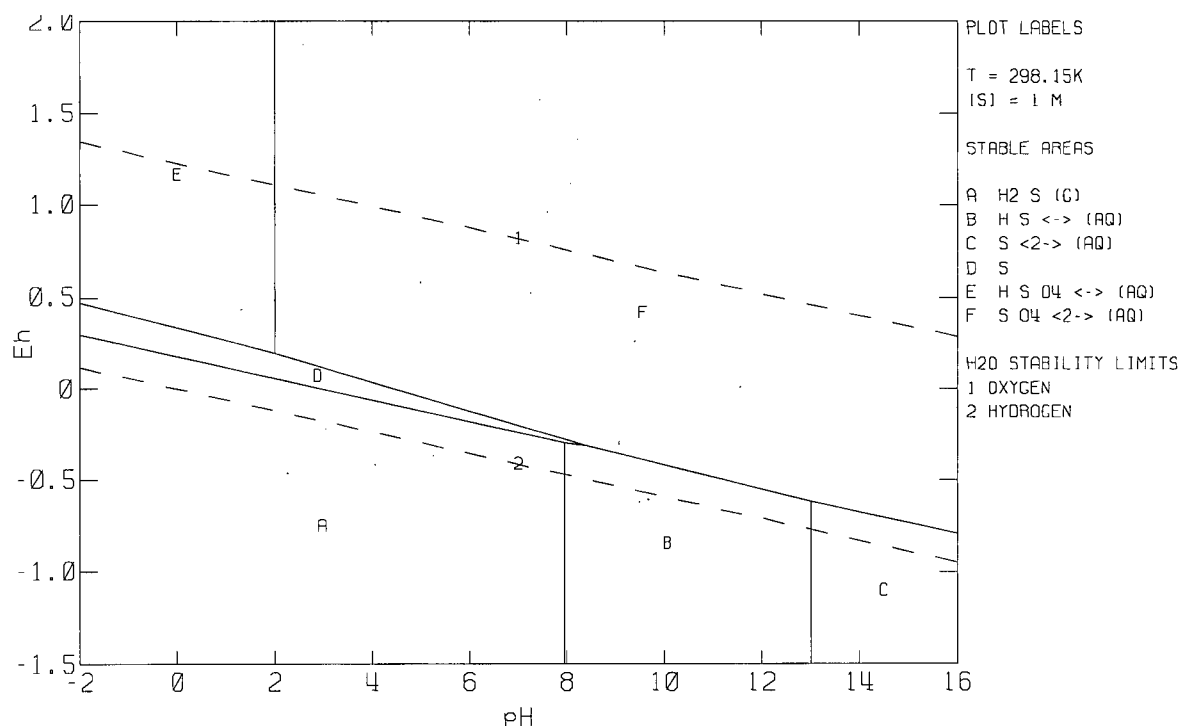
Figure 3-1.   "Standard" sulfur-water diagram at 25°C with 1 atm gas pressure and unit
activity of all solutes.

Although realistic in the field of geochemistry when the lines in the diagram are likely to present true equilibria reached after millions of years, Figure 3-1 is largely unuseful in hydrometallurgy. It is well known that elemental sulfur is not oxidized to sulfate by ferric ion at ambient conditions.   Relying on such experimental hindsights, the "stability" (really metastability) of elemental sulfur may be artificially increased by 300 kJ/mole (after E. Peters).   Since the sulfur-sulfide equilibria must not be disturbed, this is done by making the Gibbs free energies of formation of the sulfate and bisulfate ion less negative by this amount.   The lines for the "equilibria":

$$SO_4^{2-} + 8\,H^+ + 6e^- \leftrightarrow S^\circ + 4\,H_2O \tag{3-1}$$

and:

$$HSO_4^- + 7\,H^+ + 6e^- \leftrightarrow S^\circ + 4\,H_2O \tag{3-2}$$
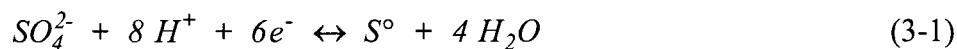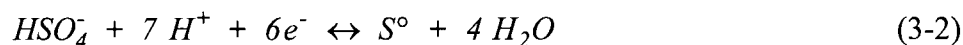
are thus shifted upwards in the diagram by 0.5 V (50 kJ/eq). The result of this operation can clearly be seen in the "extended" sulfur-water diagram of Figure 3-2.
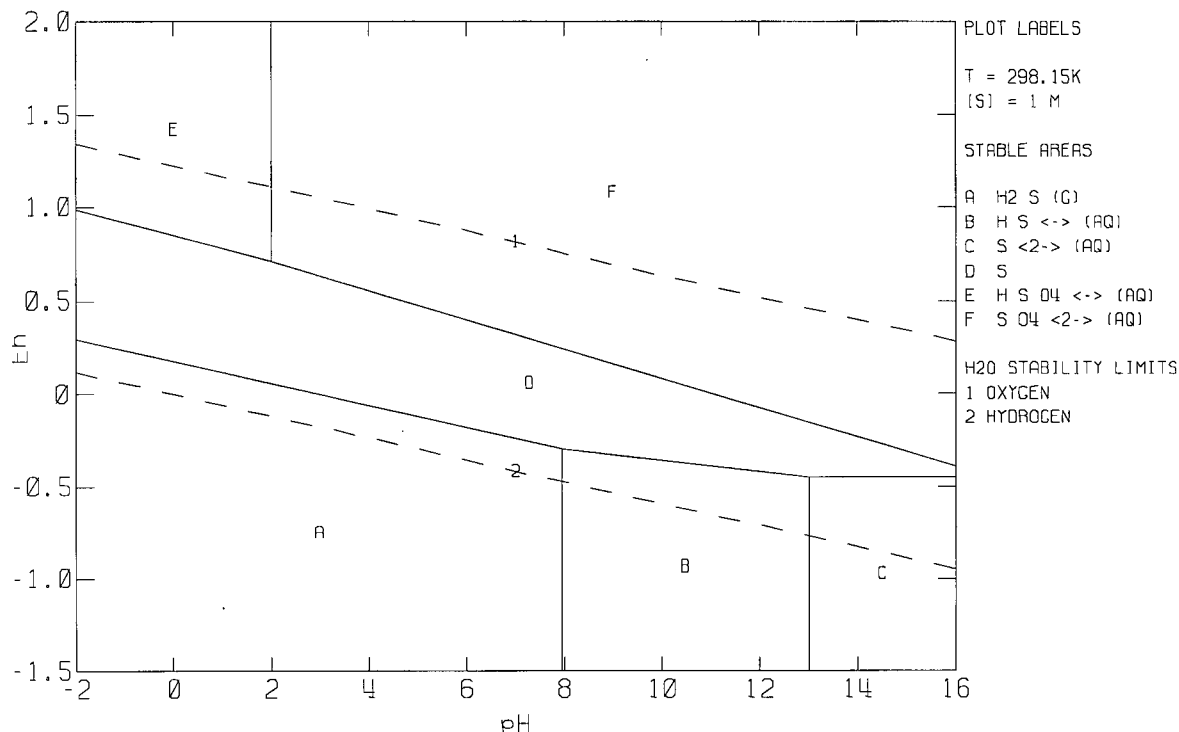
Figure 3-2.   "Extended" sulfur-water diagram at 25°C with 1 atm gas pressure and unit activity of all solutes.

In accordance with the practice in established works, particularly Pourbaix's Atlas [48], the pH scale in the sulfur-water diagrams ranges from -2 to 16. It is noted, however, that these lower and upper pH values represent physically impossible acid and alkali concentrations, respectively, and are therefore really thermodynamic fiction. Moreover, at very high acid or alkali concentrations the concept of the "aqueous" system no longer holds.

3.3   Arsenic-Sulfur-Water Diagrams

Arsenic, like sulfur, forms a large number of species in aqueous solution. Considered in the present analysis of the $As-S-H_2O$ system are arsine gas (AsH_3), the As(III) arsenyl ion (AsO^+), as well as meta-arsenious acid ($HAsO_2$), ortho-arsenious acid (H_3AsO_3) and arsenic acid (H_3AsO_4) and their deprotonation products. Left out of the calculations are other arsenic hydrides, such as diarsane (As_2H_4), the As(V) arsenyl ion (AsO_2^+), the perarsenyl ion (AsO_3^+) and all thioarsenite and thioarsenate species.

The only solid phases included in the development of the diagrams are the grey, rhombohedral allotropic form of metallic arsenic, claudetite (monoclinic As_2O_3), realgar (AsS) and orpiment (As_2S_3).

3.3.1 Ambient temperature

Figure 3-3 shows the extended As-S-H_2O diagram at 25°C with 1 atm gas pressure and unit activity of all solutes.
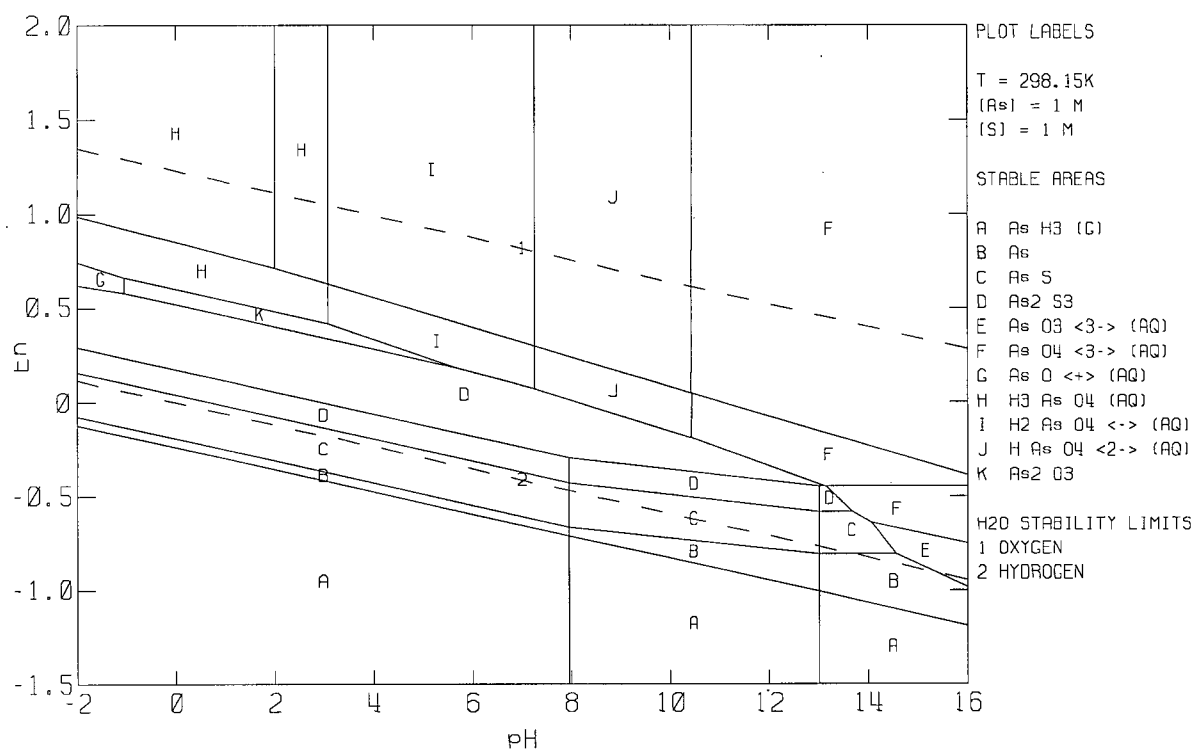
Figure 3-3.   Extended arsenic-sulfur-water diagram at 25°C with 1 atm gas pressure and
                1 molal activity of aqueous arsenic and sulfur species.

The number of unstable aqueous species at the conditions for which Figure 3-3 is generated is limited to monomeric meta-arsenious acid and its dissociation product, and the mono- and di-protonated ortho-arsenious acid ions.

Realgar does not appear in the diagram when Barin's Gibbs free energy of -133.004 kJ per mole As_4S_4 is used. Since the mineral is commonly found in natural deposits, this value seems to be unreliable. Indeed, mineralogical thermodynamic data compiled by Robie *et al.* [51] and Vaughan and Craig [52] list a free energy of approximately -71 kJ per mole AsS. The adopted USGS value of -70.32 kJ/mole does produce the expected rim of realgar below the As_2S_3 region.

Unfortunately, no high-temperature USGS data are available, and a Barin value will be used in the As-S-H$_2$O diagram at 160°C.

Upon lowering of the metalloid activity to 10^{-3} molal, the stability region of As$_2$O$_3$ is "replaced" by that of H$_3$AsO$_3$. Moreover, a window for the di-ortho arsenite ion then appears, which, like the areas of predominance of all other aqueous arsenic species, grows at the expense of the orpiment domain when the arsenic solute activity is further decreased.

3.3.2   Elevated temperature

In order to calculate the high-temperature As-S-H$_2$O diagram, the Gibbs free energies of formation of all aqueous species at 160°C have to be computed using the Criss and Cobble theory [53,54,55].

The Criss and Cobble theory was developed in the mid 1960's. It is based on the so-called entropy correspondence principle. This principle implies that a standard state can be chosen at every temperature such that the entropies of a certain category of ions at that temperature are linearly related to their corresponding standard entropies at some reference temperature (usually 25°C). The standard state has to be chosen properly by fixing the entropy of H$^+$ at each temperature [53]. Once the entropy of an ion at elevated temperature has been estimated, the average value of its heat capacity can be calculated [54]. The change in heat capacity of the ion formation reaction is then combined with values of ΔS°_{298K} and $\Delta G^{\circ}_{f,298K}$ for that reaction to calculate $\Delta G^{\circ}_{f,TK}$.

Two problems arise when the empirical theory is applied to the present system: (1) unknown standard ionic entropies, and (2) classification of oxy-cations, complex non-oxy-anions and undissociated species.

The Criss and Cobble calculations require an initial value of the standard entropy of each aqueous species. Unfortunately, for the arsenyl, di-ortho-arsenite and ortho-arsenite ions that number is not available and needs to be estimated.

A value of 12.52 J/mole/K for S°_{298K} *(AsO$^+$)* is estimated using Latimer's method [56]. The standard entropies of the mono-protonated ortho-arsenite and ortho-arsenite ions are estimated on the basis of the dissociation series of arsenic acid. It is assumed that the stepwise decrease in entropy for the ortho-arsenious acid dissociation series is proportionally the same as for arsenic acid. This engineering approach gives -35.1 and -248.9 J/mole/K for S°_{298K} *(HAsO$_3^{2-}$)* and S°_{298K} *(AsO$_3^{3-}$)*, respectively, as rough starting values for the calculations.

Within the framework of the Criss and Cobble theory, ions are classified as simple cations, simple anions (and OH$^-$), oxy-anions and acid oxy-anions. Therefore, likely erroneous assumptions have to be made for cationic hydrolysis species such as the arsenyl ion, and acid anions like the bisulfide ion.

Since there is some evidence that the entropies of oxy-cations such as the uranyl ion (UO_2^{2+}) lie near the correspondence diagram for simple cations [53,55], AsO^+ is assumed to be part of this category in the spreadsheet calculations. Bisulfide ion is classified as a simple anion in the present analysis.

Undissociated species, such as the weak As(III) and As(V) acids, have no charge and cancel Criss and Cobble's distinction between the "conventional" and "absolute" entropy scales. Neutral aqueous complexes, therefore, must be treated separately according to Helgeson's theory [57].

Like Criss and Cobble, Helgeson utilizes entropies as an entry into the problem of predicting thermochemical properties in solutions at elevated temperatures. In his theoretical interpretation of an isothermal entropy cycle for an arbitrary dissociation reaction, Helgeson separates entropies into hypothetical electrostatic and non-electrostatic terms. Thus, the temperature dependence of the thermodynamics of dissociation for complexes is described in terms of functions involving the dielectric constant of water and a power series consistent with non-electrostatic interaction in the absence of a dielectric medium.

Although the concept of his theory may be abstract, Helgeson's equations are quite practical to use after the proper assumptions. Furthermore, they are fully compatible with the Criss and Cobble calculations.

Figure 3-4 shows the extended As-S-H$_2$O diagram at 160°C with 1 atm gas pressure and unit activity of all solutes. The equations used in the development of this figure are summarized in Appendix A. Many of the calculated free energy values at 160°C have been verified by comparison with those computed at 150°C by Barner and Scheuerman [58].

In the interpretation of Figure 3-4 it should be borne in mind that the concept of the "neutral pH" condition changes with temperature due to variation of the dissociation constant of water. It can easily be calculated that pK_w is in the vicinity of 11.5 at 160°C. This gives a pH of approximately 5.75 for equimolal activities of protons and hydroxyl ions.
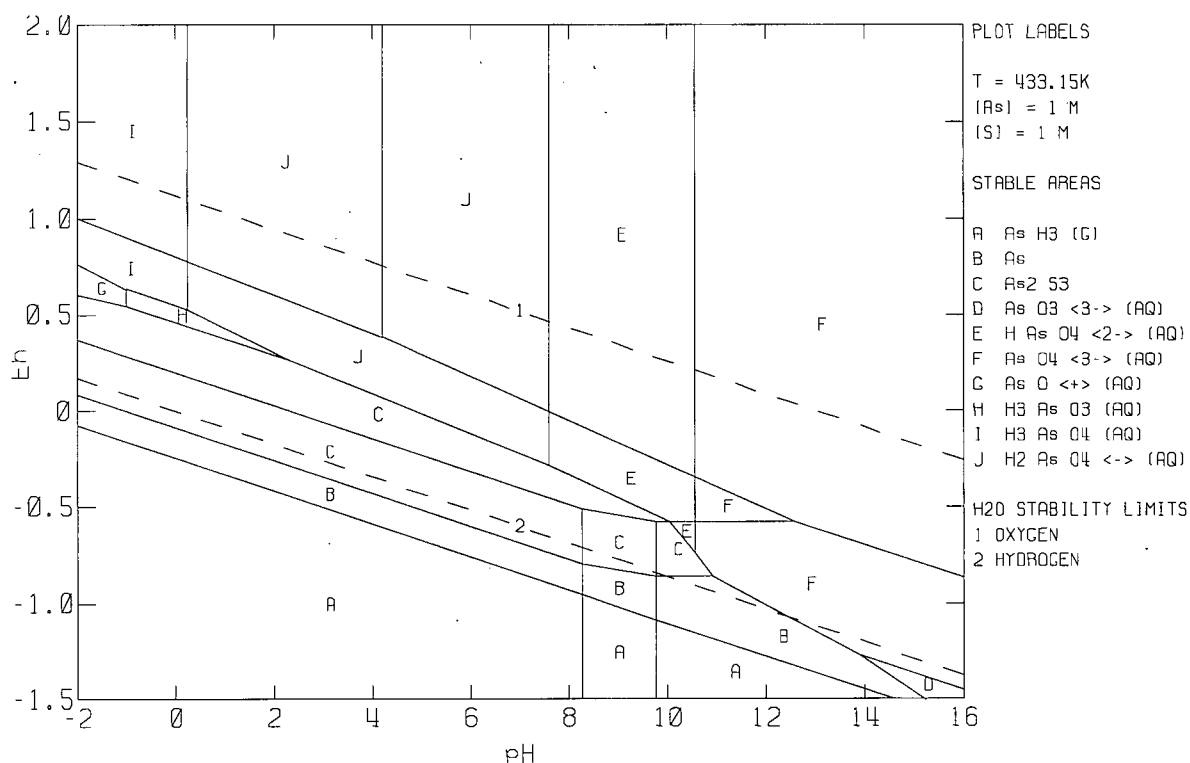
Figure 3-4.   Extended arsenic-sulfur-water diagram at 160°C with 1 atm gas pressure and
             1 molal activity of aqueous arsenic and sulfur species.

The (sulfur) ligand equilibria must be interpreted with caution. Many uncertainties surround the ambiguous ionization of the bisulfate ion. Since the association of protons and sulfate weakens with increasing ionic strength, the bisulfate buffer point for practical solutions at ambient temperature is probably closer to pH 0 than 2 (after E. Peters). Comparing the stability regions of bisulfide ion in Figure 3-3 and 3-4, it shows that HS⁻ becomes an increasingly strong acid as the temperature rises. At very high temperature it actually becomes a stronger acid than hydrogen sulfide and ceases to be an important dissolved sulfur species [55].

Realizing that the size and location of predominance areas of the arsenic species in the As-S-H_2O diagram at elevated temperature are only as accurate as the thermodynamic data they are the result of, it appears that the arsenic oxide is no longer stable at the conditions of Figure 3-4. Besides the generally steeper lines in the diagram, the large stability regions of the arsenate ion and its di-protonated counterpart are also striking features of the high-temperature system. As mentioned before, the disappearence of the realgar band can be attributed to questionable thermodynamic data.

As for the status of high-temperature aqueous thermodynamics, the Criss and Cobble theory seems to be one of the few practical ones available. It has become evident in this chapter that Criss and Cobble's theory requires revision. Despite its age and non-fundamental character, however, it remains helpful in the study of high-temperature systems in hydrometallurgy. Greater accuracy in the calculation of thermodynamic data at elevated temperature, although desirable from an academic point of view, is likely trivial to industrial processes given the variations in the temperature at which reactors such as the FSL autoclave actually operate.

3.4   Nickel-Sulfur-Water Diagram

Figure 3-5 shows the extended Ni-S-H_2O diagram at 25°C with 1 atm gas pressure and unit activity of all solutes. It is generated with the reducing conditions after copper depletion of a FSL batch in mind. This confines the aqueous nickel species of interest to those formed by the metal in its divalent state. In addition to Ni^{2+}, $NiOH^+$ (high acidity) and $HNiO_2^-$ (high alkalinity) are also considered. The solid phases included in the development of the diagram are bunsenite (NiO), millerite (NiS) and heazlewoodite (Ni_3S_2).
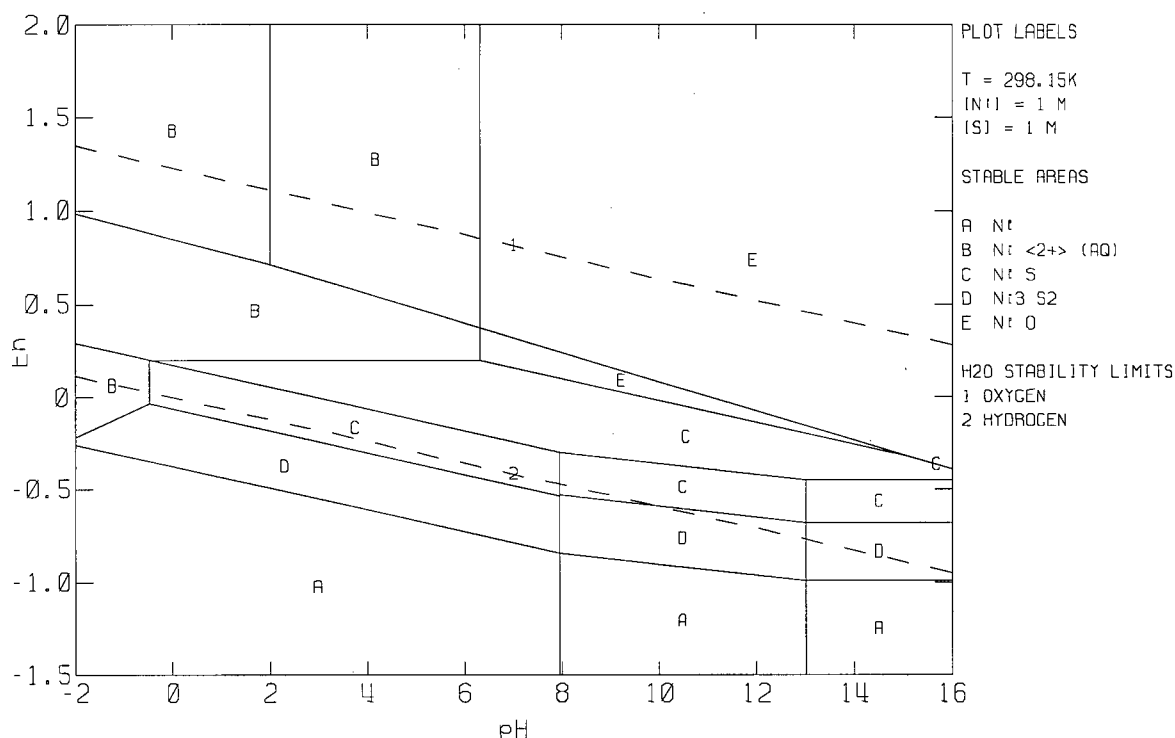
Figure 3-5.   Extended nickel-sulfur-water diagram at 25°C with 1 atm gas pressure and 1 molal activity of aqueous nickel and sulfur species.

The behavior of nickel at low potentials will be adressed in Chapter 5.

CHAPTER 4

EXPERIMENTAL WORK

4.1   Sampling Program

Since IPC residue is highly sensitive to oxidation by air, special measures have to be taken to preserve the freshness of samples of the carbonylation residue during long-term storage. On the basis of INCO's experience with various methods of sample preparation and storage, it was decided to freeze the samples as wet cakes for the present investigations.

Figure 4-1.   Sample taking from the sample point of the IPC thickener underflow line.

In May, 1994, a sampling campaign was undertaken at INCO's CRED plant in Copper Cliff, Ontario, to obtain representative IPC feeds for both the preliminary test work on site and the leaching program to be carried out at UBC. During the 16-day period from May 9 to 24, at least four slurry samples of approximately 500 mL each were drawn daily from the sample point of the IPC thickener underflow line depicted in Figure 4-1.

Sampling was done in the early morning. Two by two the bottle contents were quickly filtered over Büchner funnels under vacuum and washed thoroughly with distilled water. The IPC filter cakes were then transferred onto watch glasses.

A head sample was composed of several spatula scoops from all cakes. Bits of material were selected from several parts of the cakes and, in view of possible particle segregation within the cakes, care was taken to extract the entire cake thickness.

The filter cakes were put in nitrogen-purged double plastic bags, labeled and temporarily stored on ice in a cooler. Every 2 or 3 days all daily samples from the cooler were shipped to a freezer at the Clarabelle Mill.

The head sample was repulped in distilled water, filtered under vacuum and washed with approximately 250 mL of methanol. To ensure effective displacement of residual water in the cake pores, methanol was added just before cake cracking commenced. The methanol-treated cake was transferred quantitatively onto a watch glass and dried in a vacuum desiccator. The dry solids were submitted for assay at INCO's Copper Cliff Central Process Technology Laboratory.

The samples were trucked to UBC in frozen state on May 25. They arrived in good shape in Vancouver on May 30 and were immediately stored in a freezer in the Corrosion Laboratory. All 66 samples were kept congealed until use in the leaching program.

4.2   Leaching Program

4.2.1   Scope

The FSL process parameters investigated in the present leaching program are summarized in Table 4-1.

Table 4-1.   Summary of First-Stage Leach (FSL) parameters investigated in the leaching
program.

Physicomechanical parameters	agitation rate	
	pulp density	
	temperature	
	retention time	
Chemical parameters	composition of IPC residue	Cu : S_{tot} ratio
	composition of electrolyte	copper concentration
		acid concentration
		effect of organic additives
		effect of arsenic

In addition to the 66 autoclave tests carried out as part of this program, a number of releaching experiments were performed with FSL residues of the copper-depleted source in two different media. The purpose of those tests was to acquire more specific information on the behavior of arsenic.

Earlier proposed autoclave runs with IPC residues "doped" with particular mineral phases such as pentlandite $((Ni,Co,Fe)_9S_8)$, trevorite $(NiFe_2O_4)$ and domeykite (Cu_3As) were canceled when it became apparent that specimens of those minerals of acceptable purity were not readily available. After reconsideration, plans for a series of experiments involving air discharge of pressure leached slurry were also dropped.

4.2.2   Batch make-up

The "recipe" for the first-stage leaching tests was obtained through downscaling of the actual FSL process (Appendix B), taking into account information from shift reports on recent trends in the preparation of FSL batches. The physical limits of the Parr laboratory reactor for safe operation were also incorporated in the calculations. The "standard" laboratory FSL batch consisted of 360 g of IPC residue (dry basis), 700 mL of synthetic electrolyte, and 500 mL of either distilled or deionized water to simulate the steam condensate formed in the plant. The choice for synthetic electrolyte was based on expected undesirable aging phenomena with plant electrolyte, such as precipitation and degradation of organic additives.

Given a density of 1230 kg/m^3 for laboratory electrolyte containing 45 g/L copper and 220 g/L acid, the solids content of the "standard" slurry was 21% (wt.). Contrary to plant

practice, batch make-up was usually not modified for different IPC feed compositions in the laboratory.

4.2.3   Electrolyte preparation

Synthetic electrolyte was prepared fresh for each leaching test. It was made by dissolving the appropriate amounts of reagent-grade $CuSO_4 \cdot 5H_2O$ and concentrated H_2SO_4 in distilled (Copper Cliff) or deionized (Vancouver) water in a 1 L volumetric flask, which was diluted to volume only after cooling to room temperature.

For the autoclave runs involving the use of organic additives, aqueous stock solutions of 10 g/L of both leveling agent (Crodaglu 1M44) and anti-misting agent (Dowfax 2A0) were prepared. Small quantities of both reagents were received from the CRED plant. Crodaglu was carefully dissolved in hot water of 40-50°C, and all animal glue "solutions" were stored in a refrigerator to avoid degradation of the natural macromolecules. After three days of storage they were discarded. Solutions of the Dow surfactant were gently homogenized to avoid excessive foaming. The desired quantity of organic reagents was pipetted into the electrolyte from dilute additive solutions.

Since the oxidation state +3 of arsenic is predominant at FSL conditions, reagent-grade anhydrous sodium meta-arsenite ($NaAsO_2$) was utilized as a source of arsenic for electrolytes "spiked" with this element. It was found that As(III) can be conveniently dissolved in a neutral copper sulfate solution through the intermediate copper arsenite "Scheele's green" [59]:

$$CuSO_4 + 2\ NaAsO_2 + x\ H_2O \rightarrow Cu(AsO_2)_2 \cdot xH_2O + Na_2SO_4 \qquad (4\text{-}1)$$
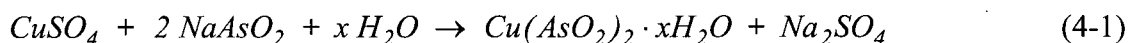
The hydrated green precipitate was obtained by mixing $CuSO_4$ and $NaAsO_2$ in a small volume of water. It redissolved instantaneously upon acidification with the simultaneous release of copper and trivalent arsenic into solution:

$$Cu(AsO_2)_2 \cdot xH_2O + 2\ H_2SO_4 \rightarrow CuSO_4 + (AsO)_2SO_4 + (2+x)\ H_2O \qquad (4\text{-}2)$$
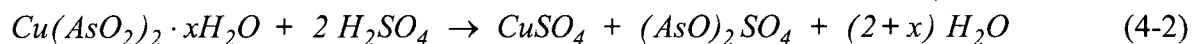
Oxidation of As(III) to As(V) by air is negligible at room temperature because of unfavorable kinetics [47]. Let it also be noted that, contrary to oxidative sodium-iron-sulfate-containing leaching systems, the precipitation of sodium jarosite is not of concern under the metathetic conditions prevalent in the FSL process.

4.2.4   Equipment

4.2.4.1 Autoclaves

At the CRED laboratory a standard 2 L all-titanium Parr autoclave with Teflon liner was used. Temperature control was achieved manually both by adjusting the amount of electric current admitted to the heating mantle with a transformer, and by regulating the flow of cooling water through serpentine coils. The presence of the poorly heat-conducting Teflon body in the autoclave bomb greatly complicated this manual operation due to build-up of residual heat between the titanium container wall and the liner. Not surprisingly, the liner gradually deformed in the course of the preliminary autoclave experiments as a result of localized "hot spots" and thermoshock phenomena upon introduction of water to the cooling coils. During test #13 it became so severely dented that it obstructed the impeller. Thus, a Pyrex glass liner was used for the leaching program in Vancouver.

Given the occurrence of reducing FSL conditions due to copper depletion, titanium is most certainly not the preferred autoclave construction material. Therefore, several Carpenter and Hastelloy alloys were considered for the pressure leaching program at UBC. Since these were all too expensive, stainless steel (SS) type 316 ultimately became the construction material of choice.

The 2 L autoclave in Vancouver was assembled from an assortment of custom-made and old and new Parr parts with optimum suitability for laboratory first-stage leaching in mind. Figure 4-2 shows the complete reactor set-up.

The reactor was fitted with a magnetic agitator drive. The stirring shaft - the only non-SS part of the reactor internals - was made of highly resistant Hastelloy-C. It was held in place by two stirrer brackets, and two 6-bladed, axial-flow (45° pitch, down-draft) propellers were attached to it.

An important safety feature of the autoclave was the SS flexible high-pressure hose attached to the head of the bomb. In case of a blow-out through failure of the rupture disc, this hose would guide the flashing slurry into the "autoclave safety vessel" filled with water.
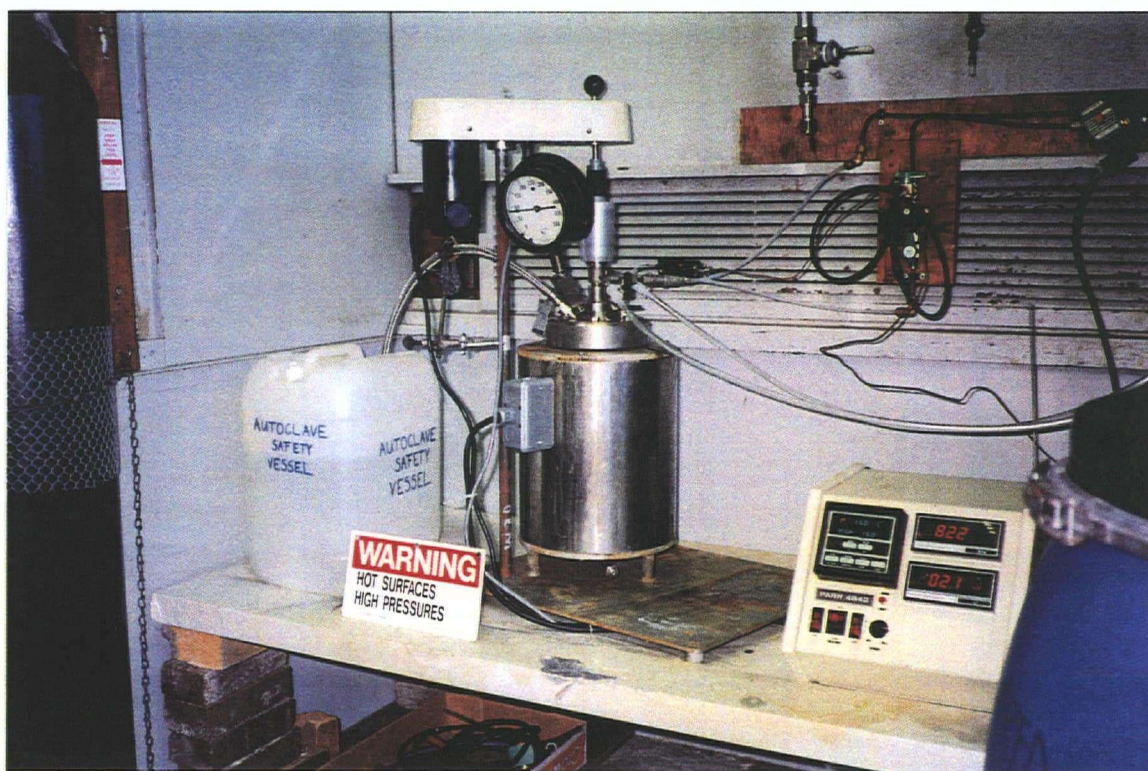
Figure 4-2.   Autoclave set-up for the leaching program at UBC.

It was found that the fit of Parr manufactured serpentine cooling coils into the glass liner was too tight.   Therefore, single thick-walled SS coils machined at the shop of the Department were utilized instead.   Despite the presence of the Pyrex liner in the reactor bomb, excellent temperature control (±2°C) was achieved with the closed feed-back system comprising the Parr 4842 controller, thermocouple, electronically operated cooling water valve and coil.   Air cooling with ascending air between the container and the heating mantle proved to be unnecessary.

Thanks to thorough cleaning of the autoclave internals after each experiment, visual inspection for excessive corrosion and wear, preventive maintenance and periodic pressure tests with water for leak detection, the SS pressure reactor has performed satisfactorily throughout the entire leaching campaign.   Nevertheless, corrosion was severe, and all agitator parts have been replaced twice in the course of the test work.

4.2.4.2 Vacuum desiccators

As all residues dealt with during this thesis project were prone to oxidation, reliable operation of vacuum desiccators was essential.   The desiccators utilized in Copper Cliff were simply

connected to the general vacuum system of the CRED plant. In the absence of such utility in the laboratory in Vancouver, special provisions had to be made. Figure 4-3 shows the complete vacuum desiccator set-up for drying of methanol-treated residues and thawing of IPC samples at UBC.
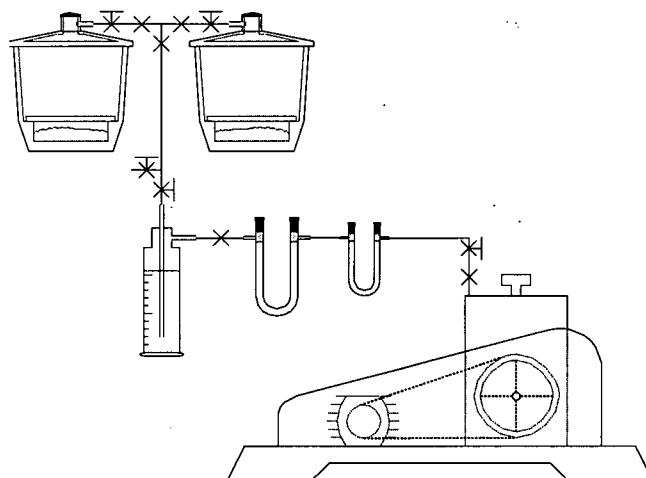
Figure 4-3.   Vacuum desiccator set-up for the leaching program at UBC.

Two Vaseline-greased Pyrex desiccators were connected to a powerful rotary vacuum pump via a sorption system consisting of a washing bottle and two U-tubes in series. Since all vapors released by residues inside the desiccators passed through the pump's oil reservoir (2.5 L capacity), the drying tubes were implemented to avoid pump damage by fouling of the lubricant with condensation products from the gaseous phase. Poisoning of the oil by methanol was feared to be particularly harmful. Thus, the washing bottle was put into place to lower the concentration of methanol within the vapor phase and decrease the overall vapor pressure at the same time.

The sorption system was equipped with several stopcocks and quick connectors to regulate build-up and release of vacuum as desired. Silica gel from the desiccators and U-tubes was periodically regenerated by heating and reused.

4.2.5   Autoclave leaching procedure

Since the effective volumes of the Parr autoclaves in Copper Cliff and Vancouver were practically identical, no modifications had to be made in the laboratory FSL batch make-up as described earlier. However, minor improvements in the experimental method were brought about throughout this project, and the autoclave leaching procedure outlined here is the finally adopted one.

The IPC residue sample was thawed overnight in its plastic bags in a vacuum desiccator to minimize atmospheric exposure. Following moisture analysis, the desired quantity of wet IPC filter cake was introduced to the glass autoclave liner and hand-stirred briefly with electrolyte and water in order to disperse the solids. Obviously, the amount of water added was corrected for the pore water volume of the cake.

Using a high-impedance volt meter, the slurry oxidation-reduction potential (ORP) at ambient temperature was measured between a self-made platinum electrode and a Fisher saturated calomel electrode (SCE). The quality of the reading of this electrode couple was verified regularly with the aid of electrochemical set-ups of other graduate students at the laboratory. Moreover, the calomel electrode was refilled periodically with fresh saturated KCl.

The liner was then cautiously lowered into the autoclave container and the bomb was assembled. The leaching experiment commenced only after heating to the desired temperature. The flow of cooling water to the agitator, temperature and pressure were repeatedly checked. At the end of the run, the electronically operated cooling water valve was opened to quench the slurry. As in the heat-up phase, the agitator was kept running during cooling. Generally, it took about 20 minutes to lower the apparent temperature of the leached pulp to $\approx 30°C$. Subsequently, the autoclave container was removed from the heating mantle and immersed in a cold water bath for 10 minutes to dissipate residual heat.

Following slow depressurization, the bomb was dissembled in a fume hood. Known quantities of a dilute sulfuric acid wash solution were utilized to recover any solids sticking to the agitator, cooling coil and bomb head in a separate beaker. During this rinsing process the solids in the liner settled, allowing measurement of the ORP of the supernatant leach solution at ambient temperature. While hand-stirring the sedimented pulp, the ORP of the leached slurry was also measured.

The contents of the liner and the additional solids collected from the autoclave internals were filtered together using a large water-aspirated conical flask with Büchner funnel. After washing of the cake, it was repulped with wash solution, refiltered and rewashed to remove any residual entrained leach liquor. The volumes of the leach and repulp filtrates were measured. Duplicate samples of approximately 100 mL each were taken of both filtrates and submitted for assay.

The mass of the "clean" wet cake was also recorded. The cake was then split into three fractions. One fraction was used for moisture analysis. It was dried in a small oven at roughly 60°C and 90% vacuum. Another fraction was repulped in 500 mL of analytical-grade methanol, filtered under vacuum and dried in a desiccator. The dry leach residue sample was distributed over two air-tight plastic containers sealed with tape. One vial was submitted for assay, while

the other one was kept as a back-up and for the SEM and XRD analyses discussed in Chapter 5. The third portion of the cake was discarded.

Regarding the variety of IPC feeds utilized in the leaching program, it is emphasized here that a series of autoclave tests for the study of a particular FSL process parameter was performed with IPC residue samples of the same day, hence, of equal composition. Moreover, the effect of feed composition on extractions and leaching behavior can be compared between most series on the basis of the "standard" autoclave experiment. Such run involved leaching of the "standard" batch at 160°C and 820 rpm for 1 hour.

4.2.6   Releaching procedures

4.2.6.1 Releaching with sodium hydroxide

Four alkaline releaching experiments were carried out with vacuum-dried "normal" leach residue and an arsenic-enriched leach residue of the copper-depleted source, both prepared according to the autoclave leaching procedure previously described. The releaching response of the "normal" residue served as a blank.

Leaching was done in a nitrogen-sparged, agitated beaker covered with a Styrofoam lid. To prevent excessive evaporation of the leach solution, the N_2 flow was saturated with water prior to introduction to the beaker by bubbling it through deionized H_2O in a gas washing bottle. The sparger was a glass frit of medium porosity. Agitation was provided by an overhead stirrer rather than a stirring magnet to avoid excessive grinding of the residue particles. A temperature of 50°C was maintained by water circulating through a thermostatic bath and the double-walled Pyrex glass beaker. The pH was kept at either 11 or 12 with the aid of a Fisher combined pH electrode and a Radiometer titrator pumping a $1M$ NaOH solution.

Using fresh Fisher buffer solutions, the pH electrode was first calibrated at pH 7 and 10 at room temperature. The temperature dial on the titrator was used to adjust the readings to 50°C.

The 300 mL starting volume of water was then heated. Following the addition of the desired amount of solids at 50°C, the natural pH of the slurry was recorded.

The releaching experiments with "normal" residue were carried out at 20% (wt.) initial pulp density. This proved to be rather high in view of the unfavorable hydrodynamic conditions prevailing in the beaker. Subsequently, a solids concentration of 10% (wt.) was employed for the "copper-depleted" residue in order to attain better suspension of the particles.

Only after adjustment of the pH to 11 or 12, the first solution sample, marking time 0, was taken. The agitator was stopped during sample taking to allow the solids to settle, whereas the sparger was raised so as to provide a blanket of nitrogen between the atmosphere and the solution interface. A syringe equipped with a 0.22 μm disposable nylon disc filter was utilized to extract 10 mL of the alkaline supernatant solution through the sample hole in the lid. An additional sample was taken after 30 minutes, while the 60 minutes sample was the releach filtrate.

Washing of the filter cakes was conducted in a similar manner as with the autoclave tests, however, deionized water was utilized as the washing solution. After methanol treatment and drying, the whole cakes were submitted for assay.

4.2.6.2 Releaching with pregnant electrolyte

Contrary to the alkaline releaching experiments performed with *dry residue* of the copper-depleted source, the releaching experiment with synthetic pregnant copper electrolyte involved the introduction of hot, concentrated $CuSO_4$-H_2SO_4 solution to a freshly prepared copper-depleted FSL *slurry*. In view of the direct importance of this test to CRED process control (Chapter 5) it was carried out in duplicate.

After quenching of the arsenic-enriched autoclave slurry to an apparent temperature of 80°C, the autoclave liner was removed from the reactor bomb and immersed in a circulating hot water bath of the same temperature. The hot slurry was then covered with the same Styrofoam lid and agitated and sparged as described before. The water bath was filled with small plastic balls to reduce evaporation and heat losses.

Following heating of the liner contents to exactly 80°C, a solution head sample was taken according to the method outlined above. Expecting the incremental recoveries of cobalt, nickel and iron achieved during releaching to be negligible compared to the extractions of these elements attained in autoclave leaching at 160°C, it was hoped that this sample could be utilized for volume calibration.

The slurry ORP was manually adjusted to and maintained at +85 mV_{SCE} by pipetting pregnant copper electrolyte into the liner. The electrolyte contained 100 g/L copper and 130 g/L acid and was kept at 65°C in a separate water bath to prevent crystallization.

The solution sample at time 0 was taken immediately after the desired ORP was reached. Additional samples were taken after 5, 15, 30, 60, 120 and 180 minutes, the latter being the filtrate sample. After 3 hours the slurry was cooled and filtered, washed and treated with methanol according to the usual practice.

4.2.7   Hydrogen sulfide analyses

As part of the preliminary leaching program at the CRED laboratory, it was examined if Dräger tubes could be successfully used to measure the concentration of H_2S in the reactor freeboard after a copper-depleted leach experiment. To do this, the autoclave pressure release valve was fitted with tubing to connect it to a Dräger tube inserted into a hand-held pump.

The measurements proved to be unpractical and unsatisfactory for three reasons. First of all, the choice for a Dräger tube with a H_2S concentration range of either 0.5-20 or 20-200 ppm had to be made prior to the actual determination. Secondly, the tubes could not be used at temperatures above 40°C. This implied that the autoclave slurry had to be cooled down almost to ambient temperature, causing a significant shift in the equilibrium:

$$H_2S(g) \leftrightarrow H_2S(aq) \tag{4-3}$$
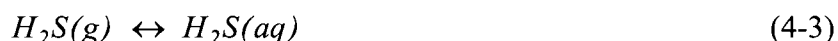
Finally, the amount of gas present in the autoclave plenum was not always sufficient for the completion of the prefixed number of pump strokes necessary for the H_2S analysis. This led to unreliable concentration measurements on the one hand, and undesirable underpressurization of the autoclave bomb on the other hand.

In view of these difficulties the Dräger tube measurements were soon abandoned. Nevertheless, the presence of H_2S in the reactor freeboard under severe copper-depleted FSL conditions was clearly demonstrated. Several other ideas for quantitative H_2S analysis were put forward, but none of those was ever pursued.

4.3   Sample and Waste Management

Every sample taken in the course of the leaching program was registered in the laboratory sample log. When shipped to Copper Cliff for assay, the samples were labeled and packaged according to UN regulations. A small number of solutions and residues were analyzed at the International Plasma Laboratory (IPL) in Vancouver.

All FSL solutions were collected in two 50 gallon drums. They were intended for processing at CRED. Unfortunately, the barrels became contaminated with other waste and will now be discarded via UBC authorities instead.

Methanol waste was accumulated in large glass bottles. A distillation column will be set up to separate an impure methanol fraction from aqueous bottoms containing the majority of the

(base) metal values. The distillate will be disposed of as simple organic waste, whereas the bottoms will be mixed with the FSL solutions.

Leach residue rejects and IPC residue leftovers were stored in a bucket. Water was added periodically to prevent drying of the solids, because they are mildly pyrophoric. Although methods for elimination of this solid waste have not been looked into in detail yet, it will likely be shipped to the CRED plant.

CHAPTER 5

RESULTS AND DISCUSSION

5.1   Introduction

After a brief discussion of the chemical composition of the IPC residue samples utilized in the experimental program, this chapter describes the effect of various physicomechanical and chemical parameters on the impurity extractions achieved and leaching phenomena observed during first-stage leaching. On the basis of the experimental results and the thermodynamics of Chapter 3 a tentative reaction model is then proposed for first-stage leaching after copper depletion. Subsequently, an entire section is devoted to the behavior of arsenic under copper-deficient FSL conditions and releaching studies of residues enriched with this element. Finally, an attempt is made to quantify the effect of air discharging of first-stage autoclaves. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) work is integrated with the results of the leaching program.

Although no metallurgical balances are written out here, it is pointed out that, in conformity with common metallurgical practice, impurity recoveries attained are reported both on the basis of the element's assay head grade as well as its calculated head grade. The latter is considered to be more representative of a given leaching system as it is computed using both solution and residue assays. The comparison of assay head and calculated head extractions, of course, is essential to recognize systematic errors in an experimental procedure or to identify questionable chemical analyses.

From the worksheets attached in Appendix C it can be seen that, despite the substantial absolute and relative errors between the two grades for many tests, the respective nickel, cobalt and iron recoveries calculated on the basis of either grade generally do not differ more than $\approx 2.5\%$ absolute. Such a difference is certainly acceptable in view of (1) the high concentration of these metals encountered in first-stage leaching, and (2) the limited accuracy of the Inductively Coupled Plasma (ICP) technique, the analytical method utilized with most samples. Except for the arsenic series, greater absolute errors are tolerated with arsenic considering its relatively low concentration amid the other impurities and copper. The more pronounced discrepancy in many of the iron balances can be attributed to autoclave corrosion, hydrolysis after long-term sample storage, or even systematically incorrect analyses. The relative difference between the assay head and calculated head grade of copper is usually well within 5%.

Without exception, the extractions tabulated or shown graphically in this chapter are based on the calculated head grade. Disregarding a few isolated cases, serious deviation of the arbitrarily set threshold error of 2.5% for cobalt, nickel and iron recoveries for a series of autoclave tests is mentioned in the discussion of the experimental results.

It is also noted that the metal and acid concentrations of the leach filtrates are backcalculated values, computed from mass balances that incorporate the assays of the total leach filtrate (leach filtrate plus wash water) and the repulp filtrate, and the moisture content of the wet leach residue. Since some oxidation of the wet FSL cakes may have taken place during repulping and refiltering, the reported residual copper concentrations of the leach filtrates can be slightly inflated. This means that the final copper levels cannot be unambiguously related to the measured ORP's.

5.2   Sample Composition

The minimum, maximum and average grades of the main constituents of the IPC residue samples obtained during the sampling program at INCO's CRED plant in May, 1994, are shown in Table 5-1. The "balance" is made up of a host of elements which were not studied in this project, including other base metals such as lead, alkali metals such as magnesium and calcium, precious and platinum group metals, and selenium and tellurium.

Table 5-1.   Minimum, maximum and average grades of the main constituents of IPC residue samples taken from May 9 to 24, 1994.

element	Co	Ni	Fe	As	Cu	S_{tot}	O	balance
min. grade, %	6.06	7.44	4.03	0.67	53.59	12.50	4.88	0.55
max. grade, %	7.61	9.99	5.39	0.79	59.22	17.05	7.94	2.71
avg. grade, %	7.13	8.79	4.70	0.73	56.17	14.69	6.42	1.37

The heterogeneous nature of the feed to the CRED plant also becomes apparent from the histograms of Figure 5-1, which demonstrate the variability in the cobalt, nickel, iron and arsenic grades of IPC residue during the 16-day sampling period. Obviously, such daily changes in the feed composition are highly undesirable for the batch leaching process currently operated.
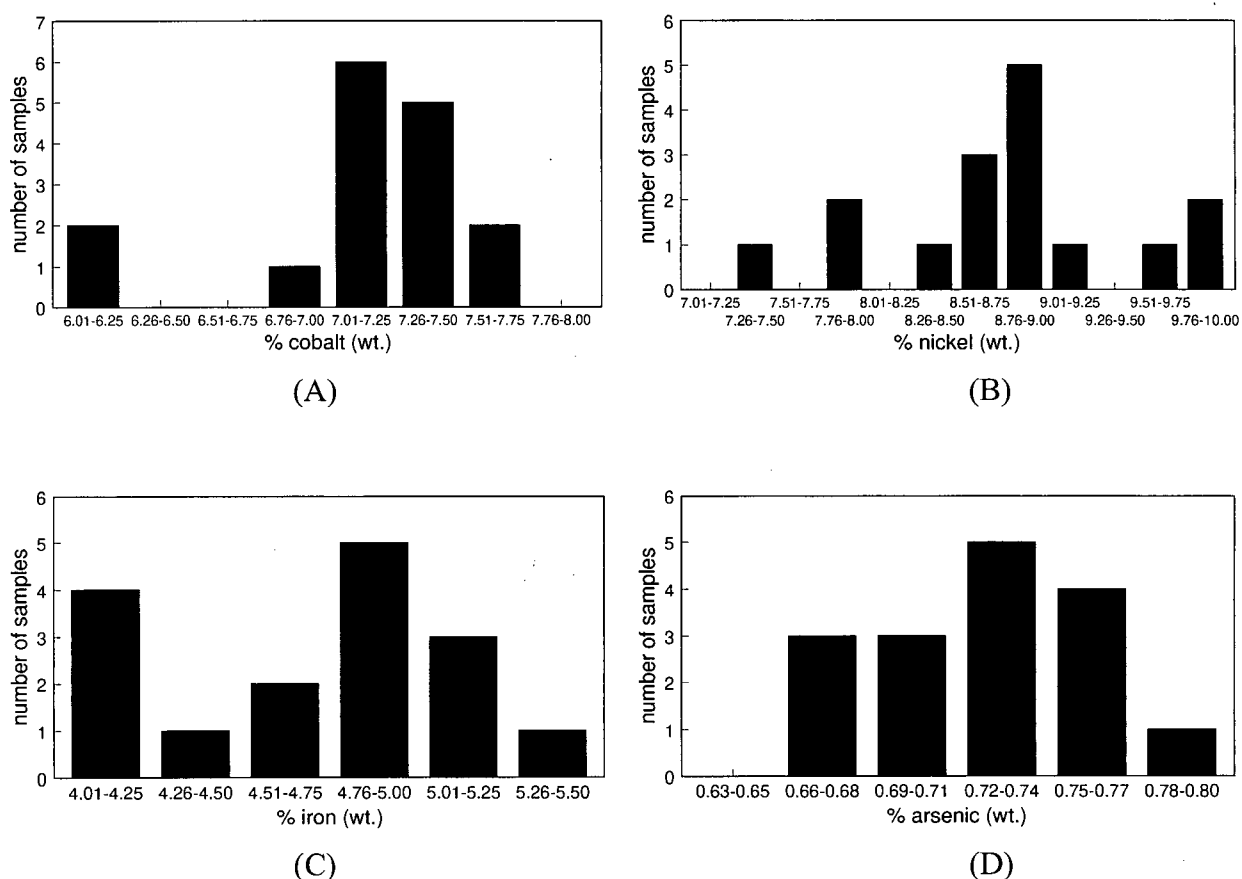
Figure 5-1.   Variability in the grades of the principal impurity elements in IPC residue
samples of May 9-24, 1994: (A) cobalt, (B) nickel, (C) iron and (D) arsenic.

5.3   Effect of Agitation and Pulp Density

5.3.1   Agitation series

The agitation series comprised four autoclave experiments of 1 hour at stirring rates of 600, 725, 850 and 1000 rpm, using the "standard" batch make-up with IPC residue of May 18.   A frequency of 600 rpm was thought to be the lowest possible for effective particle suspension, whereas the maximum of 1000 rpm was dictated by the power of the agitator motor and available pulleys.   The impurity extractions obtained are shown in Figure 5-2.
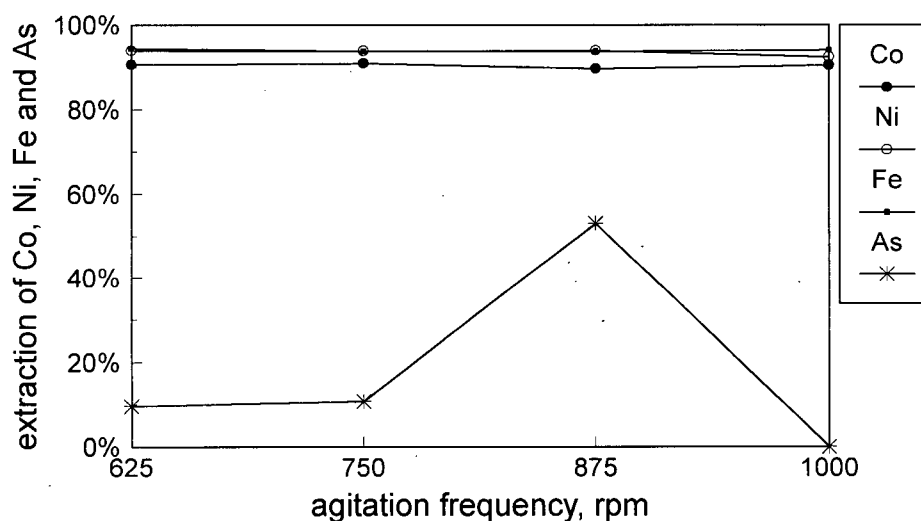
Figure 5-2.   Effect of agitation rate on the extraction of cobalt, nickel, iron and arsenic.

Figure 5-2 displays virtually horizontal lines representing ≈95% extraction each of nickel and iron and 90% cobalt, and great variation in the recovery of arsenic. The erratic arsenic extractions are not due to the different agitation intensities of the slurry, but rather are the result of the level of residual copper ion in solution at the end of the autoclave test. Although no reliable slurry ORP readings are available, it is evident that all tests but #20 at 875 rpm ended under mildly or strongly reducing conditions, causing partial or quantitative removal of arsenic from solution.

Indeed, copper depletion frequently occurred throughout the leaching campaign. As emphasized in Chapter 4, however, batch make-up was not a variable in the present investigations.

Figure 5-2 indicates that the FSL process is insensitive to the agitation rate as long as good particle suspension is provided. It can be speculated that the explanation for this finding lies in the skeletal morphology of the carbonylation residue: Figure 5-3 shows the typical "honeycomb" structure of IPC residue grains.

Leaching of the finely dispersed impurity elements from the IPC copper sulfide matrix involves both intergrain and intragrain diffusion. Excluding any chemical effects for now, it is plausible that the movement of ions through the bulk of the solution is much faster than the diffusion of protons, cupric ion and impurity ions through the stagnant solution in the voids of the residue. In other words, more vigorous agitation of FSL slurry may increase the diffusion rate in the bulk solution ("macroscopic" diffusion), but the overall leaching rate remains limited by the movement of ions within the pores of the solid particles ("microscopic" diffusion).
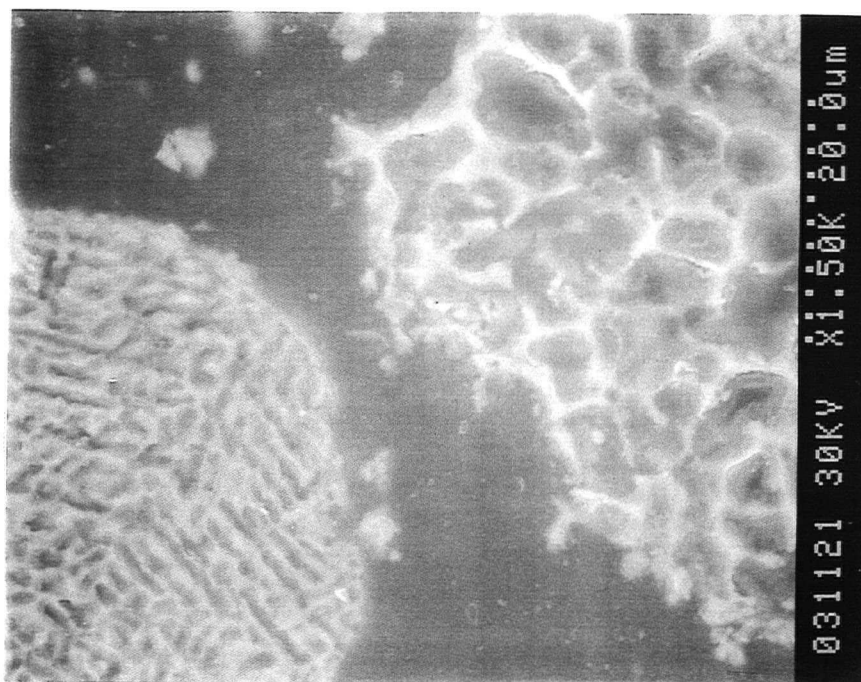
Figure 5-3. SEM photograph showing "honeycomb" structures of different porosity (1500x magnification).

The "topography" depicted in Figure 5-3 hampers quantitative analysis of individual IPC or FSL residue grains by the energy-dispersive X-ray (EDX) technique. On the one hand, X-rays emitted from valleys and hollows may not be able to reach the detector. On the other hand, high-energy X-rays may penetrate a thick barrier while X-rays from lighter elements are blocked. The result in both instances is a distorted element concentration measurement.

An intermediate stirring frequency of 820 rpm - on the Parr controller display - was chosen for all autoclave tests. The autoclave controller reading was verified with a tachometer and was less than 5% off the true rate of about 860 rpm.

From previous test work it is known that at 820 rpm all second-stage gas-liquid mass transfer limitations are overcome. Although the FSL system is not the same, it was felt that this could be relevant to the study of the behavior of arsenic in the presence of H_2S. Furthermore, it was found that the autoclave runs smoothly at such agitation rate and does not vibrate or shake too much.

5.3.2 Pulp Density series

The pulp density series consisted of five runs of 60 minutes at 5.0, 10.0, 15.0, 20.9 and 29.5% (wt.) slurry solids content. They were all carried out with IPC residue of May 22. Respecting the maximum allowable slurry volume of the Parr reactor for safe operation, the pulp density was changed by varying the amount of water added while keeping the electrolyte : residue mass ratio constant at 2.39. The impurity extractions obtained are shown in Figure 5-4.
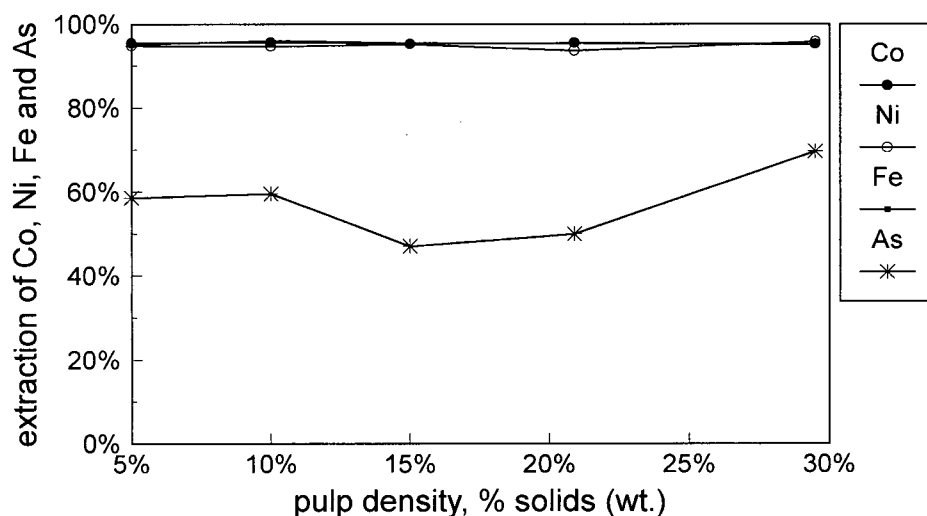
Figure 5-4.   Effect of pulp density on the extraction of cobalt, nickel, iron and arsenic.

Figure 5-4 shows that the FSL process is essentially unaffected by changes in the slurry solids content. In terms of the earlier diffusion concept this indicates that bulk diffusion is not influenced by solids concentrations of 5 to 30% (wt.).

There is no obvious reason as to why the arsenic extractions peak at around 50 to 60%. On the basis of the present results, two scenarios for first-stage leaching of arsenic can be postulated: (1) the extraction of arsenic is kinetically slower than the solubilization of the other impurities, (2) the element is distributed over two or more separate minerals, at least one of which leaches favorably compared to the other(s) that is (are) refractory towards dissolution in the $CuSO_4$-H_2SO_4 medium.

The second scenario seems more likely. For instance, one could speculate that arsenic exists both in solid solution in the copper sulfide matrix as well as in a discrete nanocrystalline phase such as an arsenide. However, using SEM or XRD it is already a near impossible task to identify a single arsenic compound in IPC or FSL residue, let alone distinguish between two or more of them.

In test #27 at 30% solids - an impossible pulp density in present plant practice - an anomalously high arsenic extraction was achieved: 69.6%. The dried residue utilized in that particular test must have been very oxidized considering the low copper and high acid consumptions of 16.3 and 299.4 kg/t IPC residue, respectively.

The effect of grinding or attritioning action on the impurity extractions at the higher solids concentrations is hard to discern, however, particle reduction by such mechanisms is unwanted with regard to the filtration characteristics of FSL slurry.

5.4   Effect of Temperature and Residence Time

5.4.1   Kinetic studies on IPC residue with a high Cu : S_{tot} ratio

In older INCO correspondence, second-stage leaching difficulties were sometimes attributed to the action of the mineral cuprite, the presence of which in IPC residue with a high Cu : S_{tot} mass ratio can be explained as follows. With insufficient sulfur available to accommodate all of the copper as sulfides in the IPC reactor feed, the remaining metallic (nickel) phase becomes richer in copper. Therefore, after selective removal of the nickel by carbonylation, the IPC residue contains more "exposed" copper metallics. These fine copper metal particles are very amenable to oxidation to cuprite during wet grinding, transport and storage prior to first-stage leaching.

The FSL process supposedly left Cu_2O intact. It was postulated that the oxide locally rendered the surface of the chalcocite to be leached more alkaline, which led to the formation of an adhering coating of BCS that impeded further oxidation of the sulfides.

As outlined in Chapter 1, it is now known that high-(Cu : S) feeds to the SSL process can result in elevated concentrations of BCS, increased slurry viscosities and slower gas-liquid mass transfer in the reactor.

With both the obsolete and the recent theory in mind, a comprehensive leaching study of high-(Cu : S_{tot}) IPC residue was undertaken. In addition, the mineralogy of various FSL residues produced in interruptive and extended autoclave tests was investigated by XRD.

Nineteen individual autoclave runs at 80, 120, 140 and 160°C were performed with IPC feed material from May 11-14 using the "standard" batch make-up. The Cu : S_{tot} ratio for each of these residues was around 4.3, while their overall chemical composition was very similar. Grinding data from the CCNR indicated that the grind size of IPC residue from May 11, 12 and 14 was ≈70% passing 325 mesh, whereas residue of May 13 was coarser at 86% passing the same screen size. In view of the buffer capacity of the IPC thickener and surge tanks at the CRED facility, however, these data are unlikely to represent the true fineness of the

carbonylation residue samples of May 11-14. No screening analyses were performed on these and any other IPC residues, since grind size is not a process parameter that can be easily controlled or modified at the leaching plant.

The extraction curves are shown in Figure 5-5. In the interpretation of this figure it should be realized that the errors in the nickel, cobalt and iron balances for the kinetic experiments at 80 and 120°C are greater than for any other test. After re-analysis of all filtrate samples, the consistency of the discrepancy between assay head and calculated head extractions seems to point to incorrect concentrations of the three metals in either the IPC or the leach residues. Since assays for the head samples submitted during the sampling campaign in Copper Cliff have proven very reliable, the FSL residue analyses are believed to be inaccurate. However, due to time and budget constraints this has not been verified.

No other possible sources of error have been identified. The experimental procedure was not changed. Since no anomalous increase in the chromium content of the FSL filtrates was observed, excessive corrosion of the SS autoclave internals is also ruled out; one would rather expect an inhibiting action by copper as a result of the higher concentrations of this metal in FSL slurries at lower leaching temperatures. Analyses of the methanol filtrates showed that the coloring of those solutions was due to negligible concentrations of impurity elements that could not possibly have been responsible for the great biases in the metallurgical balances.

In Figure 5-5 only cobalt and iron follow the expected temperature-residence time trend. Long retention times at a temperature of 160°C without replenishment of the copper level in solution are detrimental to the arsenic recovery, and, interestingly, also appear to adversely affect the nickel extraction. Reducing conditions at the end of 4-hour leaching test #28 were indicated by the 35 psi (H_2S) pressure increase recorded by the gauge. During the same experiment a bronze-colored precipitate was deposited on the stirring shaft, which unfortunately could not be scraped off for SEM and XRD analysis.

Figure 5-5 implies that in the plant large quantities of cobalt, nickel, iron and arsenic are solubilized from high-($Cu : S_{tot}$) IPC residue during first-stage batch make-up and preheating to 80°C and batch heating to 160°C. In fact, the vast majority of "leachable" arsenic values has already been extracted once the current FSL operating temperature is reached. The iron and nickel recoveries achieved after heating-up to 160°C are as high as 78.3 and 76.2%, respectively, clearly suggesting the presence of these metals in oxide phases. The dissolution of cobalt is more dependent on metathesis reactions, which are known to require autoclave rather than atmospheric leaching conditions to take place at industrially acceptable rates.

(A)

(B)

(C)

(D)
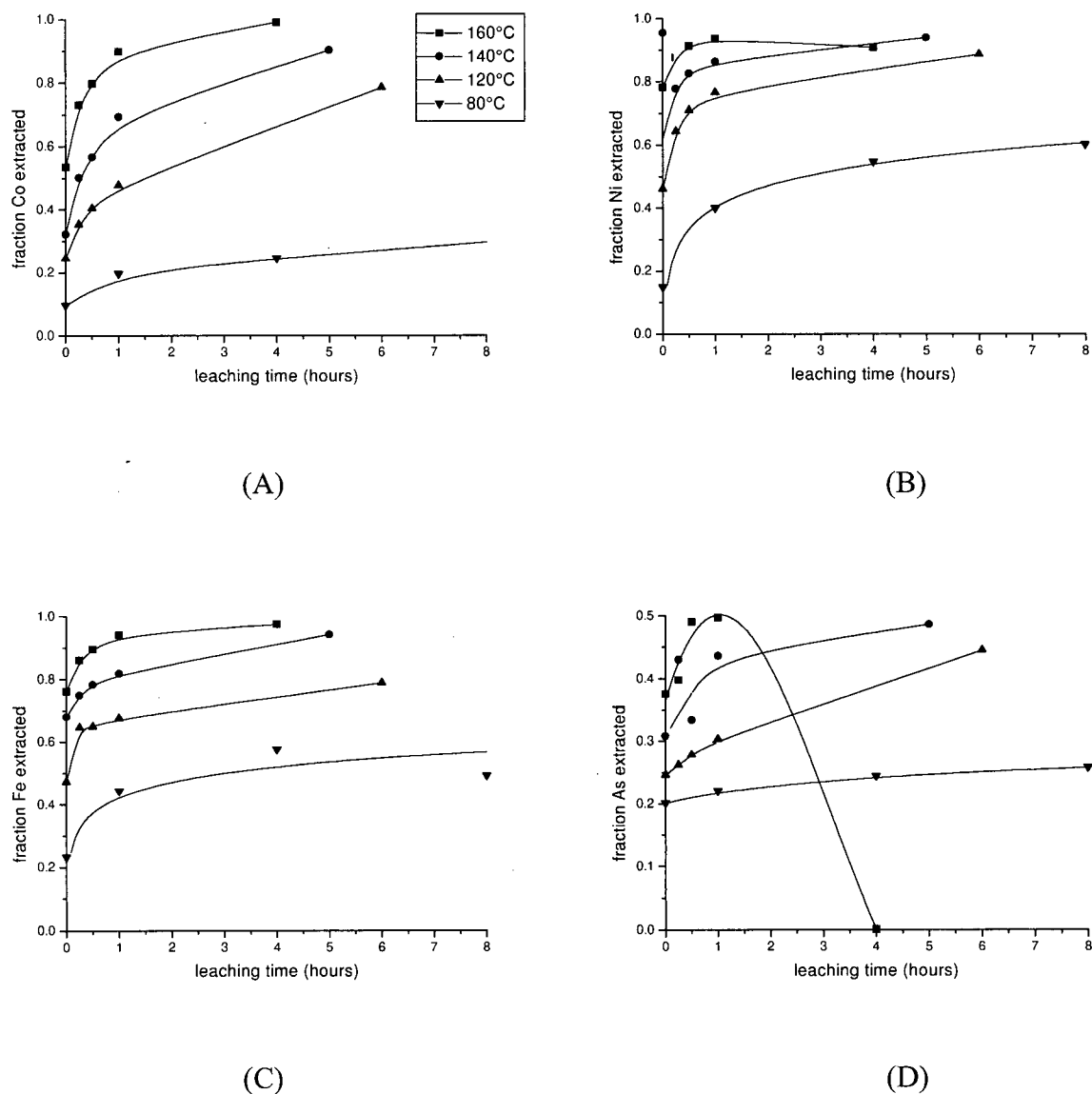
Figure 5-5. Fraction of metal extracted from IPC residues with an average Cu : S_{tot} mass
ratio of 4.3, as a function of leaching time: (A) cobalt, (B) nickel, (C) iron
and (D) arsenic. Note the different extraction scale in the arsenic graph.

In early INCO studies [60] it was established that the overall first-stage leaching rate is first order
with respect to the residual concentration c of impurities in the leach residue:

$$. - \frac{dc}{dt} = K_T (c - c_\infty)$$

(5-1)

In equation (5-1) c_∞ represents the "unleachable" impurity content of IPC residue, and K_T is the apparent overall rate constant. Bearing in mind the changes in the composition of IPC residue over the twenty years the CRED plant has been in operation, the extraction curves shown in Figure 5-5 do not follow equation (5-1) at all.

One could argue that the experimental method employed in this leaching campaign has failed to provide useful data for the derivation of a kinetic model describing first-stage leaching of IPC residue with a high Cu : S_{tot} mass ratio within the temperature range investigated. Indeed, in the present study the most important part of the kinetic information is lost by the time the first data are generated; the slopes of the cobalt, nickel and iron extraction curves merely reveal that the leaching rate is largely independent of temperature after heating-up to the desired leaching temperature. Moreover, the similar slopes make the calculation of apparent activation energies from Arrhenius plots impossible.

One could also challenge the usefulness of the concept of the overall rate constant with respect to first-stage leaching. The FSL process is a highly complex system that comprises simultaneous leaching of various impurity metals from a multi-phase material according to at least three different mechanisms: (1) oxide dissolution, (2) metathesis, and (3) cementation. The system is further complicated by electrochemical interactions such as galvanic conversion.

Therefore, even if apparent rate constants and activation energies could have been computed, it would have been extremely hard to assign any specific physical meaning to them. Although it is recognized at this point that leaching experiments with pure minerals would certainly give a better insight into the kinetic contributions of individual phases, it must be emphasized that IPC residue is not a naturally occurring material and has a unique composition and morphology.

XRD studies on IPC and leach residues of the high-(Cu : S_{tot}) kinetic series were performed at Geological Sciences at UBC using a Siemens D-5000 diffractometer with Diffrac/AT software. Prior to taking a spatula tip of residue sample, the sample vial was thoroughly shaken. The small quantity of residue was then wet-ground in methanol in an agate mortar, quickly dried under a hot lamp, and transferred onto a glass slide using wax paper. After cutting of the sample with a razor blade, several drops of methanol were added to allow the solids to be smeared out evenly. Once the methanol had evaporated again the slide was inserted into the sample holder of the diffractometer.

IPC residue samples of May 12 and 13 were first scanned from $2\theta = 5$ to 75° in steps of 0.02° with a counting time of 1 second. On the basis of those patterns it was decided to reduce the 2θ scale to 28-58° as all major peaks are located within that range, while increasing the

counting time to 2.5 seconds to improve the peak : noise ratio.   Following calculation and
subtraction of the background noise, all patterns were smoothed.

The XRD patterns for the leaching tests at 160°C with IPC residue of May 12 are shown in
Figure 5-6.
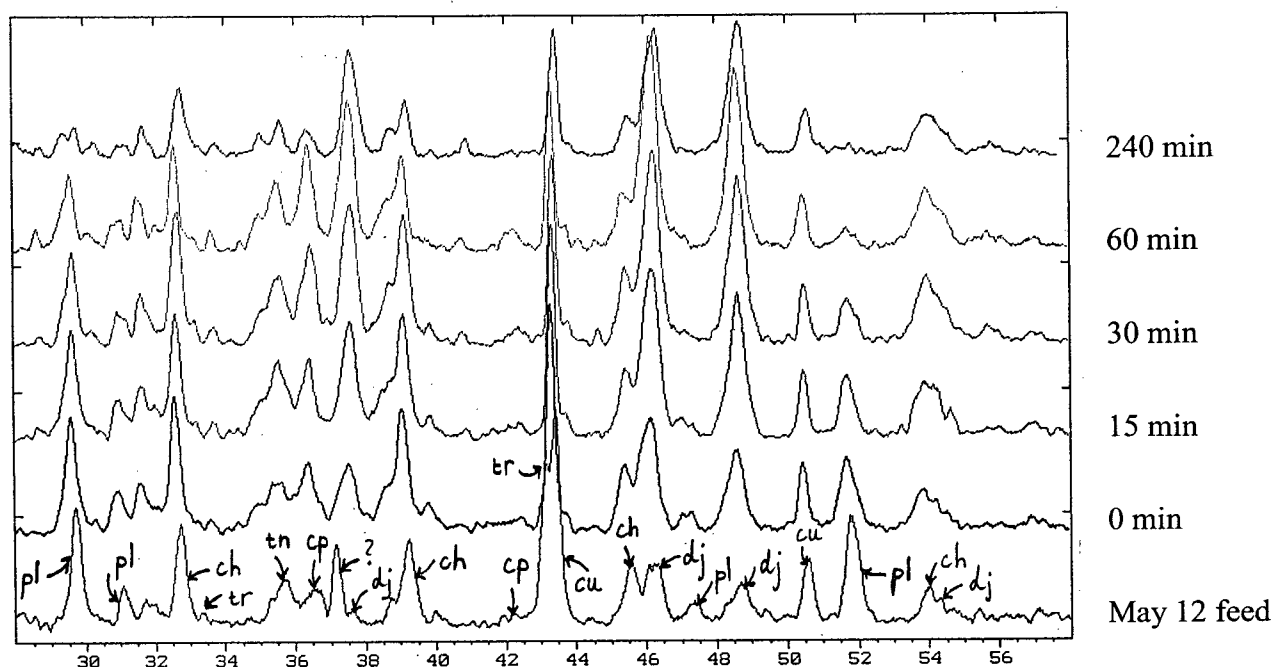
Figure 5-6.   Stacked XRD patterns showing mineralogical changes in the leach residue
                over time at 160°C.   Key: ch = chalcocite, cp = cuprite, cu = copper,
                dj = djurleite, pl = pentlandite and tn = tenorite.

As anticipated, elemental copper is one of the major phases present in the IPC and leach residues
of Figure 5-6.   The shoulder in the main copper peak (2θ = 43.3°; d = 2.09 Å) as well as other
smaller peaks are evidence for the presence of troilite (FeS).   The high intensity of the principal
copper peak may be due in part to the presence of minor amounts of iron-rich trevorite,
$(Fe,Ni)Fe_2O_4$, or, more likely, bunsenite (NiO), to which the mysterious peak at 2θ = 37.2°
(d = 2.42 Å) could possibly also be ascribed.   This peak might also belong to another, still
unidentified (synthetic) mineral phase.

        Chalcocite $(Cu_{1.96}S)$ is the main copper sulfide mineral in the IPC feed, but djurleite
$(Cu_{1.93}S)$ is formed during leaching.   Tenorite (CuO) and cuprite (Cu_2O) are the chief oxide
phases, yet XRD is inconclusive as to whether the latter was really formed prior to lixiviation in
the $CuSO_4$-H_2SO_4 medium or just through handling of the leach residues.

From the extraction curves in Figure 5-5 it can be deduced that the removal of arsenic from solution after several hours of leaching at 160°C was initiated by a persistant demand for an oxidant for the leaching of a residual cobalt- and iron-bearing phase. As can be seen from Figure 5-6, there is indeed less cobaltiferous pentlandite $((Co,Ni,Fe)_9S_8)$ present in the leach residue after 4 hours than after 1 hour of leaching. Unfortunately, no arsenic minerals could be identified.

The mineralogical composition of the other high-$(Cu : S_{tot})$ IPC feed materials was almost identical, while the inversely proportional relationship between impurity extraction and peak intensity was evident.

5.4.2   Kinetic studies on IPC residue with a low Cu : S_{tot} ratio

For comparison to the results reported in section 5.4.1, kinetic experiments at 160°C on IPC residue with a Cu : S_{tot} ratio of only 3.2 were also performed. To avoid the highly reducing conditions encountered in the course of test #28, 800 mL of electrolyte instead of 700 mL was utilized in the batch make-up for these series. Four-hour autoclave run #49 had to be stopped prematurely because of agitation problems.

Although the sulfide minerals in IPC residue of May 19 matched those present in the high-$(Cu : S_{tot})$ feeds, the oxide mineralization consisted entirely of spinel-type phase(s) and bunsenite; no evidence for the presence of either cuprite or tenorite was found in the diffractogram. Surprisingly, elemental copper was also a component of the low-$(Cu : S_{tot})$ residue, although the intensity of its peaks was somewhat lower.

The extraction curves obtained are shown in Figure 5-7. The low-$(Cu : S_{tot})$ material proved to be highly reactive, and the increased concentration of cupric ion in the slurry was not quite enough to eliminate copper depletion. The maximum arsenic extraction of 59.5% was attained only after 30 minutes of leaching. Again the nickel and iron recoveries were near 80% at time zero, whereas the metathesis reactions for the solubilization of cobalt took longer to reach such a level.
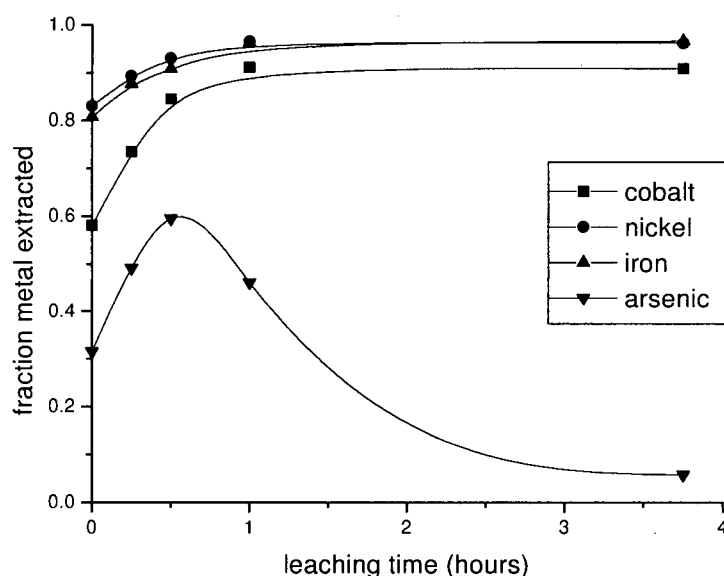
Figure 5-7.   Fraction of metal extracted from IPC residue with a Cu : S_{tot} mass ratio of
3.2, as a function of leaching time.

5.5   Effect of Electrolyte Composition

5.5.1   Copper series

The copper series comprised five 1-hour leaching tests with electrolyte copper concentrations of
60, 45, 30, 15 and 0 g/L, together with 220 g/L H_2SO_4. Unlike all other experiments discussed in
this chapter they were carried out at the CRED laboratory. Each batch was composed of 360 g
IPC residue of May 20, 700 mL of electrolyte and 500 mL deionized water. From the pulp
density series it follows that the changes in the slurry solids concentration caused by the different
electrolyte copper levels have had negligible impact on the leaching results of the copper series.

In the course of the preheating phase of test #13 at 0 g/L copper, the Teflon liner employed in
Copper Cliff became so severely deformed that it blocked the agitator. The autoclave run was
discontinued and never repeated since its academic value was found not to weigh up to the risk of
equipment damage due to the large quantity of H_2S (and possibly H_2) formed under zero copper
conditions. Indeed, at initial electrolyte copper contents of 30 and 15 g/L the reactor gauge
displayed pressure increases of 25 and 160 psi, respectively, from the normal 80 psi. The
presence of hydrogen sulfide gas in the freeboard for those tests was demonstrated with the aid of
Dräger tubes. The formation of H_2S is also reflected by the steady increase in acid consumption
with decreasing copper concentration.

The copper series leaching results are plotted in Figure 5-8.
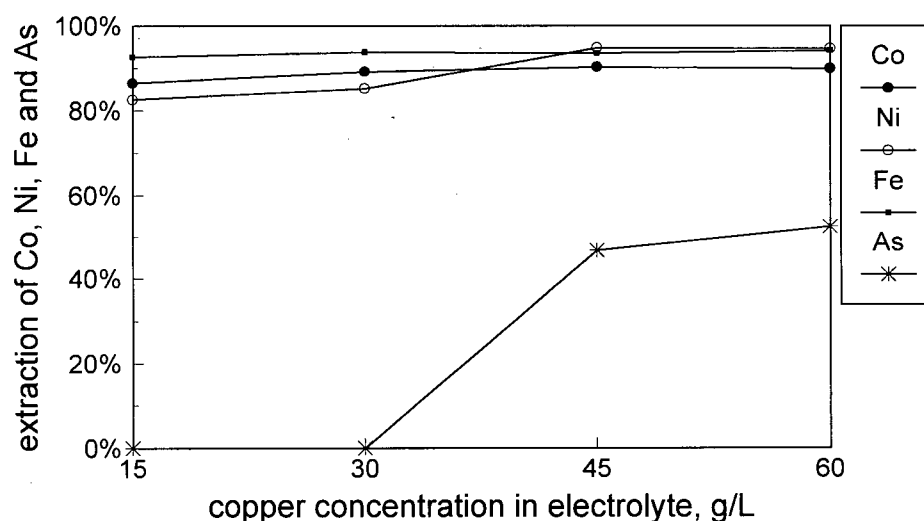
Figure 5-8.   Effect of electrolyte copper concentration on the extraction of cobalt, nickel, iron and arsenic.

Figure 5-8 shows that the iron extraction is barely influenced by the level of cupric ion in the electrolyte, which supports previous comments on the presence of this metal in IPC residue oxide minerals. The consistently high cobalt recoveries are due to metathesis of this metal with arsenic or acid once copper has been depleted from solution.

At the low-copper side it is not clear if arsenic is leached in the first place or if it is "reprecipitated" at a later stage. In the case of severely reducing conditions, dissolved nickel is also removed from solution. The decrease in the arsenic and nickel recovery is 52.4 and 12.1%, respectively, when the copper content of the electrolyte is lowered from 60 to 15 g/L. In contrast, a large excess of copper ions seems to have a beneficial effect on the arsenic extraction, yet no duplicate test was carried out to assess the reproducibility of the results of test #9 at 60 g/L.

Strikingly, the leach residues obtained with low-copper electrolyte are lighter than the ones produced when electrolyte with an elevated copper level is utilized. This finding can be attributed to the lower grade of "heavy" copper of the former.

5.5.2   Acid series

The acid series consisted of five leaching tests with electrolyte acid concentrations of 0, 50, 100, 150 and 220 g/L, while the copper level was maintained at 45 g/L. IPC residue of May 9 was chosen for these series because of its high oxygen content of about 8%. As with the copper

series, the variation in pulp density arising from the changing acid content of the electrolyte in each experiment can be ignored. The impurity extractions obtained are shown in Figure 5-9.
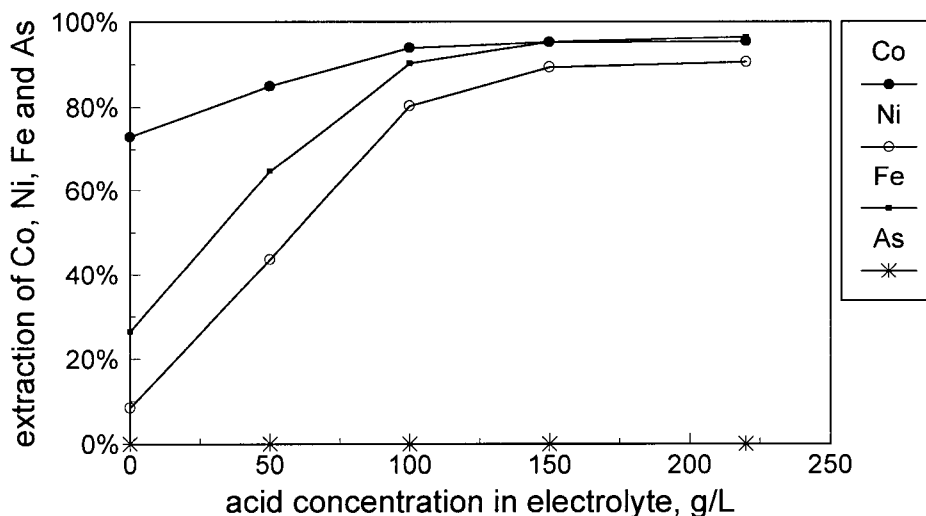
Figure 5-9. Effect of electrolyte sulfuric acid concentration on the extraction of cobalt, nickel, iron and arsenic.

The dependency of iron extractions on the electrolyte acid concentration is further substantiated in Figure 5-9. Since the cobalt extractions achieved do not differ more than approximately 20% over the entire range of acid levels investigated, it can be concluded that this metal is solubilized from May 9 residue predominantly by metathesis reactions. This was really already evident from the color of the leach filtrates, which changed from deep red to the usual dark brown with increasing H_2SO_4 levels in the electrolyte.

Unfortunately, the acid series results for arsenic and nickel are masked by copper depletion. Arsenic is likely "reprecipitated" quantitatively and, although a link between the nickel recovery and the availability of acid is established, the extractions of this metal are biased by partial reprecipitation. At the regular electrolyte acid concentration of 220 g/L its recovery is some 5% lower than the extractions of iron and cobalt.

Nevertheless, Figure 5-9 demonstrates that the sensitivity of the impurities to the amount of acid in solution decreases in the order Fe > Ni > Co, which is believed to be true for first-stage leaching in general. For all three metals the extraction is almost linear with the acid concentration until it levels off at 100 g/L. Considering the spinel-type structure of most impurity oxides in IPC residue, in a broader sense this behavior is analogous to the leaching of franklinite ($ZnFe_2O_4$) in the zinc industry. Although leaching of this zinc spinel is practiced at

atmospheric conditions in a $ZnSO_4$-H_2SO_4 lixiviant, its break-up is also strongly affected by acidity.

Test #14 at 0 g/L acid produced the sole leach residue in the entire leaching program heavier than 360 g, the mass of IPC residue used in most batches. Strangely, XRD studies showed no evidence for the presence of copper hydrolysis products or basic nickel or cobalt sulfates in the dry cake. This means that its large mass is due to a combination of incomplete dissolution of oxide minerals, as indicated by its high oxygen content and low Cu : O mass ratio, and the replacement of lighter base metals (cobalt) by heavier copper through metathesis reactions. It is also worth noting that in the same experiment a minor quantity of sulfuric acid was produced.

Although high impurity extractions can be obtained at 150 g/L, the acid surplus is certainly necessary to prevent massive hydrolysis of dissolved metals during cooling in general and filtration in particular.

5.5.3   Additives series

Originally, two autoclave experiments with IPC residue of May 10 were planned for the additives series: a blank run without organic reagents, and a "worst case" run with 5 ppm Crodaglu 1M44 and 100 ppm Dowfax 2A0 in the electrolyte. Utilizing the usual 700 mL of electrolyte, the leach conditions became so reducing at the end of both tests that it was decided to repeat them with 800 mL instead. When the slurry ORP's measured upon completion of the additional experiments were still negative, the additives series was ceased since higher priority was given to other test work. The leaching results, which are not less informative, are summarized in Table 5-2.

As anticipated, the presence of additives in the electrolyte has no impact on first-stage leaching, even at the uncommonly high levels used in tests #48 and #55. Crodaglu degrades rapidly at temperatures higher than 60-70°C, so that glue essentially decomposes during preheating of the batch. Although Dowfax has been attributed good thermal stability and resistance to deactivation by other ions even in concentrated electrolytes [61], the combination of the high leaching temperature and the harsh FSL solution is likely detrimental to Dowfax's di-phenyl oxide di-sulfonate structure. Moreover, the surfactant acts at the solution/gas interface rather than at the solution/solids interface. It is noted, however, that minor quantities of elemental sulfur-like flakes were observed floating on the supernatant solution during filtration, yet assays for S° in the additives residues were zero.

Table 5-2. Effect of organic electrowinning additives on the extraction of cobalt, nickel, iron and arsenic.

electrolyte volume	impurity extractions no additives added	impurity extractions additives added
700 mL	93.6% Co	93.8% Co
	87.2% Ni	87.9% Ni
	0.0% As	0.0% As
	96.2% Fe	95.8% Fe
800 mL	93.4% Co	93.5% Co
	92.2% Ni	94.5% Ni
	0.0% As	0.0% As
	95.4% Fe	95.8% Fe

5.6   Reaction Model for First-Stage Leaching under Reducing Conditions

Interestingly, the results of the additives series suggest that 95% nickel extractions can still be obtained at a slurry potential as low as -263 mV_{SCE} at room temperature, when all copper and arsenic have already been depleted. In addition to the results of the agitation series, this is strong evidence for a sequence of "precipitation" reactions rather than "co-precipitation" of arsenic and nickel after copper depletion.

On the basis of the experimental results so far, it is postulated that dissolved arsenic takes over the role of copper in the metathesis reactions once the copper level in the FSL solution has been reduced to zero. Since the slurry ORP is proportional to the logarithm of the activity of dissolved species, a major shift in the slurry potential is observed whenever the last traces of a certain metal are removed from solution and another redox system becomes the controlling one. With the successive depletion of copper and arsenic, the FSL moves to progressively lower potentials.

From the E_h-pH diagrams in Chapter 3 it follows that the aforementioned slurry ORP of -263 mV_{SCE} is well within the stability region of H_2S at the residual filtrate acidity of 95.2 g/L of test #55. It is believed that the removal of arsenic from solution is dominated by exchange reactions with unleached sulfides until the point of hydrogen sulfide formation is reached and the element is readily precipitated.

After arsenic, nickel also precipitates according to:

$$Ni^{2+} + H_2S \rightarrow NiS + 2H^+ \qquad (5\text{-}2)$$

but this reaction is both thermodynamically and kinetically much less favorable. Using thermodynamic data from Appendix A, an equilibrium constant of only 82.4 at 25°C can be calculated for reaction (5-2). The observed build-up of H_2S in the autoclave freeboard and the decreased filterability of reducing FSL slurries could both be indicative of the fact that the precipitation of millerite is homogeneous.

There is one more scenario regarding the behavior of arsenic and nickel that must be considered. Under the right conditions, two co-existing sulfide minerals will react to form a mixed sulfide phase with a more negative Gibbs free energy (greater stability) than obtained by the sum of the Gibbs values of the individual minerals (after E. Peters).

Thermodynamically speaking, the conditions for the formation of gersdorffite or wolfachite (both NiAsS) are quite favorable. First of all, when Figures 3-3 and 3-5 are superimposed a significant overlap of the arsenic and nickel sulfide predominance areas becomes apparent. Secondly, a strong reductant R (metallic copper) is present in the FSL system, allowing reactions of the type:

$$2NiS + As_2S_3 + 6R + 6H^+ \rightarrow 2NiAsS + 6R^+ + 3H_2S \qquad (5\text{-}3)$$

From a kinetic point of view, it remains to be determined at what rate reaction (5-3) would proceed at the FSL temperature of 160°C.

5.7   Behavior of Arsenic

5.7.1   Arsenic series

The aim of the arsenic series was to gain better insight into the relationship between end-of-leach slurry potentials and reprecipitation of arsenic. Furthermore, it was hoped that the series would produce FSL residues more suitable for SEM and XRD work.

The arsenic series comprised six autoclave runs of 0, 10, 20, 30, 60 and 240 minutes duration. They were carried out with IPC residue of May 24, and an electrolyte containing 35 g/L copper, 220 g/L sulfuric acid and a 10 g/L arsenic "spike". The choice for the May 24 feed was solely

based on the availability of sample, whereas the copper level of 35 g/L was selected to achieve acceptable extractions of nickel, cobalt and iron (copper series) while deliberately inducing arsenic precipitation.

During the preparation of electrolyte with 25 g/L each of copper and arsenic for additional test #66, the solubility product of either sodium arsenite or arsenic(III) oxide was exceeded. This leaching experiment was therefore canceled.
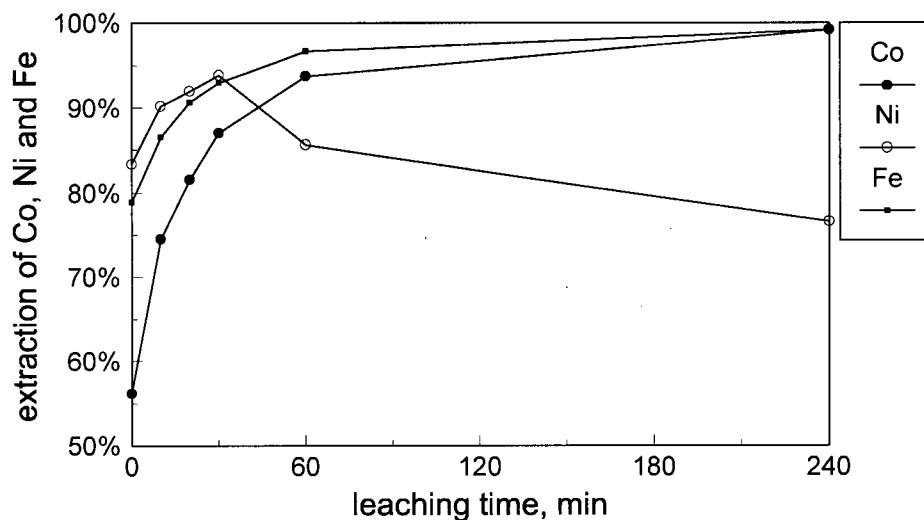
Figure 5-10. Extraction of cobalt, nickel and iron achieved in the arsenic series, as a function of leaching time.
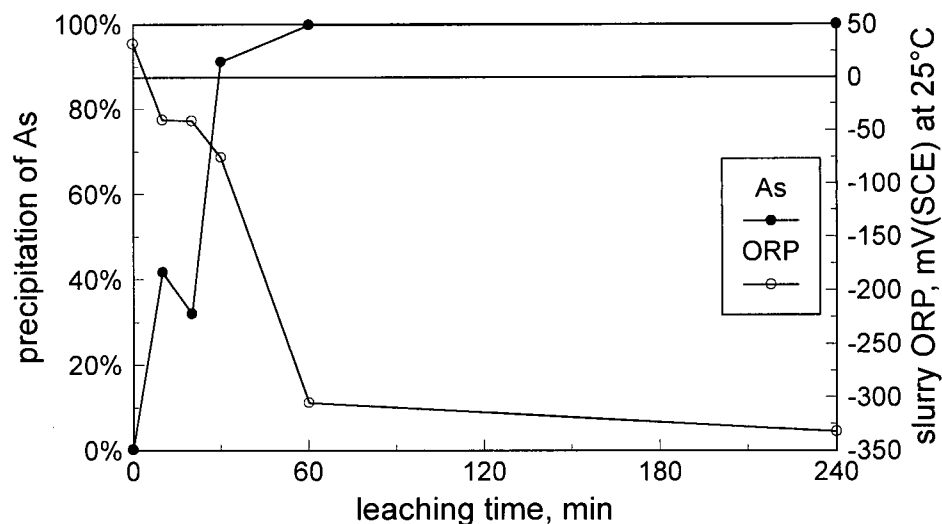
Figure 5-11. Arsenic precipitation and end-of-leach slurry potentials as a function of leaching time.

The results of the arsenic series are shown in Figure 5-10 and Figure 5-11.   Looking at Figure 5-10, two features are evident immediately: (1) reprecipitation of nickel, and (2) a steady increase in the recovery of cobalt and iron even when copper and arsenic are completely and nickel is partially removed from solution.   The reason for the substantial rise in the extraction of cobalt (as in Figure 5-5) and iron is due to exchange reactions between unleached sulfides and acid.   The behavior of nickel is in agreement with the reaction model described in the previous section.

From Figures 5-10 and 5-11 it follows that after 30 minutes of leaching 94% nickel has been extracted from the IPC residue, while more than 90% of the arsenic has precipitated.   Thus, arsenic precipitation is almost completed at -75 mV_{SCE} at 25°C, whereas - in accordance with Figure 3-5 - nickel removal from solution is initiated between -75 and -305 mV.

The existence of a plateau in Figure 5-11 at roughly -40 mV is unlikely.   The discontinuity in the precipitation curve is presumably due to the small difference in the autoclave leaching times for which the data were collected.

In the arsenic series, the distinction between precipitation and reprecipitation of arsenic is unnecessary.   This is shown by both the invariably positive percentage of arsenic removed from solution, as well as by the value of the weight ratio As in IPC residue : As in leach residue, which never becomes significantly smaller than 1.   Hence, either no arsenic at all is extracted from the feed or any dissolved arsenic from the IPC residue has already reprecipitated after heating of the batch to 160°C.   The fact that the mass of leach residue first declines with time and later on increases again is indicative of the competition between extraction and precipitation.

Several loose powder mounts and polished sections of arsenic series residues were examined by SEM with EDX.   Despite the relatively high arsenic content (≈3%) of some of those residues, the SEM work can be considered unsuccessful.   No rims of arsenic sulfides were found; instead, the element seems to be distributed quite evenly throughout the sample.   This is believed to be due to the extremely high specific surface area of the "honeycombs", which offer an almost infinite number of sites for precipitation.   Since lead peaks overlap part of the arsenic spectrum in EDX, mapping for arsenic was rendered virtually impossible by the presence of lead in the samples.

The chemical composition and morphology of IPC and FSL residue varies significantly from grain to grain.   Dense grains are usually much smaller than particles with the porous skeletal structure.   The latter cannot be analyzed reliably by the EDX technique in view of the earlier explained topographic effects.

Using the most promising residue (produced in the arsenic series) in XRD studies, slow scanning around arsenic sulfide peaks did not provide the information hoped for. No decisive phase identification was achieved with residue #61 containing 3.2% arsenic and 2.2% nickel.

5.7.2   Releaching with sodium hydroxide

Leaching experiments and SEM and XRD work together have failed to provide physical evidence that explicitly points to the precipitation of arsenic sulfide compounds under copper-depleted FSL conditions. The only true experimental indication of the formation of such precipitates is the presence of H_2S in the autoclave. Thus, in the absence of *direct* proof for the occurrence of As_xS_y, the goal of the alkaline releaching experiments was to gather additional *indirect* evidence for the existence of arsenic sulfide precipitates. Time constraints have limited the number of re-extraction tests carried out in a NaOH medium to the four described in this section.

In cyanidation circuits all over the world, arsenic sulfide minerals are known to be troublesome gold ore components. Indeed, orpiment and realgar are capable of fouling caustic solutions through the formation of arsenites and thioarsenites:

$$As_2S_3 + 6\ NaOH \rightarrow Na_3AsO_3 + Na_3AsS_3 + 3\ H_2O \tag{5-4}$$

$$2\ AsS + 6\ NaOH \rightarrow Na_3AsO_3 + Na_3AsS_2 + 3\ H_2O \tag{5-5}$$
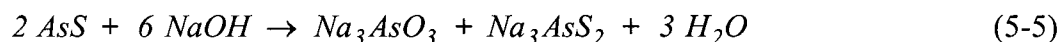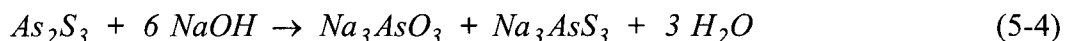
As part of the present investigations into the behavior of arsenic, redissolution of the element from an arsenic-enriched dry FSL residue was tested at pH 11 and 12. For comparison, the amenability of a "normal" residue to leaching in caustic soda solutions of the same alkalinity was also tested. The arsenic re-extractions achieved in the 1-hour experiments are shown in Table 5-3.

Table 5-3.   Effect of residue type and alkalinity on the re-extraction of arsenic.

residue type	pH	arsenic re-extraction
low-arsenic	11	0.0%
0.53% As	12	1.9%
high-arsenic	11	11.0%
2.88% As	12	16.0%

Contrary to the excellent balances of the arsenic series, poor arsenic accountability was attained in the alkaline releaching experiments. This is due to the low concentrations of the metalloid in the NaOH solutions.

The redissolution results are disappointing and essentially inconclusive. It is believed that the low arsenic recoveries reported in Table 5-3 are caused by unfavorable experimental conditions, such as a low temperature, a short leaching time and insufficient alkalinity, rather than by the presence of non-sulfidic arsenic compounds in the residue. This view is supported by the fact that no other elements solubilized in the high-pH solutions.

The unsatisfactory arsenic extractions could equally be attributed to the conversion of one arsenic sulfide compound into another with the release of sulfide ion instead of arsenic. However, no sulfide assays are available to confirm such a theory. Finally, the different reactivity of wet and dry FSL residue might have played a role.

5.7.3   Releaching with pregnant electrolyte

The purpose of this important releaching experiment was to investigate the possibility of arsenic redissolution from copper-depleted FSL slurry through the introduction of pregnant electrolyte to the first-stage autoclave pressure let-down tank. Since a line for Durco Filtrate to the first-stage Product Holding Tank (PHT) could easily be put in place at the CRED plant, this would be a convenient way to "correct" reducing batches prior to filtration and alleviate the arsenic related problems during second-stage leaching.

In the laboratory simulation of this electrolyte addition option, the mass balances over the autoclave are corrupted by unavoidable losses of leach residue to the autoclave internals. Therefore, the releaching results in Appendix C are reported as the relative distribution of arsenic over the liquid and solid phases as a function of time. It is noted that any arsenic removed from the liner through sample taking has been accounted for.

The duplicate releaching experiment with hot $CuSO_4$-H_2SO_4 solution was carried out at a slurry ORP of 85 mV_{SCE} at 80°C. This redox potential was suggested by CRED staff and is based on a study at the JRGRL, which recommended such a value for optimum ($\approx$50%) arsenic extraction in the FSL process.

Unfortunately, the arsenic re-extractions of 1.4% and 6.2% attained after 3 hours clearly indicate that arsenic redissolution at 85 mV is unsuccessful. In fact, this had already become evident in the course of the test since negligible changes in the slurry ORP were observed once

the desired redox value was reached. Thus, similar to the concentration of other impurities in solution, the elevated copper levels of about 17.5 g/L and 10.5 g/L, respectively, remained basically constant.

It is believed that the conditions at which the re-extraction experiments with synthetic Durco Filtrate were done are both thermodynamically and kinetically unfavorable. From the potential-pH diagrams of Figure 3-3 and 3-4 it can be deduced that the potential of 85 mV at high acidity is *thermodynamically* well within the stability region of arsenic sulfide. Furthermore, metathesis reactions generally require autoclave conditions to take place at industrially acceptable rates. Hence, the temperature of 80°C, or, the assumed temperature in the first-stage flash tank, is *kinetically* disadvantageous.

Two process control options for resolubilization of arsenic remain to be examined, namely (1) releaching with pregnant electrolyte at other potentials and temperatures, and (2) intermittent electrolyte injection during first-stage leaching.

With regard to the first option it is advocated the experimental method be improved by connecting the platinum electrode in the releach vessel with an external calomel reference electrode using a salt bridge. The additional potential drop so introduced is negligible, while the life of the reference electrode is greatly prolonged as thermal degradation through disproportionation of the calomel is eliminated. Moreover, the risk of unreliable potential measurements caused by desaturation of the KCl solution is much smaller.

The second option calls for changes in batch make-up, and the installation of ORP probes and a high-pressure electrolyte injection system. Before the implementation of these changes, the incremental arsenic recovery achieved by the introduction of copper electrolyte needs to be investigated. Obviously, intermittent electrolyte injection would be an important first step towards a continuous leaching process.

In the meantime, the installation of an ORP probe between the first-stage PHT and Filter Feed Tank seems to be the best option. On-line potential measurements would be a suitable way to identify copper-depleted batches and adapt the make-up of following batches.

5.8   Air Discharge Series

In recent years, staff at the CRED plant have considered the use of compressed air instead of "push steam" to discharge the first-stage autoclaves. Ball park estimates for compressor capacity and cost for air discharge were made back in 1992, together with a proposal for the mode of operation [62].

The important disadvantage of the current practice is overheating of the leach solution, and hence, the acid-resistant lining, to temperatures as high as 175°C by "push steam" entering the FSL reactor. This makes the bricks and mortar prone to cracking and spalling upon introduction of a new batch of only 80-90°C almost directly after discharge of the hot slurry. It is believed that the use of air would circumvent this heat management problem and ultimately result in longer lining life.

As mentioned in Chapter 4, the projected series of laboratory pressure leaching experiments followed by air discharge of the autoclave were dropped. The basis for this decision is the outcome of the simplified calculations attached in Appendix D. These show that air discharge of a typical FSL batch would cause an unwanted rise in the copper level in solution of *at least* 0.35 g/L, and a multiple thereof should the discharge pressure indeed be *maintained* at 115 psig.

The exothermic heat effect associated with air discharge is hard to compute; it would likely be small and pose no threat to the brick lining. In view of significant redissolution of cupric ion, however, setting up a detailed energy balance over a FSL autoclave would be a futile exercise.

Thus, it can be concluded that air discharge of the FSL reactors would result in both considerable copper losses to the tailings and a higher copper content of the mixed carbonate product. Moreover, even if the the increase in the copper concentration was acceptable, the use of air would be unsafe considering the possible presence of H_2S or H_2 in the freeboard after a copper-depleted leach.

For the same reason, controlled air injection into the first-stage reactor has been ruled out as a method to dissolve reprecipitated arsenic. Finally, the current practice of mixing of the off gases from the FSL and SSL could be dangerous in case of severely reducing first-stage conditions caused by process upsets.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

1)   The impurity extractions achieved in the FSL process are independent of the agitation rate and pulp density as long as residue particles are freely suspended. Although more intense stirring of FSL slurry may enhance the diffusion rate of ions in the bulk of the solution, the overall leaching rate remains limited by the movement of ions participating in the leaching reactions inside the skeletal residue structure.

2)   The sensitivity of the impurities to the amount of acid in solution decreases in the order Fe > Ni > Co, indicating that a significant portion of the iron and, to a lesser extent, nickel are present in oxide phases in the IPC feeds, whereas the dissolution of cobalt is largely due to metathesis reactions. As anticipated, the efficiency of the FSL process is not affected by the presence of organic electrowinning additives such as Crodaglu 1M44 and Dowfax 2A0 in the slurry, since these decompose at the high temperature and acidity prevailing in the first-stage reactor.

3)   Regardless of the copper level in solution at the end of the first-stage leach, the arsenic recovery generally peaks at about 50 to 60%. On the basis of the present results, two scenarios for first-stage leaching of the metalloid can be postulated: (1) the extraction of arsenic is kinetically slower than the solubilization of the other impurities, (2) the element is distributed over two or more separate minerals, at least one of which leaches favorably compared to the other(s) that is (are) refractory towards dissolution in the $CuSO_4$-H_2SO_4 medium. As both SEM and XRD have not proven useful for the identification of arsenic phases in this project, a series of extended leaching experiments with intermittent electrolyte addition should be carried out to investigate both scenarios in more detail. Simultaneously, the test results would provide insight into the leaching response of the first-stage process in a continuous operation.

4)   Kinetic studies have not produced useful data for the derivation of a kinetic model describing overall first-stage leaching. However, they have shown that the leaching of IPC residue does not or no longer satisfy the first order relationship proposed by INCO in the early 1970's. Moreover, only cobalt and iron follow the expected temperature-retention time trend; long residence times at a temperature of 160°C without

replenishment of the copper level in solution are not only detrimental to the arsenic recovery, but, interestingly, also adversely affect the nickel extraction.

On the basis of thermodynamics and the behavior of arsenic and nickel observed in the experimental work, a rudimentary model has been proposed to describe the presumably sequential processes taking place after copper depletion. The model suggests that dissolved arsenic takes over the role of copper in the metathetic exchange reactions with unleached sulfides once this metal has been quantitatively consumed. As the potential becomes progressively lower, H_2S becomes stable and precipitates any residual arsenic in solution. In both ways arsenic reports to the leach residue as an arsenic sulfide.

After arsenic, nickel is also precipitated, but the formation of millerite (NiS) is thermodynamically much less favorable as can be deduced from the small equilibrium constant at 25°C for the reaction between nickelous ion and dissolved hydrogen sulfide gas. Furthermore, the observed accumulation of H_2S in the autoclave plenum and the inferior filtration characteristics of severely reduced FSL slurries could point to kinetically slow homogeneous precipitation.

Unfortunately, neither direct nor indirect proof of the presence of arsenic sulfides in FSL residues of the copper-depleted type has been produced. Using SEM, mapping of arsenic in residues enriched with this element was made impossible by the presence of lead. The concentration of arsenic phases is generally too low for identification by XRD. Finally, the results of releaching experiments aimed at the selective re-extraction of arsenic from leach residues in NaOH solutions are essentially inconclusive.

5)   Arsenic redissolution from a copper-depleted FSL batch cannot be accomplished by the introduction of pregnant electrolyte (Durco Filtrate) to the first-stage autoclave pressure let-down vessel under the conditions of the laboratory simulation.

Two options for the re-extraction of arsenic remain to be studied, namely (1) releaching with pregnant electrolyte at higher slurry potentials than 85 mV_{SCE} and temperatures than 80°C, although the latter likely already approximates the temperature in the flash tank, and (2) intermittent electrolyte injection during first-stage leaching.

In the meantime, the installation of an ORP probe between the first-stage PHT and Filter Feed Tank seems to be the best option. On-line potential measurements would be a suitable way to identify copper-depleted batches and adapt the make-up of following batches.

6)   Simplified calculations have shown that the use of air instead of "push steam" for discharging of a typical FSL batch would cause an unwanted rise in the copper level in solution. The increase in the copper content of the solution is estimated at 0.35 g/L in case the compressor would shut down once it reaches the desired discharge pressure of 115 psig. Should the discharge pressure be maintained at 115 psig the incremental copper concentration would be several times higher.

Considering the reduced nature of FSL residues, the effect of agitation is trivial; the cuprous sulfide slurry can be expected to react with any oxygen introduced to the reactor almost instantaneously, whether it is stirred or not.

Even if the increase in the copper concentration was acceptable, the use of air would be unsafe in view of the possible presence of H_2S and H_2 in the autoclave freeboard after a copper-depleted leach.

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APPENDIX A

THERMOCHEMICAL CALCULATIONS

I   Species and thermodynamic data

Tables A-1 through A-4 show the complete set of species considered and thermodynamic data used in the calculations of Chapters 3 and 5.

Table A-1.   Thermodynamic data of water species; ¶ on "conventional" scale, § calculated by CSIRO software.

Species	S°_{298K}	$\Delta G^{\circ}_{f,298K}$	Source	$\Delta G^{\circ}_{f,433K}$ (calc'd)
	J/mole/K	kJ/mole		kJ/mole
H_2O	69.950	-237.141	[50]	- §
H_2	130.680	0	[50]	0
O_2	205.147	0	[50]	0
H^+	0 ¶	0	[45]	0
OH^-	-10.75	-157.293	[45]	-119.9

Table A-2.   Thermodynamic data of sulfur species; ¶ before extension of sulfur metastability, § destabilized prior to Criss and Cobble calculations, † classified as a simple anion.

Species	S°_{298K}	$\Delta G^{\circ}_{f,298K}$	Source	$\Delta G^{\circ}_{f,433K}$ (calc'd)
	J/mole/K	kJ/mole		kJ/mole
H_2S (g)	205.753	-33.328	[50]	-38.284
H_2S (aq)	129	-27.87	[45]	-
HS^-	62.9	12.05	[45]	30.3 †
S^{2-}	-16.3	86.31	[45]	111.4
S (rhombic)	32.056	0	[50]	0
HSO_4^-	131.8	-756.01 ¶	[45]	-397.4 §
SO_4^{2-}	20.1	-744.63 ¶	[45]	-362.5 §

Table A-3.   Thermodynamic data of arsenic species; ¶ estimated value, § classified as a simple cation.

Species	S°_{298K} J/mole/K	$\Delta G^{\circ}_{f,298K}$ kJ/mole	Source	$\Delta G^{\circ}_{f,433K}$ (calc'd) kJ/mole
AsH_3	222.782	69.109	[50]	71.101
As (rhombohedral)	35.706	0	[50]	0
AsO^+	12.52 ¶	-163.8	[45]	-156.7 §
$HAsO_2$	126.6	-402.7	[45]	-373.1
AsO_2^-	41.2	-350.2	[45]	-304.4
H_3AsO_3	196.6	-639.9	[45]	-597.0
$H_2AsO_3^-$	110.4	-587.5	[45]	-528.2
$HAsO_3^{2-}$	-35.1 ¶	-524.3	[47]	-435.5
AsO_3^{3-}	-248.9 ¶	-447.7	[47]	-323.9
H_3AsO_4	184.1	-766.1	[46]	-707.0
$H_2AsO_4^-$	117.0	-748.5	[45]	-705.0
$HAsO_4^{2-}$	3.76	-707.1	[45]	-642.1
AsO_4^{3-}	-162.7	-647.5	[45]	-554.4
As_2O_3 (claudetite)	117.001	-576.641	[50]	-541.548
As_4S_4 (realgar)	254.053	-133.004	[50]	-129.357
AsS	63.51	-70.32	[51]	-
As_2S_3 (orpiment)	163.594	-166.172	[50]	-164.679

Table A-4.   Thermodynamic data of nickel species.

Species	S°_{298K} J/mole/K	$\Delta G^{\circ}_{f,298K}$ kJ/mole	Source
Ni	29.874	0	[50]
$NiOH^+$	-71.1	-227.6	[46]
Ni^{2+}	-159.0	-46.4	[45]
$HNiO_2^-$	-	-349.2	[48]
NiO (bunsenite)	37.991	-211.539	[50]
Ni_3S_2 (heazlewoodite)	133.888	-210.396	[50]
NiS (millerite)	53.011	-85.205	[50]

II   Entropy estimations

Arsenyl ion: Latimer's method

According to Latimer [56], the standard entropy of a complex aqueous species can be approximated by adding the individual entropy contributions of the element and the ligand. Whereas the former is usually known, the latter may be calculated from available data for similar species. Thus, for the arsenyl ion, the entropy contribution of the ligand (oxygen) is calculated from the antimonyl ion:

Table A-5.   Thermodynamic data used in the calculation of the standard entropy of the arsenyl ion.

complex aqueous species	S°_{298K} (species) J/mole/K	S°_{298K} (element) J/mole/K	S°_{298K} (ligand) J/mole/K
SbO^{+}	22.33	45.522	-23.19
AsO^{+}	?	35.706	-23.19

Hence:

$$S^{\circ}_{298K}(AsO^{+}) \; = \; 35.706 \; + \; (-23.19) \; = \; 12.52 \, J.mole^{-1}.K^{-1} \qquad \text{(A-1)}$$

If more entropy data for similar species are available they all should be used to calculate a more accurate average value for the entropy contribution of the ligand.

Di-ortho-arsenite and ortho-arsenite ions

It is assumed that the stepwise decrease in entropy for the ortho-arsenious acid dissociation series is proportionally the same as for arsenic acid:

Table A-6.   Thermodynamic data used in the calculation of the standard entropy of the di-ortho-arsenite and ortho-arsenite ions.

Species	S°_{298K}	S°_{298K}	Species
	J/mole/K	J/mole/K	
H_3AsO_4	184.1	196.6	H_3AsO_3
$H_2AsO_4^-$	117.0	110.4	$H_2AsO_3^-$
$HAsO_4^{2-}$	3.76	?	$HAsO_3^{2-}$
AsO_4^{3-}	-162.7	?	AsO_3^{3-}

Hence:

$$S^{\circ}_{298K}(HAsO_3^{2-}) = 110.4 - \frac{117.0 - 3.76}{184.1 - 117.0}(196.6 - 110.4) = -35.1 \; J.mole^{-1}.K^{-1} \qquad (A\text{-}2)$$

$$S^{\circ}_{298K}(AsO_3^{3-}) = -35.1 - \frac{3.76 - (-162.7)}{184.1 - 117.0}(196.6 - 110.4) = -248.9 \; J.mole^{-1}.K^{-1} \qquad (A\text{-}3)$$

III   Criss and Cobble's theory

Correct application of the Criss and Cobble theory requires the formation reactions of all charged aqueous species from their elements be written as full-cell reactions. In this way ambiguities in defining the properties of electrons are avoided. As an example, consider the half-cell reaction for the formation of the arsenyl ion:

$$As + H_2O \rightarrow AsO^+ + 2H^+ + 2e^- \qquad (A\text{-}4)$$
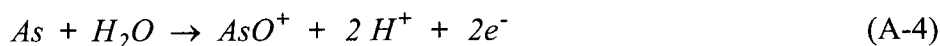
Equation (A-4) is combined with the hydrogen half-cell reaction:

$$H^+ + e^- \rightarrow \tfrac{1}{2}H_2 \qquad (A\text{-}5)$$

and the water formation reaction:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \qquad (A\text{-}6)$$

to give:

$$As + \tfrac{1}{2} O_2 + H^+ \rightarrow AsO^+ + \tfrac{1}{2} H_2 \tag{A-7}$$
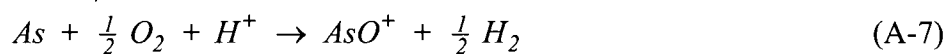
Since, by definition, the Gibbs free energies of formation of the elements and protons are zero at 25°C, it follows that:

$$\Delta \dot{G}^\circ_{f,298K} = \Delta G^\circ_{f,298K} (AsO^+) \tag{A-8}$$

The formation reactions for the other ions are written in a similar fashion:

$$As + O_2 + \tfrac{1}{2} H_2 \rightarrow AsO_2^- + H^+ \tag{A-9}$$

$$As + \tfrac{3}{2} O_2 + \tfrac{3}{2} H_2 \rightarrow H_2AsO_3^- + H^+ \tag{A-10}$$

$$As + \tfrac{3}{2} O_2 + \tfrac{3}{2} H_2 \rightarrow HAsO_3^{2-} + 2 H^+ \tag{A-11}$$

$$As + \tfrac{3}{2} O_2 + \tfrac{3}{2} H_2 \rightarrow AsO_3^{3-} + 3 H^+ \tag{A-12}$$

$$As + O_2 + \tfrac{3}{2} H_2 \rightarrow H_2AsO_4^- + H^+ \tag{A-13}$$

$$As + O_2 + \tfrac{3}{2} H_2 \rightarrow HAsO_4^{2-} + 2 H^+ \tag{A-14}$$

$$As + O_2 + \tfrac{3}{2} H_2 \rightarrow AsO_4^{3-} + 3 H^+ \tag{A-15}$$

$$S^\circ + H_2 \rightarrow HS^- + H^+ \tag{A-16}$$

$$S^\circ + H_2 \rightarrow S^{2-} + 2 H^+ \tag{A-17}$$

$$S^\circ + 2 O_2 + H_2 \rightarrow HSO_4^- + H^+ \tag{A-18}$$

$$S^\circ + 2 O_2 + H_2 \rightarrow SO_4^{2-} + 2 H^+ \tag{A-19}$$

$$\tfrac{1}{2} O_2 + H_2 \rightarrow OH^- + H^+ \tag{A-20}$$
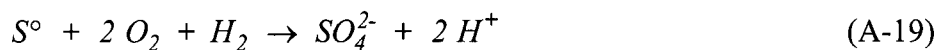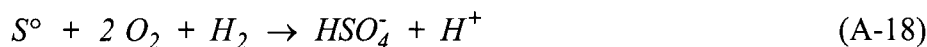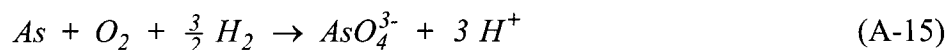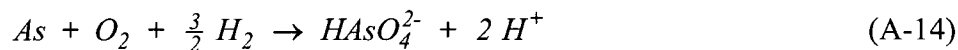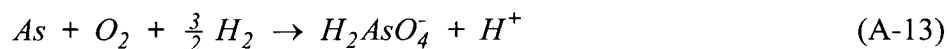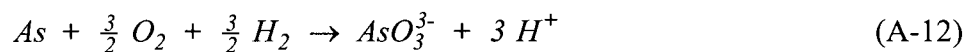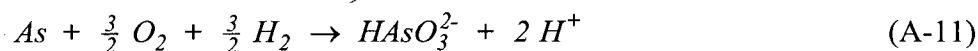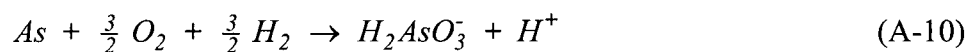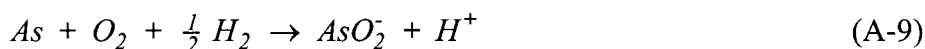
Criss and Cobble's entropy correspondence principle [53] is mathematically expressed as:

$$S^{\circ}_{TK} = a(T) + b(T)S^{\circ}_{298K} \qquad (A\text{-}21)$$

The tabulated coefficients a and b are functions of both temperature and the type of ion [53,54]. Equation (A-21) is only satisfied when the "conventional" standard entropies of the ions (in cal/mole/K) are converted to the "absolute" scale [54] through the relationship:

$$S^{\circ}_{298K}(abs) = S^{\circ}_{298K} - 5.0z \qquad (A\text{-}22)$$

wherein z is the ionic charge.

The average heat capacity of ions is given by:

$$C^{\circ}_{p}\Big|^{TK}_{298K} = \frac{S^{\circ}_{TK} - S^{\circ}_{298K}(abs)}{\ln\dfrac{T}{298.15}} \qquad (A\text{-}23)$$

The great usefulness of this extension of the entropy correspondence principle, of course, is that it does not require any direct information on the heat capacity for electrolytes at any temperature.

The average heat capacities of the non-ionic species - except for undissociated complexes - are calculated from existing C°_{p} data:

$$C^{\circ}_{p}\Big|^{TK}_{298K} = \frac{\displaystyle\int_{298K}^{TK} C^{\circ}_{p}(T)\, dT}{T - 298.15} \qquad (A\text{-}24)$$

wherein:

$$C^{\circ}_{p}(T) = A + BT + CT^{-2} \qquad (A\text{-}25)$$

The heat capacity functions (in J/mole/K) used in the spreadsheet calculations are taken from Rao [49]:

$$C^{\circ}_{p}(T, H_2) = 27.280 + 3.264 \times 10^{-3}\,T + 0.502 \times 10^{5}\,T^{-2} \qquad (A\text{-}26)$$

$$C_p^o(T, O_2) = 29.957 + 4.184 \times 10^{-3} T - 1.674 \times 10^5 T^{-2} \qquad (A\text{-}27)$$

$$C_p^o(T, As) = 23.179 + 5.523 \times 10^{-3} T \qquad (A\text{-}28)$$

$$C_p^o(T, S) = 14.811 + 24.058 \times 10^{-3} T + 0.728 \times 10^5 T^{-2} \qquad (A\text{-}29)$$

The change in heat capacity of the ion formation reaction is obtained by summing the average heat capacities of products minus reactants. $\Delta G_{f,TK}^o$ for the ion formation reaction can then readily be calculated according to:

$$\Delta G_{f,TK}^o = \Delta G_{f,298K}^o - \Delta S_{298K}^o (T - 298.15) + \Delta C_p^o \Big|_{298K}^{TK} \Theta \qquad (A\text{-}30)$$

with:

$$\Theta = T - 298.15 - T \ln \frac{T}{298.15} \qquad (A\text{-}31)$$

Since the free energies of the elements and protons at all temperatures are zero by convention, $\Delta G_{f,TK}^o$ for the reaction is equal to the Gibbs free energy of formation of the ion at temperature T. The calculated values of $\Delta G_{f,433K}^o$ for all ions considered are reported in Tables A-1 to A-3.

IV   Helgeson's theory

In Helgeson's analysis [57] the total interaction between complex, ions and solvent dipoles contributing to the entropy change of dissociation of an undissociated species in aqueous solution is regarded as the sum of electrostatic (long range) and non-electrostatic (short range) interaction:

$$\Delta S_T^o (diss) = \Delta S_e^o (T) + \Delta S_n^o (T) = \Delta S_e^o (T_r) f(T) + \Delta S_n^o (T_r) g(T) \qquad (A\text{-}32)$$

wherein T_r is the reference temperature (25°C).

The combination of a general form of the Born or Bjerrum equation and a mathematical relationship expressing the variation of the dielectric constant of water with temperature in the 0-370°C interval gives the following equation for the electrostatic entropy term:

$$\Delta S_e^{\circ}(T) = \Delta S_e^{\circ}(T_r) \exp\left[\exp(b + aT) - \exp(b + aT_r) + \frac{T - T_r}{\Theta} \right] \times$$

$$\frac{1 + a\Theta \exp(b + aT)}{1 + a\Theta \exp(b + aT_r)} \tag{A-33}$$

with $a = 0.01875$, $b = -12.741$ and $\Theta = 219$.

$\Delta S_e^{\circ}(T)$ is equal to the net difference in the entropy change attending solvation of the neutral complex and its dissociated species as long as the hydration process is entirely electrostatic. The standard state adopted in Helgeson's theory is based on infinite dilution. Consequently, ion-ion and ion-complex interaction are negligible, and $\Delta S_e^{\circ}(T)$ refers solely to the electrostatic interaction of water dipoles with the complex and its dissociated ions.

Assuming that for dissociational reactions in aqueous solutions the non-electrostatic contribution to the heat capacity of dissociation can be represented by:

$$\Delta C_{p,n}^{\circ}(T) = \alpha + \beta T + \gamma T^2 \tag{A-34}$$

in which α, β and γ are reaction-dependent coefficients, then equation (A-34) can be divided by T and integrated to give the following approximation to the non-electrostatic entropy term:

$$\Delta S_n^{\circ}(T) = \Delta S_n^{\circ}(T_r) + \alpha \ln \frac{T}{T_r} + \beta(T - T_r) + \frac{\gamma}{2}(T^2 - T_r^2) \tag{A-35}$$

Substitution of equations (A-33) and (A-35) into equation (A-32) yields:

$$\Delta S_T^{\circ}(diss) = \Delta S_e^{\circ}(T_r) \exp\left[\exp(b + aT) - \exp(b + aT_r) + \frac{T - T_r}{\Theta} \right] \times$$

$$\frac{1 + a\Theta \exp(b + aT)}{1 + a\Theta \exp(b + aT_r)} + \Delta S_n^{\circ}(T_r) + \alpha \ln \frac{T}{T_r} + \beta(T - T_r) + \frac{\gamma}{2}(T^2 - T_r^2) \tag{A-36}$$

The general expression for the dissociation constant of dissociational reactions as a function of temperature resulting from this analysis is cumbersome and unpractical. However, $\log K_T (diss)$ for many complexes below $\approx 200°C$ can be closely approximated by assuming that:

$$\frac{\Delta S_e^{\circ}(T)}{\Delta S_e^{\circ}(T_r)} \approx \frac{\Delta S_n^{\circ}(T)}{\Delta S_n^{\circ}(T_r)} \tag{A-37}$$

which is consistent with the statement that:

$$\frac{\Delta C^{\circ}_{p,T}\,(diss)}{\Delta C^{\circ}_{p,e}\,(T)} \;=\; constant \tag{A-38}$$

The effectiveness of this approximation is partly due to the insensitivity of $\log K_T\,(diss)$ to substantial departures from the above constant ratio, and partly to the similar behavior of the non-electrostatic power function of temperature and the electrostatic exponential function at low temperatures.

The assumption that $\Delta C^{\circ}_{p,T}\,(diss)$ is proportional to $\Delta C^{\circ}_{p,e}\,(T)$ leads to:

$$\log K_T\,(diss) \;=\; \left[T_r \,-\, \frac{\Theta}{\omega}\left[1 \,-\, \exp\left[\exp(b+aT) \,-\, \exp(b+aT_r) \,+\, \frac{T-T_r}{\Theta}\right]\right]\right] \times$$

$$\frac{\Delta S^{\circ}_T(T_r)}{RT\ln 10} \,+\, \frac{\Delta H^{\circ}_T(T_r)}{RT\ln 10} \tag{A-39}$$

where:

$$\omega \;=\; 1 \,+\, a\Theta\exp(a+bT_r) \;=\; 1.00322 \tag{A-40}$$

Only when the entropy and enthalpy of dissociation at 25°C are both negative, close approximations of $\log K_T\,(diss)$ (or $\Delta G^{\circ}_T\,(diss)$) to about 200°C can be made assuming $\Delta C^{\circ}_{p,T}\,(diss)\big/\Delta C^{\circ}_{p,e}\,(T)$ is constant. The negative entropy value reflects the major contribution of solvent interaction to complex stability. On the contrary, if the heat capacity of dissociation and (or) $\Delta S^{\circ}_T\,(T_r)$ and $\Delta H^{\circ}_T\,(T_r)$ are positive, the non-electrostatic contribution to $\Delta C^{\circ}_{p,T}\,(diss)$ is considerable and an approximation to $\log K_T\,(diss)$ (or $\Delta G^{\circ}_T\,(diss)$) using equation (A-39) is not warranted. In the borderline case, *i.e.* negative entropy and large positive enthalpy of dissociation (*e.g.* the water equilibrium), the approximation of equation (A-38) also holds. In such case the effectiveness of equation (A-39) is primarily due to the fact that $\log K_T\,(diss)$ is dominated by the enthalpy term.

Since:

$$\Delta G^{\circ}_T\,(diss) \;=\; -RT\ln K_T\,(diss) \;=\; -RT\ln 10\log K_T\,(diss) \tag{A-41}$$

it follows that:

$$\Delta G_T^{\circ}(diss) = \left[T_r - \frac{\Theta}{\omega} \left[1 - \exp\left[\exp(b + aT) - \exp(b + aT_r) + \frac{T - T_r}{\Theta} \right] \right] \right] \times$$
$$\Delta S_T^{\circ}(T_r) + \Delta H_T^{\circ}(T_r) \quad\quad\quad (A\text{-}42)$$

Hence, the free energy of formation of the neutral complex is calculated using the equation:

$$\Delta G_{f,T}^{\circ}(complex) = \sum \Delta G_{f,T}^{\circ}(ions) - \Delta G_T^{\circ}(diss) \quad\quad\quad (A\text{-}43)$$

The free energies of formation of the ions are calculated by the method of Criss and Cobble as previously described.

The reactions treated according to the simplified Helgeson equations are:

$$HAsO_2 \rightarrow H^+ + AsO_2^- \quad\quad\quad (A\text{-}44)$$

$$H_3AsO_3 \rightarrow H^+ + H_2AsO_3^- \quad\quad\quad (A\text{-}45)$$

$$H_3AsO_4 \rightarrow H^+ + H_2AsO_4^- \quad\quad\quad (A\text{-}46)$$
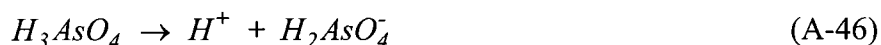
Not considered are the dissociation reactions:

$$H_2(g) \rightarrow H_2(aq) \quad\quad\quad (A\text{-}47)$$

$$O_2(g) \rightarrow O_2(aq) \quad\quad\quad (A\text{-}48)$$

$$H_2S(g) \rightarrow H_2S(aq) \quad\quad\quad (A\text{-}49)$$

$$AsH_3(g) \rightarrow AsH_3(aq) \quad\quad\quad (A\text{-}50)$$

For these reactions involving molecular gases the situation is more complicated due to large non-electrostatic contributions. Moreover, the CSIRO Thermochemistry software utilizes data for non-hydrated oxygen and hydrogen gas for the computation of the water stability lines at all temperatures.

APPENDIX B

EXPERIMENT DESIGN CALCULATIONS

CRED PLANT DATA

Densities:

IPC slurry	1.89E+03 kg/m3	{dilution due to pump flange water not included}
IPC solids	5.5E+03 kg/m3	
water	1.0E+03 kg/m3	
electrolyte	1.26E+03 kg/m3	

Constant Density Tank:

tank volume	6550 L		
water volume	5255 L		
water mass	5255 kg =	11584 lbs	
solids volume	1295 L		
solids mass	7125 kg =	15708 lbs	
% solids in slurry	57.6% (wt.)		

First-Stage Batch Make-Up Tank:

steam condensate volume	600 L	{heating to 80°C}
steam mass	600 kg =	1323 lbs
electrolyte volume	12500 L	{mixture of spent and pregnant}
electrolyte mass	15750 kg =	34722 lbs
% solids in batch	33.0% (wt.)	{at the end of preheating}

First-Stage Autoclave:

steam condensate volume	3500 L	{heating to 160°C}
steam mass	3500 kg =	7716 lbs
total batch mass	32230 kg =	71053 lbs
total batch volume	23150 L	{at the beginning of leaching}

% solids in autoclave	22.1% (wt.)	5.6% (vol.)
% water in autoclave	29.0% (wt.)	40.4% (vol.)
% electrolyte in autoclave	48.9% (wt.) +	54.0% (vol.) +
	100%	100%

LABORATORY BATCH MAKE-UP

MAWL	1.3 L	{from Parr manuals}		
add solids	0.073 L =	400 g	take 360 g
add water	0.525 L =	525 mL	take 500 mL
add electrolyte	0.702 L =	702 mL	take 700 mL

APPENDIX C

EXPERIMENT WORKSHEETS

This appendix contains the worksheets of autoclave runs and releaching experiments carried out as part of the present investigations, in chronological order. The results of both unsuccessful tests and experiments which are now considered irrelevant are not included. In case mechanical difficulties were encountered during a certain test, the nature of the problem is specified on the worksheet. There was generally not enough sample available to repeat those experiments. It goes without saying that data generated by such tests were utilized with prudence in Chapter 5.

The reported assays are a collection of chiefly ICP analyses, copper electrodeposition tests, acid titrations and LECO analyses, the vast majority of which was performed by INCO's Copper Cliff Central Process Technology Laboratory. A small number of solutions and residues generated during INCO's summer shutdown were analyzed at the International Plasma Laboratory (IPL) in Vancouver.

RELEACHING TEST WORKSHEET

test ID: #F
date: Monday, July 10, 1995

medium: NaOH

natural pH: 6.40
test pH: 12.00

temperature:	50	°C	122	°F
leaching time at T:	60	min	1	h

initial pulp density: 10% solids

REAGENT BALANCE

Beaker feed   Beaker products

FSL residue #62:	33.3	g	leach residue:	33.6	g
deionized water:	300	mL	leach filtrate:	298	mL
1M NaOH solution:	53.6	mL	wash water:	205	mL
			total filtrate:	503	mL
			repulp volume:	438	mL

ARSENIC ASSAYS

time minutes	leach sol'n ppm	solids ppm	repulp sol'n ppm
-	0	28833	
0	347		
30	396		
60	456	25068	0

ARSENIC BALANCE

time minutes	As in beaker mg	As in sol'n mg	As in solids mg	As distribution solution	As distribution solids
-	960.14	0	960.14	0.0%	100.0%
0	960.14	122.68	837.46	12.8%	87.2%
30	956.67	136.05	820.62	14.2%	85.8%
60	952.71	152.01	800.70	16.0%	84.0%

Assay head As extraction   12.4%

RELEACHING TEST WORKSHEET

test ID: #E
date: Monday, July 10, 1995

medium: NaOH

natural pH: 6.75
test pH: 11.00

temperature: 50 °C   122 °F
leaching time at T: 60 min   1 h

initial pulp density: 10% solids

REAGENT BALANCE

Beaker feed   Beaker products

FSL residue #62:   33.3 g   leach residue: 32.9 g
deionized water: 300 mL   leach filtrate: 255 mL
1M NaOH solution: 7.8 mL   wash water: 215 mL
                                                  total filtrate: 470 mL

                                                  repulp volume: 401 mL

ARSENIC ASSAYS

time	leach sol'n	solids	repulp sol'n
minutes	ppm	ppm	ppm
-	0	28833	
0	0		
30	277		
60	367	27255	0

ARSENIC BALANCE

time	As in beaker	As in sol'n	As in solids	As distribution	
minutes	mg	mg	mg	solution	solids
-	960.14	0	960.14	0.0%	100.0%
0	960.14	0	960.14	0.0%	100.0%
30	960.14	82.49	877.65	8.6%	91.4%
60	957.37	105.56	851.81	11.0%	89.0%

Assay head As extraction   6.8%

RELEACHING TEST WORKSHEET

test ID: #D
date: Friday, July 7, 1995

medium: NaOH

natural pH: 4.18
test pH: 11.98

| temperature: | 50 °C | 122 °F |
| leaching time at T: | 60 min | 1 h |

initial pulp density: 20% solids

REAGENT BALANCE

Beaker feed   Beaker products

FSL residue #63:	75 g	leach residue:	74.8 g
deionized water:	300 mL	leach filtrate:	283 mL
1M NaOH solution:	61.1 mL	wash water:	232 mL
		total filtrate:	515 mL
		repulp volume:	437 mL

ARSENIC ASSAYS

time minutes	leach sol'n ppm	solids ppm	repulp sol'n ppm
-	0	5298	
0	14		
30	21		
60	21.8	4969	0

ARSENIC BALANCE

time minutes	As in beaker mg	As in sol'n mg	As in solids mg	As distribution solution	solids
-	397.35	0	397.35	0.0%	100.0%
0	397.35	5.05	392.30	1.3%	98.7%
30	397.21	7.37	389.84	1.9%	98.1%
60	397.00	7.45	389.55	1.9%	98.1%

Assay head As extraction   6.5%

RELEACHING TEST WORKSHEET

test ID: #C
date: Friday, July 7, 1995

medium: NaOH

natural pH: 3.77
test pH: 11.01

temperature: 50 °C   122 °F
leaching time at T: 60 min   1 h

initial pulp density: 20% solids

REAGENT BALANCE

Beaker feed   Beaker products

FSL residue #63:   75 g   leach residue: 73.2 g
deionized water: 300 mL   leach filtrate: 235 mL
1M NaOH solution: 10.7 mL   wash water: 140 mL
                                       total filtrate: 375 mL

                                       repulp volume: 333 mL

ARSENIC ASSAYS

time minutes	leach sol'n ppm	solids ppm	repulp sol'n ppm
-	0	5298	
0	0		
30	0		
60	0	5753	0

ARSENIC BALANCE

time minutes	As in beaker mg	As in sol'n mg	As in solids mg	As distribution solution	solids
-	397.35	0	397.35	0.0%	100.0%
0	397.35	0	397.35	0.0%	100.0%
30	397.35	0	397.35	0.0%	100.0%
60	397.35	0	397.35	0.0%	100.0%

Assay head As extraction   -6.0%

COMBINED AUTOCLAVE AND RELEACHING TEST WORKSHEET

date: Friday, June 30, 1995

AUTOCLAVE TEST				RELEACHING TEST		

AUTOCLAVE TEST

| test ID: | #65 |
| series ID: | Releaching |

temperature:	160 °C		320 °F
heat-up time:	49 min		
leaching time:	60 min		1 h
initial pressure:	5.9 bar		85 psig
final pressure:	5.9 bar		85 psig
stirring rate:	13.7 1/s		820 rpm

RELEACHING TEST

test ID:	#B	
medium:	"Durco filtrate" with	100 g/L CuSO4
		130 g/L H2SO4
temperature:	80 °C	176 °F
leaching time:	180 min	3 h

REAGENT BALANCE

Test feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL
"Durco filtrate":	150 mL at 65°C

Test products

releach residue:	274 g
releach filtrate:	957 mL
wash solution:	421 mL
total filtrate:	1378 mL
repulp volume:	498 mL

SLURRY POTENTIALS

before autoclave leaching:	65 mV (SCE)	310 mV (SHE)
after autoclave leaching:	-168 mV (SCE)	77 mV (SHE) at 80°C
releaching:	85 mV (SCE)	330 mV (SHE) at 80°C

ASSAYS

component	electrolyte g/L	IPC residue May 21, 199	releach residue	time minutes	releach solution ppm As	repulp filtrate ppm As
Cu	35	55.21%	74.86%	-	22	
Co		7.05%	0.70%	0	170	
Ni		8.75%	0.55%	5	204	
As	10	0.79%	2.79%	15	212	
Fe		5.09%	0.26%	30	224	
O		6.82%		60	244	
Stot		15.15%	17.74%	120	284	
H2SO4	220			180	386	8

ARSENIC BALANCE

time minutes	As in liner g	As in sol'n g	As in solids g	As distribution solution	As distribution solids
-	8.013	0.030	7.984	0.4%	99.6%
0	8.013	0.230	7.784	2.9%	97.1%
5	8.012	0.273	7.738	3.4%	96.6%
15	8.010	0.282	7.728	3.5%	96.5%
30	8.007	0.296	7.712	3.7%	96.3%
60	8.005	0.320	7.686	4.0%	96.0%
120	8.003	0.369	7.634	4.6%	95.4%
180	8.000	0.498	7.502	6.2%	93.8%

COMBINED AUTOCLAVE AND RELEACHING TEST WORKSHEET

date: Thursday, June 29, 1995

AUTOCLAVE TEST				RELEACHING TEST			

test ID: #64   test ID: #A
series ID: Releaching

                                                           medium: "Durco filtrate" with   100 g/L CuSO4
                                                                                                        130 g/L H2SO4
temperature: 160 °C   320 °F   temperature: 80 °C   176 °F
heat-up time: 49 min
leaching time: 60 min   1 h   leaching time: 180 min   3 h

initial pressure: 5.9 bar   85 psig
final pressure: 5.9 bar   85 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Test feed   Test products

IPC residue: 360 g   releach residue: 286 g
electrolyte: 700 mL   releach filtrate: 1083 mL
deionized water: 500 mL   wash solution: 347 mL
                                        total filtrate: 1430 mL
"Durco filtrate": 220 mL at 65°C
                                        repulp volume: 542 mL

SLURRY POTENTIALS

before autoclave leaching: 65 mV (SCE)   310 mV (SHE)

after autoclave leaching: -310 mV (SCE)   -65 mV (SHE) at 80°C

releaching: 85 mV (SCE)   330 mV (SHE) at 80°C

ASSAYS

component	electrolyte g/L	IPC residue May 21, 199	releach residue		time minutes	releach solution ppm As	repulp filtrate ppm As
Cu	35	55.21%	74.35%		-	5	
Co		7.05%	0.93%		0	34	
Ni		8.75%	0.79%		5	31	
As	10	0.79%	3.55%		15	36	
Fe		5.09%	0.33%		30	43	
O		6.82%			60	53	
Stot		15.15%	17.74%		120	70	
H2SO4	220				180	107	6

ARSENIC BALANCE

time minutes	As in liner g	As in sol'n g	As in solids g	As distribution solution	solids
-	10.271	0.007	10.264	0.1%	99.9%
0	10.271	0.048	10.222	0.5%	99.5%
5	10.270	0.044	10.227	0.4%	99.6%
15	10.270	0.050	10.220	0.5%	99.5%
30	10.270	0.060	10.210	0.6%	99.4%
60	10.269	0.073	10.196	0.7%	99.3%
120	10.269	0.096	10.173	0.9%	99.1%
180	10.268	0.146	10.122	1.4%	98.6%

AUTOCLAVE TEST WORKSHEET

test ID: #61
series ID: Arsenic
date: Saturday, May 13, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	50 min		
leaching time at T:	240 min	4 h	
initial pressure:	5.8 bar	84 psig	
final pressure:	5.8 bar	84 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g	leach residue:	336 g	residue ratio:	1.07 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL	leach filtrate:	930 mL		
		wash solution:	1014 mL	wash acidity:	11 g/L H2SO4
		total filtrate:	1944 mL		
		repulp volume:	746 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	60 mV (SCE)	305 mV (SHE)
after:	slurry:	-332 mV (SCE)	-87 mV (SHE)
	supernatant:	-186 mV (SCE)	59 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 24, 1994	leach residue	leach filtrate		repulp filtrate
Cu	35 g/L	57.04%	73.65%	0 g/L	0 M	0 g/L
Co		7.10%	0.06%	28.5 g/L	0.484 M	0.137 g/L
Ni		7.90%	2.19%	25.9 g/L	0.442 M	0.289 g/L
As	10 g/L	0.74%	3.21%	0 g/L	0 M	0.004 g/L
Fe		4.03%	0.05%	22.2 g/L	0.398 M	0.108 g/L
O		5.55%	1.06%			
Stot		16.34%	17.63%			
H2SO4	220 g/L			57.3 g/L	0.584 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 24, 1994	leach residue
Cu : O	10.28	69.48
Cu : Stot	3.49	4.18
Stot : O	2.94	16.63

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		68.1	61.93%		4.89%	8.58%
Co	99.2%		7.43%	99.2%	0.33%	4.66%
Ni	74.1%		8.75%	76.6%	0.85%	10.72%
As			1.06%		0.32%	42.83%
Fe	98.9%		5.79%	99.2%	1.76%	43.68%
H2SO4		248.9				

detailed arsenic balance

As in	9.664 g	
As out	10.805 g	
difference	1.141 g	10.56%
As precipitated		100%
As in leach res. : As in IPC res.	4.05 (wt./wt.)	

AUTOCLAVE TEST WORKSHEET

test ID: #60
series ID: Arsenic
date: Thursday, May 11, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	51 min		
leaching time at T:	60 min	1 h	
initial pressure:	5.8 bar	84 psig	
final pressure:	5.8 bar	84 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g		leach residue:	310 g	residue ratio:
electrolyte:	700 mL				
deionized water:	500 mL		leach filtrate:	949 mL	
			wash solution:	971 mL	wash acidity:
			total filtrate:	1920 mL	
			repulp volume:	704 mL	

residue ratio: 1.16 wt./wt.
wash acidity: 11 g/L H2SO4

POTENTIAL MEASUREMENTS

before:	slurry:	60 mV (SCE)	305 mV (SHE)
after:	slurry:	-305 mV (SCE)	-60 mV (SHE)
	supernatant:	-86 mV (SCE)	159 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 24, 1994	leach residue	leach filtrate		repulp filtrate
Cu	35 g/L	57.04%	74.87%	0.05 g/L	0.001 M	0.072 g/L
Co		7.10%	0.50%	24.8 g/L	0.421 M	0.171 g/L
Ni		7.90%	1.43%	27.9 g/L	0.475 M	0.202 g/L
As	10 g/L	0.74%	3.17%	0.01 g/L	0.000 M	0.008 g/L
Fe		4.03%	0.19%	18.7 g/L	0.335 M	0.125 g/L
O		5.55%	1.05%			
Stot		16.34%	18.39%			
H2SO4	220 g/L			61.8 g/L	0.630 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 24, 1994	leach residue
Cu : O	10.28	71.30
Cu : Stot	3.49	4.07
Stot : O	2.94	17.51

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades)	
					absolute	relative
Cu		67.9	57.68%		0.64%	1.12%
Co	93.9%		6.97%	93.8%	0.13%	1.79%
Ni	84.4%		8.58%	85.6%	0.68%	8.58%
As			0.79%		0.05%	6.10%
Fe	95.9%		5.10%	96.7%	1.07%	26.50%
H2SO4		235.2				

detailed arsenic balance

As in	9.664 g		
As out	9.826 g		
difference	0.162 g	1.65%	
As precipitated		99.9%	
As in leach res. : As in IPC res.		3.69 (wt./wt.)	

AUTOCLAVE TEST WORKSHEET

test ID: #59
series ID: Arsenic
date: Wednesday, May 10, 1995

temperature: 160 °C   320 °F
heat-up time to T: 49 min
leaching time at T: 30 min   0.5 h

initial pressure: 5.8 bar   84 psig
final pressure: 5.8 bar   84 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g	leach residue:	308 g	residue ratio:	1.17 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL	leach filtrate:	927 mL		
		wash solution:	1020 mL	wash acidity:	11 g/L H2SO4
		total filtrate:	1947 mL		
		repulp volume:	627 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	60 mV (SCE)	305 mV (SHE)
after:	slurry:	-75 mV (SCE)	170 mV (SHE)
	supernatant:	177 mV (SCE)	422 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 24, 1994	leach residue	leach filtrate		repulp filtrate
Cu	35 g/L	57.04%	75.81%	0.01 g/L	0.000 M	0.009 g/L
Co		7.10%	1.11%	24.7 g/L	0.419 M	0.451 g/L
Ni		7.90%	0.58%	30.0 g/L	0.511 M	0.552 g/L
As	10 g/L	0.74%	2.81%	0.66 g/L	0.009 M	0.092 g/L
Fe		4.03%	0.39%	17.5 g/L	0.313 M	0.351 g/L
O		5.55%	0.97%			
Stot		16.34%	18.63%			
H2SO4	220 g/L			66.5 g/L	0.678 M	12 g/L

element ratio (wt./wt.)	IPC residue of May 24, 1994	leach residue
Cu : O	10.28	78.15
Cu : Stot	3.49	4.07
Stot : O	2.94	19.21

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		68.0	58.06%		1.02%	1.78%
Co	86.6%		7.30%	87.0%	0.20%	2.84%
Ni	93.7%		8.22%	93.9%	0.32%	4.05%
As			0.63%		0.11%	14.92%
Fe	91.6%		4.83%	93.0%	0.80%	19.92%
H2SO4		225.3				

detailed arsenic balance

As in	9.664 g	
As out	9.267 g	
difference	0.397 g	4.29%
As precipitated		91.3%
As in leach res. : As in IPC res.	3.25 (wt./wt.)	

AUTOCLAVE TEST WORKSHEET

test ID: #58
series ID: Arsenic
date: Thursday, May 5, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	51 min		
leaching time at T:	20 min	0.33 h	
initial pressure:	5.8 bar	84 psig	
final pressure:	5.8 bar	84 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	307 g	residue ratio:	1.17 wt./wt.
leach filtrate:	965 mL		
wash solution:	945 mL	wash acidity:	11 g/L H2SO4
total filtrate:	1910 mL		
repulp volume:	617 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	60 mV (SCE)	305 mV (SHE)
after:	slurry:	-41 mV (SCE)	204 mV (SHE)
	supernatant:	135 mV (SCE)	380 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 24, 1994	leach residue	leach filtrate		repulp filtrate
Cu	35 g/L	57.04%	75.51%	0.17 g/L	0.003 M	0.191 g/L
Co		7.10%	1.56%	22.1 g/L	0.374 M	0.130 g/L
Ni		7.90%	0.80%	29.2 g/L	0.497 M	0.142 g/L
As	10 g/L	0.74%	1.63%	4.92 g/L	0.066 M	0.062 g/L
Fe		4.03%	0.51%	15.9 g/L	0.285 M	0.105 g/L
O		5.55%	1.40%			
Stot		16.34%	18.55%			
H2SO4	220 g/L			72.6 g/L	0.740 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 24, 1994	leach residue
Cu : O	10.28	53.94
Cu : Stot	3.49	4.07
Stot : O	2.94	13.25

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		67.6	57.63%		0.59%	1.04%
Co	81.2%		7.25%	81.6%	0.15%	2.04%
Ni	91.4%		8.50%	92.0%	0.60%	7.64%
As			0.76%		0.02%	3.12%
Fe	89.2%		4.70%	90.7%	0.67%	16.58%
H2SO4		204.4				

detailed arsenic balance

As in	9.664 g	
As out	9.747 g	
difference	0.083 g	0.85%
As precipitated		32.1%
As in leach res. : As in IPC res.		1.87 (wt./wt.)

AUTOCLAVE TEST WORKSHEET

test ID: #57
series ID: Arsenic
date: Thursday, May 4, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	51 min		
leaching time at T:	10 min	0.17 h	
initial pressure:	5.8 bar	84 psig	
final pressure:	5.8 bar	84 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g	leach residue:	315 g	residue ratio:	1.14 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL	leach filtrate:	956 mL		
		wash solution:	899 mL	wash acidity:	11 g/L H2SO4
		total filtrate:	1855 mL		
		repulp volume:	719 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	60 mV (SCE)	305 mV (SHE)
after:	slurry:	-40 mV (SCE)	205 mV (SHE)
	supernatant:	127 mV (SCE)	372 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 24, 1994	leach residue	leach filtrate		repulp filtrate
Cu	35 g/L	57.04%	75.49%	0.26 g/L	0.004 M	0.282 g/L
Co		7.10%	2.21%	21.2 g/L	0.360 M	0.300 g/L
Ni		7.90%	1.13%	34.1 g/L	0.581 M	0.453 g/L
As	10 g/L	0.74%	1.84%	4.26 g/L	0.057 M	0.128 g/L
Fe		4.03%	0.74%	15.7 g/L	0.281 M	0.250 g/L
O		5.55%	1.63%			
Stot		16.34%	18.33%			
H2SO4	220 g/L			69.4 g/L	0.708 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 24, 1994	leach residue
Cu : O	10.28	46.31
Cu : Stot	3.49	4.12
Stot : O	2.94	11.25

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		67.4	59.32%		2.28%	3.99%
Co	72.8%		7.56%	74.5%	0.46%	6.50%
Ni	87.5%		10.04%	90.2%	2.14%	27.10%
As			0.80%		0.06%	8.11%
Fe	83.8%		4.82%	86.5%	0.79%	19.70%
H2SO4		215.9				

detailed arsenic balance

As in	9.664 g	
As out	9.880 g	
difference	0.216 g	2.19%
As precipitated		41.8%
As in leach res. : As in IPC res.		2.18 (wt./wt.)

AUTOCLAVE TEST WORKSHEET

test ID: #56
series ID: Arsenic
date: Wednesday, May 3, 1995

temperature: 160 °C   320 °F
heat-up time to T: 50 min
leaching time at T: 0 min   0 h

initial pressure: 5.8 bar   84 psig
final pressure: 5.8 bar   84 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue: 360 g   leach residue: 319 g   residue ratio: 1.13 wt./wt.
electrolyte: 700 mL
deionized water: 500 mL   leach filtrate: 972 mL
                                   wash solution: 869 mL   wash acidity: 11 g/L H2SO4
                                   total filtrate: 1841 mL

                                   repulp volume: 738 mL

POTENTIAL MEASUREMENTS

before: slurry: 60 mV (SCE)   305 mV (SHE)

after: slurry: 32 mV (SCE)   277 mV (SHE)
           supernatant: 42 mV (SCE)   287 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 24, 1994	leach residue	leach filtrate		repulp filtrate
Cu	35 g/L	57.04%	72.67%	2.96 g/L	0.047 M	0.350 g/L
Co		7.10%	3.48%	14.7 g/L	0.249 M	0.036 g/L
Ni		7.90%	1.98%	32.6 g/L	0.556 M	0.041 g/L
As	10 g/L	0.74%	0.82%	7.19 g/L	0.096 M	0.013 g/L
Fe		4.03%	1.09%	13.5 g/L	0.241 M	0.031 g/L
O		5.55%	2.32%			
Stot		16.34%	17.84%			
H2SO4	220 g/L			81.2 g/L	0.828 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 24, 1994	leach residue
Cu : O	10.28	31.32
Cu : Stot	3.49	4.07
Stot : O	2.94	7.69

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		60.1	58.39%		1.35%	2.36%
Co	56.6%		7.04%	56.2%	0.06%	0.84%
Ni	77.8%		10.56%	83.4%	2.66%	33.62%
As			0.72%		0.02%	2.18%
Fe	75.9%		4.60%	78.9%	0.57%	14.24%
H2SO4		181.9				

detailed arsenic balance
As in   9.664 g
As out   9.606 g
difference   0.058 g   0.60%

As precipitated   0.19%

As in leach res. : As in IPC res.   0.98 (wt./wt.)

AUTOCLAVE TEST WORKSHEET

test ID: #55
series ID: Additives
date: Saturday, April 29, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	50 min		
leaching time at T:	60 min	1 h	
initial pressure:	5.9 bar	85 psig	
final pressure:	5.9 bar	85 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	800 mL
deionized water:	400 mL

Autoclave products

leach residue:	308 g	residue ratio:	1.17 wt./wt.
leach filtrate:	959 mL		
wash solution:	871 mL	wash acidity:	11 g/L H2SO4
total filtrate:	1830 mL		
repulp volume:	696 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	67 mV (SCE)	312 mV (SHE)
after:	slurry:	-263 mV (SCE)	-18 mV (SHE)
	supernatant:	89 mV (SCE)	334 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 10, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.90%	77.45%	.0.06 g/L	0.001 M	0.079 g/L
Co		7.07%	0.58%	26.8 g/L	0.456 M	0.181 g/L
Ni		9.76%	0.67%	37.4 g/L	0.638 M	0.296 g/L
As		0.73%	0.82%	0 g/L	0 M	0 g/L
Fe		4.46%	0.25%	18.2 g/L	0.326 M	0.125 g/L
O		6.75%	1.62%			
Stot		14.83%	18.26%			
H2SO4	220 g/L			95.2 g/L	0.970 M	11 g/L
Crodaglu	5 ppm					
Dowfax	100 ppm					

element ratio (wt./wt.)	IPC residue of May 10, 1994	leach residue
Cu : O	8.13	47.81
Cu : Stot	3.70	4.24
Stot : O	2.20	11.27

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		99.8	56.28%		1.38%	2.51%
Co	92.9%		7.65%	93.5%	0.58%	8.22%
Ni	94.1%		10.55%	94.5%	0.79%	8.06%
As	3.8%		0.70%	0.0%	0.03%	3.77%
Fe	95.3%		5.06%	95.8%	0.60%	13.56%
H2SO4		208.7				

AUTOCLAVE TEST WORKSHEET

test ID: #54
series ID: Additives
date: Friday, April 28, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	51 min		
leaching time at T:	60 min	1 h	
initial pressure:	5.9 bar	85 psig	
final pressure:	5.9 bar	85 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	800 mL
deionized water:	400 mL

Autoclave products

leach residue:	310 g	residue ratio:	1.16 wt./wt.
leach filtrate:	948 mL		
wash solution:	882 mL	wash acidity:	11 g/L H2SO4
total filtrate:	1830 mL		
repulp volume:	664 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	66 mV (SCE)	311 mV (SHE)
after:	slurry:	-259 mV (SCE)	-14 mV (SHE)
	supernatant:	76 mV (SCE)	321 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 10, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.90%	77.32%	0.06 g/L	0.001 M	0 g/L
Co		7.07%	0.55%	25.6 g/L	0.434 M	0.112 g/L
Ni		9.76%	0.94%	36.1 g/L	0.615 M	0.269 g/L
As		0.73%	0.89%	0 g/L	0 M	0 g/L
Fe		4.46%	0.25%	17.0 g/L	0.305 M	0.077 g/L
O		6.75%	1.50%			
Stot		14.83%	18.4%			
H2SO4	220 g/L			94.3 g/L	0.962 M	11 g/L
Crodaglu	0 ppm					
Dowfax	0 ppm					

element ratio (wt./wt.)	IPC residue of May 10, 1994	leach residue
Cu : O	8.13	51.55
Cu : Stot	3.70	4.20
Stot : O	2.20	12.27

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		99.8	56.60%	93.4%	1.70%	3.09%
Co	93.3%		7.21%	93.4%	0.14%	1.92%
Ni	91.7%		10.31%	92.2%	0.55%	5.67%
As	-4.6%		0.76%	0.0%	0.03%	4.64%
Fe	95.2%		4.70%	95.4%	0.24%	5.46%
H2SO4		213.6				

AUTOCLAVE TEST WORKSHEET

test ID: #53
series ID: Kinetics, Low Cu : S
date: Thursday, April 27, 1995

temperature:	160 °C	320 °F
heat-up time to T:	51 min	
leaching time at T:	15 min	0.25 h
initial pressure:	5.9 bar	85 psig
final pressure:	5.9 bar	85 psig
stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	800 mL
deionized water:	400 mL

Autoclave products

leach residue:	306 g	residue ratio:	1.18 wt./wt.
leach filtrate:	980 mL		
wash solution:	785 mL	wash acidity:	11 g/L H2SO4
total filtrate:	1765 mL		
repulp volume:	738 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	69 mV (SCE)	314 mV (SHE)
after:	slurry:	50 mV (SCE)	295 mV (SHE)
	supernatant:	55 mV (SCE)	300 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 19, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	53.59%	73.31%	11.2 g/L	0.176 M	0.251 g/L
Co		7.52%	2.38%	20.6 g/L	0.350 M	0.144 g/L
Ni		8.93%	1.18%	31.1 g/L	0.530 M	0.188 g/L
As		0.77%	0.47%	1.44 g/L	0.019 M	0.013 g/L
Fe		5.39%	0.80%	17.9 g/L	0.321 M	0.122 g/L
O		5.88%	1.06%			
Stot		16.73%	20.12%			
H2SO4	220 g/L			88.7 g/L	0.904 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 19, 1994	leach residue
Cu : O	9.11	69.16
Cu : Stot	3.20	3.64
Stot : O	2.85	18.98

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		69.6	55.36%		1.77%	3.29%
Co	73.1%		7.64%	73.5%	0.12%	1.62%
Ni	88.8%		9.47%	89.4%	0.54%	6.06%
As	47.6%		0.79%	49.2%	0.02%	3.20%
Fe	87.4%		5.56%	87.8%	0.17%	3.08%
H2SO4		223.5				

AUTOCLAVE TEST WORKSHEET

test ID: #52
series ID: Kinetics, Low Cu : S
date: Wednesday, April 26, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	50 min		
leaching time at T:	30 min	0.5 h	
initial pressure:	5.9 bar	85 psig	
final pressure:	5.9 bar	85 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g		leach residue:	314 g	residue ratio: 1.15 wt./wt.
electrolyte:	800 mL				
deionized water:	400 mL		leach filtrate:	977 mL	
			wash solution:	829 mL	wash acidity: 11 g/L H2SO4
			total filtrate:	1806 mL	
			repulp volume:	641 mL	

Autoclave products

POTENTIAL MEASUREMENTS

before:	slurry:	69 mV (SCE)	314 mV (SHE)
after:	slurry:	34 mV (SCE)	279 mV (SHE)
	supernatant:	42 mV (SCE)	287 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 19, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	53.59%	74.29%	4.2 g/L	0.066 M	0.125 g/L
Co		7.52%	1.41%	24.8 g/L	0.421 M	0.063 g/L
Ni		8.93%	0.78%	33.7 g/L	0.574 M	0.081 g/L
As		0.77%	0.38%	1.80 g/L	0.024 M	0.008 g/L
Fe		5.39%	0.64%	20.6 g/L	0.368 M	0.057 g/L
O		5.88%	0.94%			
Stot		16.73%	20.12%			
H2SO4	220 g/L			92.4 g/L	0.942 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 19, 1994	leach residue
Cu : O	9.11	79.03
Cu : Stot	3.20	3.69
Stot : O	2.85	21.40

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		88.6	55.94%		2.35%	4.38%
Co	83.7%		7.96%	84.6%	0.44%	5.87%
Ni	92.4%		9.82%	93.1%	0.89%	10.00%
As	56.8%		0.82%	59.5%	0.05%	6.61%
Fe	89.6%		6.14%	90.9%	0.75%	13.87%
H2SO4		212.8				

AUTOCLAVE TEST WORKSHEET

test ID: #51
series ID: Kinetics, Low Cu : S
date: Tuesday, April 25, 1995

temperature: 160 °C   320 °F
heat-up time to T: 50 min
leaching time at T: 60 min   1 h

initial pressure: 5.9 bar   85 psig
final pressure: 5.9 bar   85 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue: 360 g   leach residue: 310 g   residue ratio: 1.16 wt./wt.
electrolyte: 800 mL
deionized water: 400 mL   leach filtrate: 981 mL
                              wash solution: 941 mL   wash acidity: 11 g/L H2SO4
                              total filtrate: 1922 mL

                              repulp volume: 711 mL

POTENTIAL MEASUREMENTS

before: slurry: 70 mV (SCE)   315 mV (SHE)

after: slurry: -9 mV (SCE)   236 mV (SHE)
           supernatant: 143 mV (SCE)   388 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 19, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	53.59%	72.48%	0.09 g/L	0.001 M	0.006 g/L
Co		7.52%	0.79%	25.7 g/L	0.436 M	0.022 g/L
Ni		8.93%	0.37%	33.3 g/L	0.568 M	0.032 g/L
As		0.77%	0.45%	1.21 g/L	0.016 M	0.077 g/L
Fe		5.39%	0.27%	22.0 g/L	0.393 M	0.015 g/L
O		5.88%	0.78%			
Stot		16.73%	19.61%			
H2SO4	220 g/L			89.3 g/L	0.911 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 19, 1994	leach residue
Cu : O	9.11	92.92
Cu : Stot	3.20	3.70
Stot : O	2.85	25.14

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		99.7	52.44%		1.15%	2.15%
Co	91.0%		7.68%	91.2%	0.16%	2.07%
Ni	96.4%		9.41%	96.6%	0.48%	5.32%
As	50.0%		0.72%	46.2%	0.05%	7.14%
Fe	95.7%		6.21%	96.3%	0.82%	15.30%
H2SO4		216.7				

AUTOCLAVE TEST WORKSHEET

test ID: #50
series ID: Kinetics, Low Cu : S
date: Thursday, April 20, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	49 min		
leaching time at T:	0 min	0 h	
initial pressure:	5.9 bar	85 psig	
final pressure:	5.9 bar	85 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g		leach residue:	317 g	residue ratio: 1.14 wt./wt.
electrolyte:	800 mL				
deionized water:	400 mL		leach filtrate:	926 mL	
			wash solution:	812 mL	wash acidity: 11 g/L H2SO4
			total filtrate:	1738 mL	
			repulp volume:	727 mL	

POTENTIAL MEASUREMENTS

before:	slurry:	68 mV (SCE)	313 mV (SHE)
after:	slurry:	62 mV (SCE)	307 mV (SHE)
	supernatant:	48 mV (SCE)	293 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 19, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	53.59%	67.31%	21.9 g/L	0.344 M	0.361 g/L
Co		7.52%	3.86%	18.3 g/L	0.311 M	0.121 g/L
Ni		8.93%	1.87%	31.5 g/L	0.536 M	0.178 g/L
As		0.77%	0.66%	1.04 g/L	0.014 M	0.009 g/L
Fe		5.39%	1.23%	17.7 g/L	0.318 M	0.136 g/L
O		5.88%	1.69%			
Stot		16.73%	18.97%			
H2SO4	220 g/L			90.4 g/L	0.922 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 19, 1994	leach residue
Cu : O	9.11	39.83
Cu : Stot	3.20	3.55
Stot : O	2.85	11.22

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades)	
					absolute	relative
Cu		43.8	54.90%		1.31%	2.44%
Co	54.8%		8.11%	58.1%	0.59%	7.83%
Ni	81.6%		9.74%	83.1%	0.81%	9.12%
As	24.6%		0.85%	31.5%	0.08%	10.01%
Fe	79.9%		5.65%	80.8%	0.26%	4.78%
H2SO4		231.5				

AUTOCLAVE TEST WORKSHEET

test ID: #49
series ID: Kinetics, Low Cu : S
date: Wednesday, April 19, 1995

temperature:	160 °C	320 °F		
heat-up time to T:	51 min			loose agitator
leaching time at T:	225 min	3.75 h		
initial pressure:	5.5 bar	80 psig		
final pressure:	5.5 bar	80 psig		
stirring rate:	13.7 1/s	820 rpm		

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g	leach residue:	321 g	residue ratio:	1.12 wt./wt.
electrolyte:	800 mL				
deionized water:	400 mL	leach filtrate:	954 mL		
		wash solution:	902 mL	wash acidity:	11 g/L H2SO4
		total filtrate:	1856 mL		
		repulp volume:	629 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	79 mV (SCE)	324 mV (SHE)
after:	slurry:	16 mV (SCE)	261 mV (SHE)
	supernatant:	138 mV (SCE)	383 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 19, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	53.59%	73.85%	0 g/L	0 M	0 g/L
Co		7.52%	0.80%	27.3 g/L	0.463 M	0.093 g/L
Ni		8.93%	0.41%	35.7 g/L	0.608 M	0.131 g/L
As		0.77%	0.77%	0.16 g/L	0.002 M	0.075 g/L
Fe		5.39%	0.24%	23.4 g/L	0.419 M	0.077 g/L
O		5.88%	0.75%			
Stot		16.73%	19.79%			
H2SO4	220 g/L			83.0 g/L	0.846 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 19, 1994	leach residue
Cu : O	9.11	98.47
Cu : Stot	3.20	3.73
Stot : O	2.85	26.39

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		100.0	55.85%		2.26%	4.22%
Co	90.5%		7.95%	91.0%	0.43%	5.68%
Ni	95.9%		9.82%	96.3%	0.89%	9.98%
As	10.5%		0.73%	5.8%	0.04%	4.96%
Fe	96.0%		6.41%	96.7%	1.02%	19.00%
H2SO4		241.4				

AUTOCLAVE TEST WORKSHEET

test ID: #48
series ID: Additives
date: Wednesday, April 12, 1995

temperature: 160 °C   320 °F
heat-up time to T: 550 min
leaching time at T: 60 min   1 h

initial pressure: 5.7 bar   82 psig
final pressure: 6.6 bar   96 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue: 360 g   leach residue: 319 g   residue ratio: 1.13 wt./wt.
electrolyte: 700 mL
deionized water: 500 mL   leach filtrate: 946 mL
                                      wash solution: 961 mL   wash acidity: 11 g/L H2SO4
                                      total filtrate: 1907 mL

                                      repulp volume: 797 mL

POTENTIAL MEASUREMENTS

before: slurry: 63 mV (SCE)   308 mV (SHE)

after: slurry: -257 mV (SCE)   -12 mV (SHE)
          supernatant: 163 mV (SCE)   408 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 10, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.90%	74.83%	0 g/L	0 M	0.001 g/L
Co		7.07%	0.57%	29.2 g/L	0.495 M	0.300 g/L
Ni		9.76%	1.52%	37.2 g/L	0.634 M	0.736 g/L
As		0.73%	0.90%	0 g/L	0 M	0 g/L
Fe		4.46%	0.25%	19.3 g/L	0.345 M	0.196 g/L
O		6.75%	2.31%			
Stot		14.83%	17.84%			
H2SO4	220 g/L			71.6 g/L	0.730 M	11 g/L
Crodaglu	5 ppm					
Dowfax	100 ppm					

element ratio (wt./wt.)	IPC residue of May 10, 1994	leach residue
Cu : O	8.13	32.39
Cu : Stot	3.70	4.19
Stot : O	2.20	7.72

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		87.5	57.56%		2.66%	4.84%
Co	92.9%		8.18%	93.8%	1.11%	15.71%
Ni	86.2%		11.13%	87.9%	1.37%	14.04%
As	-9.2%		0.80%	0.0%	0.07%	9.25%
Fe	95.0%		5.29%	95.8%	0.83%	18.62%
H2SO4		210.1				

AUTOCLAVE TEST WORKSHEET

test ID: #47
series ID: Additives
date: Tuesday, April 11, 1995

temperature:	160 °C	320 °F	
heat-up time to T:	55 min		
leaching time at T:	60 min	1 h	
initial pressure:	5.7 bar	82 psig	
final pressure:	6.6 bar	95 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

Autoclave products

IPC residue:	360 g	leach residue:	314 g	residue ratio:	1.15 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL	leach filtrate:	945 mL		
		wash solution:	945 mL	wash acidity:	11 g/L H2SO4
		total filtrate:	1890 mL		
		repulp volume:	646 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	64 mV (SCE)	309 mV (SHE)
after:	slurry:	-246 mV (SCE)	-1 mV (SHE)
	supernatant:	133 mV (SCE)	378 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 10, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.90%	75.55%	0 g/L	0 M	0.001 g/L
Co		7.07%	0.58%	28.2 g/L	0.479 M	0.648 g/L
Ni		9.76%	1.44%	32.8 g/L	0.558 M	1.110 g/L
As		0.73%	0.91%	0 g/L	0 M	0 g/L
Fe		4.46%	0.22%	19.1 g/L	0.342 M	0.451 g/L
O		6.75%	1.78%			
Stot		14.83%	17.93%			
H2SO4	220 g/L			69.5 g/L	0.709 M	11.5 g/L
Crodaglu	0 ppm					
Dowfax	0 ppm					

element ratio (wt./wt.)	IPC residue of May 10, 1994	leach residue
Cu : O	8.13	42.44
Cu : Stot	3.70	4.21
Stot : O	2.20	10.07

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		87.5	57.15%		2.25%	4.09%
Co	92.8%		7.91%	93.6%	0.84%	11.94%
Ni	87.1%		9.86%	87.3%	0.10%	0.98%
As	-8.7%		0.79%	-0.0%	0.06%	8.73%
Fe	95.7%		5.20%	96.3%	0.74%	16.67%
H2SO4		216.4				

AUTOCLAVE TEST WORKSHEET

test ID: #46
series ID: Kinetics, High Cu : S
date: Friday, April 7, 1995

temperature:	80 °C	176 °F
heat-up time to T:	31 min	
leaching time at T:	240 min	4 h

initial pressure:	bar	psig
final pressure:	bar	psig

stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	335 g
leach filtrate:	949 mL
wash solution:	901 mL
total filtrate:	1850 mL
repulp volume:	758 mL

residue ratio:	1.07 wt./wt.
wash acidity:	11 g/L H2SO4

POTENTIAL MEASUREMENTS

before:	slurry:	62 mV (SCE)	307 mV (SHE)
after:	slurry:	65 mV (SCE)	310 mV (SHE)
	supernatant:	68 mV (SCE)	313 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 11, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.91%	66.03%	31.0 g/L	0.489 M	0.80 g/L
Co		7.40%	6.59%	7.5 g/L	0.128 M	0.09 g/L
Ni		8.89%	4.72%	20.1 g/L	0.342 M	0.24 g/L
As		0.72%	0.63%	0.71 g/L	0.010 M	0.011 g/L
Fe		4.73%	2.60%	12.4 g/L	0.222 M	0.13 g/L
O		6.28%	3.03%			
Stot		13.32%	15.52%			
H2SO4	220 g/L			84.8 g/L	0.865 M	11.5 g/L

element ratio (wt./wt.)	IPC residue of May 11, 1994	leach residue
Cu : O	9.22	21.79
Cu : Stot	4.35	4.25
Stot : O	2.12	5.12

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		5.7	60.88%		2.97%	5.13%
Co	17.2%		8.12%	24.5%	0.72%	9.68%
Ni	50.6%		9.68%	54.7%	0.79%	8.90%
As	18.7%		0.77%	24.4%	0.05%	7.43%
Fe	48.8%		5.70%	57.5%	0.97%	20.46%
H2SO4		176.7				

AUTOCLAVE TEST WORKSHEET

test ID: #45
series ID: Kinetics, High Cu : S
date: Thursday, April 6, 1995

temperature:	80 °C	176 °F
heat-up time to T:	31 min	
leaching time at T:	0 min	0 h

initial pressure:	bar	psig
final pressure:	bar	psig

stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

Autoclave products

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

leach residue:	354 g	residue ratio:	1.02 wt./wt.
leach filtrate:	958 mL		
wash solution:	895 mL	wash acidity:	11 g/L H2SO4
total filtrate:	1853 mL		
repulp volume:	752 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	62 mV (SCE)	307 mV (SHE)
after:	slurry:	68 mV (SCE)	313 mV (SHE)
	supernatant:	73 mV (SCE)	318 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 11, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.91%	60.35%	35.9 g/L	0.565 M	1.11 g/L
Co		7.40%	7.30%	2.9 g/L	0.049 M	0.06 g/L
Ni		8.89%	8.27%	5.3 g/L	0.091 M	0.13 g/L
As		0.72%	0.62%	0.57 g/L	0.008 M	0.011 g/L
Fe		4.73%	4.25%	4.8 g/L	0.085 M	0.12 g/L
O		6.28%	4.40%			
Stot		13.32%	14.36%			
H2SO4	220 g/L			124.4 g/L	1.268 M	12 g/L

element ratio (wt./wt.)	IPC residue of May 11, 1994	leach residue
Cu : O	9.22	13.72
Cu : Stot	4.35	4.20
Stot : O	2.12	3.26

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		-8.0	60.14%		2.23%	3.85%
Co	3.0%		7.95%	9.6%	0.55%	7.38%
Ni	8.5%		9.55%	14.8%	0.66%	7.46%
As	16.0%		0.76%	20.1%	0.04%	5.19%
Fe	11.6%		5.45%	23.2%	0.72%	15.14%
H2SO4		69.5				

AUTOCLAVE TEST WORKSHEET

test ID: #44
series ID: Kinetics, High Cu : S
date: Wednesday, April 5, 1995

temperature:	80 °C	176 °F	
heat-up time to T:	30 min		
leaching time at T:	60 min	1 h	

initial pressure:	bar	psig	
final pressure:	bar	psig	

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g		leach residue:	331 g	residue ratio: 1.09 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL		leach filtrate:	954 mL	
			wash solution:	841 mL	wash acidity: 11 g/L H2SO4
			total filtrate:	1795 mL	
			repulp volume:	762 mL	

POTENTIAL MEASUREMENTS

before:	slurry:	62 mV (SCE)	307 mV (SHE)
after:	slurry:	64 mV (SCE)	309 mV (SHE)
	supernatant:	70 mV (SCE)	315 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 11, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.91%	63.61%	32.0 g/L	0.504 M	0.77 g/L
Co		7.40%	6.93%	5.8 g/L	0.099 M	0.01 g/L
Ni		8.89%	6.17%	14.2 g/L	0.243 M	0.16 g/L
As		0.72%	0.63%	0.61 g/L	0.008 M	0.008 g/L
Fe		4.73%	3.58%	9.9 g/L	0.177 M	0.11 g/L
O		6.28%	3.37%			
Stot		13.32%	14.96%			
H2SO4	220 g/L			96.5 g/L	0.984 M	11.5 g/L

element ratio (wt./wt.)	IPC residue of May 11, 1994	leach residue
Cu : O	9.22	18.88
Cu : Stot	4.35	4.25
Stot : O	2.12	4.44

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		2.6	58.23%		0.32%	0.54%
Co	13.9%		7.92%	19.6%	0.52%	7.00%
Ni	36.2%		9.44%	40.0%	0.55%	6.22%
As	19.7%		0.74%	22.0%	0.02%	2.93%
Fe	30.4%		5.91%	44.3%	1.18%	24.91%
H2SO4		146.4				

AUTOCLAVE TEST WORKSHEET

test ID: #43
series ID: Kinetics, High Cu : S
date: Tuesday, April 4, 1995

temperature:	80 °C	176 °F	
heat-up time to T:	28 min		
leaching time at T:	480 min	8 h	

initial pressure:	bar	psig	
final pressure:	bar	psig	

stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	320 g	residue ratio:	1.13 wt./wt.
leach filtrate:	953 mL		
wash solution:	916 mL	wash acidity:	11 g/L H2SO4
total filtrate:	1869 mL		
repulp volume:	803 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	63 mV (SCE)	308 mV (SHE)
after:	slurry:	63 mV (SCE)	308 mV (SHE)
	supernatant:	66 mV (SCE)	311 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 11, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.91%	67.01%	29.8 g/L	0.470 M	0.51 g/L
Co		7.40%	6.37%	9.0 g/L	0.153 M	0.03 g/L
Ni		8.89%	4.38%	22.2 g/L	0.379 M	0.07 g/L
As		0.72%	0.62%	0.73 g/L	0.010 M	0.004 g/L
Fe		4.73%	3.91%	12.7 g/L	0.227 M	0.04 g/L
O		6.28%	3.14%			
Stot		13.32%	15.56%			
H2SO4	220 g/L			79.4 g/L	0.810 M	10.5 g/L

element ratio (wt./wt.)	IPC residue of May 11, 1994	leach residue
Cu : O	9.22	21.34
Cu : Stot	4.35	4.31
Stot : O	2.12	4.96

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		8.5	58.72%		0.81%	1.39%
Co	23.4%		8.05%	29.6%	0.65%	8.77%
Ni	56.2%		9.77%	60.2%	0.88%	9.95%
As	23.1%		0.75%	25.8%	0.03%	3.63%
Fe	26.6%		6.83%	49.1%	2.10%	44.35%
H2SO4		189.6				

AUTOCLAVE TEST WORKSHEET

test ID: #42
series ID: Kinetics, High Cu : S
date: Monday, April 3, 1995

temperature:	120 °C	248 °F	
heat-up time to T:	40 min		
leaching time at T:	0 min	0 h	
initial pressure:	1.9 bar	28 psig	
final pressure:	1.9 bar	28 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	329 g	residue ratio:	1.09 wt./wt.
leach filtrate:	926 mL		
wash solution:	868 mL	wash acidity:	11 g/L H2SO4
total filtrate:	1794 mL		
repulp volume:	691 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	62 mV (SCE)	307 mV (SHE)
after:	slurry:	68 mV (SCE)	313 mV (SHE)
	supernatant:	74 mV (SCE)	319 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 14, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	55.10%	62.27%	37.2 g/L	0.585 M	0.76 g/L
Co		7.35%	6.70%	7.7 g/L	0.131 M	0.10 g/L
Ni		8.72%	5.78%	17.6 g/L	0.300 M	0.22 g/L
As		0.71%	0.62%	0.72 g/L	0.010 M	0.012 g/L
Fe		4.99%	3.97%	12.7 g/L	0.227 M	0.15 g/L
O		7.00%	4.18%			
Stot		13.42%	15.64%			
H2SO4	220 g/L			84.2 g/L	0.858 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 14, 1994	leach residue
Cu : O	7.87	14.90
Cu : Stot	4.11	3.98
Stot : O	1.92	3.74

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		-8.1	57.72%		2.62%	4.76%
Co	16.6%		8.11%	24.5%	0.76%	10.38%
Ni	39.4%		9.81%	46.1%	1.09%	12.54%
As	19.6%		0.76%	24.6%	0.05%	6.66%
Fe	27.3%		6.89%	47.3%	1.90%	38.11%
H2SO4		184.7				

AUTOCLAVE TEST WORKSHEET

test ID: #41
series ID: Kinetics, High Cu : S
date: Friday, March 31, 1995

temperature:	120 °C	248 °F
heat-up time to T:	39 min	
leaching time at T:	15 min	0.25 h
initial pressure:	2.0 bar	29 psig
final pressure:	2.0 bar	29 psig
stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	312 g	residue ratio:	1.15 wt./wt.
leach filtrate:	956 mL		
wash solution:	886 mL	wash acidity:	11 g/L H2SO4
total filtrate:	1842 mL		
repulp volume:	784 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	64 mV (SCE)	309 mV (SHE)
after:	slurry:	63 mV (SCE)	308 mV (SHE)
	supernatant:	72 mV (SCE)	317 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 14, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	55.10%	65.68%	30.1 g/L	0.473 M	0.71 g/L
Co		7.35%	5.94%	10.6 g/L	0.180 M	0.09 g/L
Ni		8.72%	3.79%	22.3 g/L	0.380 M	0.21 g/L
As		0.71%	0.63%	0.73 g/L	0.010 M	0.009 g/L
Fe		4.99%	2.43%	14.4 g/L	0.259 M	0.12 g/L
O		7.00%	3.46%			
Stot		13.42%	16.09%			
H2SO4	220 g/L			75.0 g/L	0.765 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 14, 1994	leach residue
Cu : O	7.87	18.98
Cu : Stot	4.11	4.08
Stot : O	1.92	4.65

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		7.7	56.15%		1.05%	1.91%
Co	30.0%		7.96%	35.3%	0.61%	8.28%
Ni	62.3%		9.22%	64.3%	0.50%	5.69%
As	22.6%		0.74%	26.2%	0.03%	4.81%
Fe	57.9%		5.94%	64.6%	0.95%	18.95%
H2SO4		201.5				

AUTOCLAVE TEST WORKSHEET

test ID: #40
series ID: Kinetics, High Cu : S
date: Thursday, March 30, 1995

temperature:	120 °C	248 °F
heat-up time to T:	38 min	
leaching time at T:	30 min	0.5 h
initial pressure:	2.0 bar	29 psig
final pressure:	2.0 bar	29 psig
stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g	leach residue:	314 g	residue ratio:	1.15 wt./wt.
electrolyte:	700 mL			
deionized water:	500 mL	leach filtrate:	953 mL	
		wash solution:	849 mL	wash acidity:	11.5 g/L H2SO4
		total filtrate:	1802 mL	
		repulp volume:	702 mL	

POTENTIAL MEASUREMENTS

before:	slurry:	63 mV (SCE)	308 mV (SHE)
after:	slurry:	66 mV (SCE)	311 mV (SHE)
	supernatant:	74 mV (SCE)	319 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 14, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	55.10%	67.29%	30.2 g/L	0.476 M	0.72 g/L
Co		7.35%	5.60%	12.5 g/L	0.213 M	0.15 g/L
Ni		8.72%	3.26%	26.3 g/L	0.448 M	0.31 g/L
As		0.71%	0.62%	0.79 g/L	0.011 M	0.012 g/L
Fe		4.99%	2.54%	15.4 g/L	0.276 M	0.17 g/L
O		7.00%	3.79%			
Stot		13.42%	16.60%			
H2SO4	220 g/L			69.3 g/L	0.706 M	11 g/L

element ratio (wt./wt.)	IPC residue of May 14, 1994	leach residue
Cu : O	7.87	17.75
Cu : Stot	4.11	4.05
Stot : O	1.92	4.38

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		7.5	57.94%		2.84%	5.16%
Co	33.5%		8.20%	40.4%	0.85%	11.61%
Ni	67.4%		9.81%	71.0%	1.09%	12.48%
As	23.2%		0.76%	27.8%	0.05%	6.36%
Fe	55.7%		6.30%	64.9%	1.31%	26.18%
H2SO4		217.2				

AUTOCLAVE TEST WORKSHEET

test ID: #39
series ID: Kinetics, High Cu : S
date: Wednesday, March 29, 1995

temperature:	120 °C	248 °F
heat-up time to T:	39 min	
leaching time at T:	60 min	1 h
initial pressure:	2.0 bar	29 psig
final pressure:	2.0 bar	29 psig
stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	303 g	residue ratio:	1.19 wt./wt.
leach filtrate:	955 mL		
wash solution:	845 mL	wash acidity:	11.5 g/L H2SO4
total filtrate:	1800 mL		
repulp volume:	650 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	61 mV (SCE)	306 mV (SHE)
after:	slurry:	60 mV (SCE)	305 mV (SHE)
	supernatant:	65 mV (SCE)	310 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 14, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	55.10%	67.66%	25.7 g/L	0.404 M	0.59 g/L
Co		7.35%	4.99%	14.5 g/L	0.245 M	0.15 g/L
Ni		8.72%	2.56%	26.6 g/L	0.453 M	0.27 g/L
As		0.71%	0.60%	0.83 g/L	0.011 M	0.012 g/L
Fe		4.99%	2.40%	15.9 g/L	0.285 M	0.13 g/L
O		7.00%	3.39%			
Stot		13.42%	16.60%			
H2SO4	220 g/L			71.4 g/L	0.728 M	11.5 g/L

element ratio (wt./wt.)	IPC residue of May 14, 1994	leach residue
Cu : O	7.87	19.96
Cu : Stot	4.11	4.08
Stot : O	1.92	4.90

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		19.4	55.00%		0.10%	0.18%
Co	42.8%		8.04%	47.7%	0.69%	9.38%
Ni	75.3%		9.21%	76.6%	0.49%	5.58%
As	28.3%		0.73%	30.3%	0.02%	2.86%
Fe	59.5%		6.24%	67.6%	1.25%	25.13%
H2SO4		211.5				

AUTOCLAVE TEST WORKSHEET

test ID: #38
series ID: Kinetics, High Cu : S
date: Tuesday, March 28, 1995

temperature:	120 °C	248 °F	
heat-up time to T:	50 min		leaking cooling valve
leaching time at T:	360 min	6 h	
initial pressure:	1.9 bar	28 psig	
final pressure:	1.9 bar	28 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

Autoclave products

IPC residue:	360 g	leach residue:	309 g	residue ratio:	1.17 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL	leach filtrate:	953 mL		
		wash solution:	859 mL	wash acidity:	11.5 g/L H2SO4
		total filtrate:	1812 mL		
		repulp volume:	634 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	63 mV (SCE)	308 mV (SHE)
after:	slurry:	51 mV (SCE)	296 mV (SHE)
	supernatant:	54 mV (SCE)	299 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 14, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	55.10%	73.96%	8.2 g/L	0.129 M	0.40 g/L
Co		7.35%	2.07%	24.6 g/L	0.417 M	0.37 g/L
Ni		8.72%	1.24%	31.7 g/L	0.540 M	0.46 g/L
As		0.71%	0.48%	1.24 g/L	0.017 M	0.019 g/L
Fe		4.99%	1.55%	18.7 g/L	0.334 M	0.27 g/L
O		7.00%	2.08%			
Stot		13.42%	16.74%			
H2SO4	220 g/L			65.0 g/L	0.663 M	11.5 g/L

element ratio (wt./wt.)	IPC residue of May 14, 1994	leach residue
Cu : O	7.87	35.56
Cu : Stot	4.11	4.42
Stot : O	1.92	8.05

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		65.8	56.90%		1.80%	3.27%
Co	75.8%		8.28%	78.5%	0.93%	12.68%
Ni	87.8%		9.45%	88.7%	0.73%	8.41%
As	42.3%		0.74%	44.5%	0.03%	3.86%
Fe	73.3%		6.27%	78.8%	1.28%	25.69%
H2SO4		228.2				

AUTOCLAVE TEST WORKSHEET

test ID: #37
series ID: Kinetics, High Cu : S
date: Friday, February 3, 1995

temperature:	140 °C	284 °F	
heat-up time to T:	46 min		
leaching time at T:	15 min	0.25 h	
initial pressure:	3.6 bar	52 psig	
final pressure:	3.6 bar	52 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g	leach residue:	309 g	residue ratio:	1.17 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL	leach filtrate:	947 mL		
		wash solution:	688 mL	wash acidity:	12 g/L H2SO4
		total filtrate:	1635 mL		
		repulp volume:	485 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	65 mV (SCE)	310 mV (SHE)
after:	slurry:	60 mV (SCE)	305 mV (SHE)
	supernatant:	63 mV (SCE)	308 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 13, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	56.32%	68.0%	24.1 g/L	0.379 M	1.07 g/L
Co		7.49%	4.40%	14.4 g/L	0.244 M	0.48 g/L
Ni		8.79%	2.22%	25.4 g/L	0.434 M	0.80 g/L
As		0.68%	0.40%	0.99 g/L	0.013 M	0.036 g/L
Fe		5.01%	1.52%	14.8 g/L	0.265 M	0.54 g/L
O		7.20%	2.49%			
Stot		12.50%	16.3%			
H2SO4	220 g/L			66.8 g/L	0.681 M	13 g/L

element ratio (wt./wt.)	IPC residue of May 13, 1994	leach residue
Cu : O	7.82	27.31
Cu : Stot	4.51·	4.17
Stot : O	1.74	6.55

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		24.1	55.96%		0.36%	0.65%
Co	49.6%		7.57%	50.1%	0.08%	1.01%
Ni	78.3%		8.60%	77.8%	0.19%	2.18%
As	49.5%		0.60%	43.0%	0.08%	11.39%
Fe	74.0%		5.19%	74.9%	0.18%	3.64%
H2SO4		229.1				

AUTOCLAVE TEST WORKSHEET

test ID: #36
series ID: Kinetics, High Cu : S
date: Wednesday, February 1, 1995

temperature: 140 °C   284 °F
heat-up time to T: 44 min
leaching time at T: 300 min   5 h

initial pressure: 3.6 bar   52 psig
final pressure: 3.6 bar   52 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue: 360 g   leach residue: 312 g   residue ratio: 1.15 wt./wt.
electrolyte: 700 mL
deionized water: 500 mL   leach filtrate: 950 mL
                            wash solution: 812 mL   wash acidity: 12 g/L H2SO4
                            total filtrate: 1762 mL

                            repulp volume: 559 mL

POTENTIAL MEASUREMENTS

before: slurry: 63 mV (SCE)   308 mV (SHE)

after: slurry: 30 mV (SCE)   275 mV (SHE)
          supernatant: 130 mV (SCE)   375 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 13, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	56.32%	74.0%	0.3 g/L	0.004 M	0.26 g/L
Co		7.49%	0.84%	25.3 g/L	0.430 M	0.47 g/L
Ni		8.79%	0.60%	30.9 g/L	0.527 M	0.56 g/L
As		0.68%	0.40%	1.24 g/L	0.017 M	0.028 g/L
Fe		5.01%	0.34%	17.8 g/L	0.319 M	0.37 g/L
O		7.20%	1.87%			
Stot		12.50%	16.3%			
H2SO4	220 g/L			69.3 g/L	0.707 M	12.5 g/L

element ratio (wt./wt.)	IPC residue of May 13, 1994	leach residue
Cu : O	7.82	39.57
Cu : Stot	4.51	4.54
Stot : O	1.74	8.72

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		86.8	55.45%		0.87%	1.54%
Co	90.3%		7.41%	90.2%	0.08%	1.09%
Ni	94.1%		8.68%	94.0%	0.11%	1.22%
As	49.0%		0.67%	48.6%	0.01%	0.88%
Fe	94.1%		5.00%	94.1%	0.01%	0.16%
H2SO4		217.8				

AUTOCLAVE TEST WORKSHEET

test ID: #35
series ID: Kinetics, High Cu : S
date: Tuesday, January 31, 1995

temperature:	140 °C	284 °F	
heat-up time to T:	44 min		
leaching time at T:	0 min	0 h	
initial pressure:	3.4 bar	50 psig	
final pressure:	3.4 bar	50 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	321 g	residue ratio:	1.12 wt./wt.
leach filtrate:	871 mL		
wash solution:	701 mL	wash acidity:	14 g/L H2SO4
total filtrate:	1572 mL		
repulp volume:	480 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	65 mV (SCE)	310 mV (SHE)
after:	slurry:	67 mV (SCE)	312 mV (SHE)
	supernatant:	66 mV (SCE)	311 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 13, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	56.32%	64.0%	32.3 g/L	0.508 M	2.85 g/L
Co		7.49%	6.20%	10.9 g/L	0.184 M	0.39 g/L
Ni		8.79%	0.32%	25.1 g/L	0.428 M	0.99 g/L
As		0.68%	0.52%	0.85 g/L	0.011 M	0.040 g/L
Fe		5.01%	1.84%	14.4 g/L	0.258 M	0.59 g/L
O		7.20%	3.44%			
Stot		12.50%	16.0%			
H2SO4	220 g/L			82.7 g/L	0.843 M	16 g/L

element ratio (wt./wt.)	IPC residue of May 13, 1994	leach residue
Cu : O	7.82	18.60
Cu : Stot	4.51	4.00
Stot : O	1.74	4.65

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		9.5	56.12%		0.20%	0.36%
Co	26.2%		8.16%	32.2%	0.67%	8.90%
Ni	96.8%		6.36%	95.5%	2.43%	27.60%
As	31.8%		0.67%	30.8%	0.01%	1.49%
Fe	67.3%		5.13%	68.0%	0.12%	2.30%
H2SO4		200.4				

AUTOCLAVE TEST WORKSHEET

test ID: #34
series ID: Kinetics, High Cu : S
date: Thursday, January 26, 1995

temperature:	140 °C	284 °F	
heat-up time to T:	45 min		
leaching time at T:	30 min	0.5 h	
initial pressure:	3.8 bar	55 psig	
final pressure:	3.8 bar	55 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	313 g	residue ratio:	1.15 wt./wt.
leach filtrate:	950 mL		
wash solution:	548 mL	wash acidity:	14 g/L H2SO4
total filtrate:	1498 mL		
repulp volume:	504 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	61 mV (SCE)	306 mV (SHE)
after:	slurry:	56 mV (SCE)	301 mV (SHE)
	supernatant:	63 mV (SCE)	308 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 13, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	56.32%	68.0%	18.1 g/L	0.285 M	1.73 g/L
Co		7.49%	3.80%	16.4 g/L	0.277 M	1.10 g/L
Ni		8.79%	1.78%	27.8 g/L	0.473 M	1.80 g/L
As		0.68%	0.56%	0.93 g/L	0.012 M	0.083 g/L
Fe		5.01%	1.24%	14.7 g/L	0.263 M	0.98 g/L
O		7.20%	3.17%			
Stot		12.50%	16.4%			
H2SO4	220 g/L			66.1 g/L	0.674 M	16 g/L

element ratio (wt./wt.)	IPC residue of May 13, 1994	leach residue
Cu : O	7.82	21.45
Cu : Stot	4.51	4.15
Stot : O	1.74	5.17

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		39.7	55.15%		1.17%	2.08%
Co	55.9%		7.62%	56.6%	0.13%	1.72%
Ni	82.4%		8.87%	82.6%	0.08%	0.95%
As	28.4%		0.73%	33.4%	0.05%	7.58%
Fe	78.5%		4.96%	78.3%	0.05%	0.99%
H2SO4		232.1				

AUTOCLAVE TEST WORKSHEET

test ID: #33
series ID: Kinetics, High Cu : S
date: Wednesday, January 25, 1995

temperature:	140 °C	284 °F
heat-up time to T:	43 min	
leaching time at T:	60 min	1 h
initial pressure:	3.8 bar	55 psig
final pressure:	3.8 bar	55 psig
stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	314 g	residue ratio:	1.15 wt./wt.
leach filtrate:	949 mL		
wash solution:	540 mL	wash acidity:	14 g/L H2SO4
total filtrate:	1489 mL		
repulp volume:	626 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	64 mV (SCE)	309 mV (SHE)
after:	slurry:	58 mV (SCE)	303 mV (SHE)
	supernatant:	51 mV (SCE)	296 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 13, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	56.32%	70.0%	12.8 g/L	0.201 M	1.06 g/L
Co		7.49%	2.60%	19.4 g/L	0.330 M	0.90 g/L
Ni		8.79%	1.36%	28.3 g/L	0.483 M	1.35 g/L
As		0.68%	0.48%	1.23 g/L	0.016 M	0.075 g/L
Fe		5.01%	1.06%	15.7 g/L	0.281 M	0.75 g/L
O		7.20%	2.47%			
Stot		12.50%	16.3%			
H2SO4	220 g/L			66.6 g/L	0.679 M	15.5 g/L

element ratio (wt./wt.)	IPC residue of May 13, 1994	leach residue
Cu : O	7.82	28.34
Cu : Stot	4.51	4.29
Stot : O	1.74	6.60

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		53.8	55.67%	69.3%	0.65%	1.15%
Co	69.7%		7.39%	69.3%	0.10%	1.37%
Ni	86.5%		8.66%	86.3%	0.13%	1.49%
As	38.4%		0.74%	43.6%	0.06%	9.11%
Fe	81.5%		5.07%	81.8%	0.06%	1.14%
H2SO4		231.3				

AUTOCLAVE TEST WORKSHEET

test ID: #32
series ID: Kinetics, High Cu : S
date: Saturday, September 3, 1994

temperature: 160 °C   320 °F
heat-up time to T: 51 min
leaching time at T: 0 min   0 h

initial pressure: 5.5 bar   80 psig
final pressure: 5.5 bar   80 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g		leach residue:	308 g		residue ratio:	1.17 wt./wt.
electrolyte:	700 mL						
deionized water:	500 mL		leach filtrate:	975 mL			
			wash water:	654 mL		wash acidity:	0 g/L H2SO4
			total filtrate:	1629 mL			
			repulp volume:	545 mL			

POTENTIAL MEASUREMENTS

before:	slurry:	62 mV (SCE)	307 mV (SHE)
after:	slurry:	64 mV (SCE)	309 mV (SHE)
	supernatant:	70 mV (SCE)	315 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 12, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.89%	69.9%	21.7 g/L	0.341 M	0.537 g/L
Co		7.44%	4.30%	15.6 g/L	0.264 M	0.313 g/L
Ni		8.63%	2.14%	24.4 g/L	0.416 M	0.635 g/L
As		0.70%	0.52%	0.98 g/L	0.013 M	0.025 g/L
Fe		4.79%	1.47%	14.9 g/L	0.267 M	0.300 g/L
O		6.33%	3.4%			
Stot		13.37%	15.9%			
H2SO4	220 g/L			69.1 g/L	0.704 M	1 g/L

element ratio (wt./wt.)	IPC residue of May 12, 1994	leach residue
Cu : O	9.15	20.56
Cu : Stot	4.33	4.40
Stot : O	2.11	4.68

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		28.8	56.93%		0.96%	1.66%
Co	50.6%		7.90%	53.4%	0.46%	6.17%
Ni	78.8%		8.44%	78.3%	0.19%	2.17%
As	36.8%		0.71%	37.6%	0.01%	1.22%
Fe	73.7%		5.29%	76.2%	0.50%	10.45%
H2SO4		240.7				

AUTOCLAVE TEST WORKSHEET

test ID: #31
series ID: Kinetics, High Cu : S
date: Friday, September 2, 1994

temperature:	160 °C	320 °F
heat-up time to T:	51 min	
leaching time at T:	15 min	0.25 h

initial pressure:	5.5 bar	80 psig
final pressure:	5.5 bar	80 psig

stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	308 g	residue ratio:	1.17 wt./wt.
leach filtrate:	999 mL		
wash water:	630 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1629 mL		
repulp volume:	517 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	62 mV (SCE)	307 mV (SHE)
after:	slurry:	55 mV (SCE)	300 mV (SHE)
	supernatant:	70 mV (SCE)	315 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 12, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.89%	74.3%	10.6 g/L	0.167 M	0.709 g/L
Co		7.44%	2.45%	20.4 g/L	0.346 M	0.465 g/L
Ni		8.63%	1.19%	25.8 g/L	0.440 M	0.411 g/L
As		0.70%	0.46%	0.95 g/L	0.013 M	0.035 g/L
Fe		4.79%	0.82%	15.6 g/L	0.279 M	0.437 g/L
O		6.33%	3.4%			
Stot		13.37%	16.0%			
H2SO4	220 g/L			69.0 g/L	0.704 M	1 g/L

element ratio (wt./wt.)	IPC residue of May 12, 1994	leach residue
Cu : O	9.15	21.85
Cu : Stot	4.33	4.64
Stot : O	2.11	4.71

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		58.1	57.76%		0.13%	0.23%
Co	71.8%		7.75%	73.0%	0.31%	4.18%
Ni	88.2%		8.18%	87.6%	0.45%	5.20%
As	43.3%		0.66%	39.8%	0.04%	5.72%
Fe	85.3%		5.03%	86.0%	0.24%	5.09%
H2SO4		236.3				

AUTOCLAVE TEST WORKSHEET

test ID: #30
series ID: Kinetics, High Cu : S
date: Thursday, September 1, 1994

temperature:	160 °C	320 °F	
heat-up time to T:	50 min		
leaching time at T:	30 min	0.5 h	
initial pressure:	5.9 bar	85 psig	
final pressure:	5.9 bar	85 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	309 g	residue ratio:	1.17 wt./wt.
leach filtrate:	942 mL		
wash water:	630 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1572 mL		
repulp volume:	452 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	67 mV (SCE)	312 mV (SHE)
after:	slurry:	44 mV (SCE)	289 mV (SHE)
	supernatant:	56 mV (SCE)	301 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 12, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.89%	74.0%	5.97 g/L	0.094 M	0.896 g/L
Co		7.44%	1.58%	20.4 g/L	0.345 M	0.687 g/L
Ni		8.63%	0.89%	30.9 g/L	0.526 M	0.330 g/L
As		0.70%	0.43%	1.34 g/L	0.018 M	0.049 g/L
Fe		4.79%	0.67%	18.8 g/L	0.337 M	0.551 g/L
O		6.33%	2.7%			
Stot		13.37%	16.8%			
H2SO4	220 g/L			72.7 g/L	0.741 M	2 g/L

element ratio (wt./wt.)	IPC residue of May 12, 1994	leach residue
Cu : O	9.15	27.41
Cu : Stot	4.33	4.40
Stot : O	2.11	6.22

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		71.9	56.33%		1.56%	2.70%
Co	81.8%		6.68%	79.7%	0.76%	10.18%
Ni	91.1%		8.84%	91.3%	0.21%	2.47%
As	47.8%		0.72%	49.0%	0.02%	2.40%
Fe	88.0%		5.50%	89.5%	0.71%	14.79%
H2SO4		237.5				

AUTOCLAVE TEST WORKSHEET

test ID: #29
series ID: Kinetics, High Cu : S
date: Wednesday, August 31, 1994

temperature:	160 °C	320 °F	
heat-up time to T:	48 min		
leaching time at T:	60 min	1 h	
initial pressure:	5.9 bar	85 psig	
final pressure:	5.9 bar	85 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	310 g	residue ratio:	1.16 wt./wt.
leach filtrate:	955 mL		
wash water:	596 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1551 mL		
repulp volume:	518 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	69 mV (SCE)	314 mV (SHE)
after:	slurry:	20 mV (SCE)	265 mV (SHE)
	supernatant:	200 mV (SCE)	445 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 12, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.89%	77.1%	1.18 g/L	0.019 M	0.857 g/L
Co		7.44%	0.78%	22.4 g/L	0.381 M	0.667 g/L
Ni		8.63%	0.60%	28.6 g/L	0.487 M	0.027 g/L
As		0.70%	0.41%	1.31 g/L	0.017 M	0.046 g/L
Fe		4.79%	0.38%	19.2 g/L	0.345 M	0.534 g/L
O		6.33%	4.0%			
Stot		13.37%	16.4%			
H2SO4	220 g/L			70.4 g/L	0.718 M	1 g/L

element ratio (wt./wt.)	IPC residue of May 12, 1994	leach residue
Cu : O	9.15	19.28
Cu : Stot	4.33	4.70
Stot : O	2.11	4.10

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		84.4	58.11%		0.22%	0.37%
Co	90.9%		6.63%	89.8%	0.81%	10.89%
Ni	94.0%		8.10%	93.6%	0.53%	6.08%
As	49.9%		0.70%	49.7%	0.00%	0.36%
Fe	93.3%		5.43%	94.0%	0.64%	13.30%
H2SO4		241.1				

AUTOCLAVE TEST WORKSHEET

test ID: #28
series ID: Kinetics, High Cu : S
date: Tuesday, August 30, 1994

temperature: 160 °C   320 °F
heat-up time to T: 51 min
leaching time at T: 240 min   4 h

initial pressure: 5.9 bar   85 psig
final pressure: 8.3 bar   120 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue: 360 g   leach residue: 300 g   residue ratio: 1.20 wt./wt.
electrolyte: 700 mL
deionized water: 513 mL   leach filtrate: 980 mL
                                 wash water: 689 mL   wash acidity: 0 g/L H2SO4
                                 total filtrate: 1669 mL

                                 repulp volume: 656 mL

POTENTIAL MEASUREMENTS

before: slurry: 69 mV (SCE)   314 mV (SHE)

after: slurry: -160 mV (SCE)   85 mV (SHE)
           supernatant: 60 mV (SCE)   305 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 12, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	57.89%	76.2%	0.62 g/L	0.010 M	0.924 g/L
Co		7.44%	0.06%	19.5 g/L	0.331 M	0.665 g/L
Ni		8.63%	0.90%	27.2 g/L	0.464 M	0 g/L
As		0.70%	0.73%	0 g/L	0 M	0 g/L
Fe		4.79%	0.11%	12.2 g/L	0.218 M	0.619 g/L
O		6.33%	4.4%			
Stot		13.37%	16.6%			
H2SO4	220 g/L			60.3 g/L	0.615 M	1 g/L

element ratio (wt./wt.)	IPC residue of May 12, 1994	leach residue
Cu : O	9.15	17.32
Cu : Stot	4.33	4.59
Stot : O	2.11	3.77

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		85.8	54.92%		2.97%	5.13%
Co	99.4%		5.36%	99.1%	2.08%	27.95%
Ni	91.3%		8.16%	90.9%	0.47%	5.39%
As	12.7%		0.61%	0.1%	0.09%	12.69%
Fe	98.2%		3.41%	97.4%	1.38%	28.84%
H2SO4		263.7				

AUTOCLAVE TEST WORKSHEET

test ID: #27
series ID: Pulp Density
date: Friday, August 26, 1994

temperature:	160 °C	320 °F
heat-up time to T:	50 min	
leaching time at T:	60 min	1 h
initial pressure:	5.9 bar	85 psig
final pressure:	5.9 bar	85 psig
stirring rate:	13.7 1/s	820 rpm
pulp density:	29.5% solids	

REAGENT BALANCE

Autoclave feed

IPC residue:	617.1 g
electrolyte:	1200 mL
deionized water:	0 mL

Autoclave products

leach residue:	485.6 g	residue ratio:	1.27 wt./wt.
leach filtrate:	871 mL		
wash water:	751 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1622 mL		
repulp volume:	687 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	95 mV (SCE)	340 mV (SHE)
after:	slurry:	85 mV (SCE)	330 mV (SHE)
	supernatant:	mV (SCE)	mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 22, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	59.17%	74.3%	50.5 g/L	0.794 M	1.201 g/L
Co		6.13%	0.39%	43.1 g/L	0.731 M	0.916 g/L
Ni		7.76%	0.37%	47.1 g/L	0.803 M	1.205 g/L
As		0.68%	0.27%	3.38 g/L	0.045 M	0.085 g/L
Fe		4.07%	0.28%	30.5 g/L	0.547 M	0.709 g/L
O		5.98%	4.7%			
Stot		14.86%	19.4%			
H2SO4	220 g/L			91.0 g/L	0.927 M	2 g/L

element ratio (wt./wt.)	IPC residue of May 22, 1994	leach residue
Cu : O	9.89	15.81
Cu : Stot	3.98	3.83
Stot : O	2.48	4.13

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		16.3	56.84%		2.33%	3.93%
Co	95.0%		6.39%	95.2%	0.26%	4.26%
Ni	96.2%		6.94%	95.8%	0.82%	10.52%
As	69.3%		0.69%	69.6%	0.01%	0.86%
Fe	94.5%		4.53%	95.1%	0.46%	11.39%
H2SO4		299.4				

AUTOCLAVE TEST WORKSHEET

test ID: #26
series ID: Pulp Density
date: Thursday, August 25, 1994

temperature:	160 °C	320 °F	
heat-up time to T:	53 min		
leaching time at T:	60 min	1 h	
initial pressure:	5.9 bar	85 psig	
final pressure:	5.9 bar	85 psig	
stirring rate:	13.7 1/s	820 rpm	
pulp density:	15.0% solids		

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	229.9 g	leach residue:	198.2 g	residue ratio:	1.16 wt./wt.
electrolyte:	447 mL				
deionized water:	753 mL	leach filtrate:	1049 mL		
		wash water:	629 mL	wash acidity:	0 g/L H2SO4
		total filtrate:	1678 mL		
		repulp volume:	500 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	63 mV (SCE)	308 mV (SHE)
after:	slurry:	34 mV (SCE)	279 mV (SHE)
	supernatant:	70 mV (SCE)	315 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 22, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	59.17%	77.2%	0.25 g/L	0.004 M	0.124 g/L
Co		6.13%	0.37%	14.1 g/L	0.239 M	0.019 g/L
Ni		7.76%	0.45%	17.0 g/L	0.289 M	0.043 g/L
As		0.68%	0.36%	0.61 g/L	0.008 M	0.002 g/L
Fe		4.07%	0.23%	9.2 g/L	0.164 M	0.122 g/L
O		5.98%	5.1%			
Stot		14.86%	17.2%			
H2SO4	220 g/L			46.4 g/L	0.473 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 22, 1994	leach residue
Cu : O	9.89	15.14
Cu : Stot	3.98	4.49
Stot : O	2.48	3.37

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades)	
					absolute	relative
Cu		86.4	57.92%		1.25%	2.12%
Co	94.8%		6.74%	95.3%	0.61%	10.02%
Ni	95.0%		8.14%	95.2%	0.38%	4.84%
As	54.1%		0.59%	47.1%	0.09%	13.25%
Fe	95.1%		4.38%	95.5%	0.31%	7.72%
H2SO4		215.9				

AUTOCLAVE TEST WORKSHEET

test ID: #25
series ID: Pulp Density
date: Wednesday, August 24, 1994

temperature:	160 °C	320 °F
heat-up time to T:	53 min	
leaching time at T:	60 min	1 h
initial pressure:	6.1 bar	88 psig
final pressure:	6.1 bar	88 psig
stirring rate:	13.7 1/s	820 rpm
pulp density:	10.0% solids	

REAGENT BALANCE

Autoclave feed

IPC residue:	140.3 g
electrolyte:	273 mL
deionized water:	927 mL

Autoclave products

leach residue:	122.1 g	residue ratio:	1.15 wt./wt.
leach filtrate:	1096 mL		
wash water:	476 mL	wash acidity:	0 g/L H_2SO_4
total filtrate:	1572 mL		
repulp volume:	496 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	51 mV (SCE)	296 mV (SHE)
after:	slurry:	70 mV (SCE)	315 mV (SHE)
	supernatant:	125 mV (SCE)	370 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 22, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	59.17%	75.9%	1.24 g/L	0.019 M	0.197 g/L
Co		6.13%	0.38%	9.2 g/L	0.156 M	0.112 g/L
Ni		7.76%	0.46%	9.2 g/L	0.156 M	0.105 g/L
As		0.68%	0.32%	0.52 g/L	0.007 M	0.005 g/L
Fe		4.07%	0.23%	6.2 g/L	0.112 M	0.077 g/L
O		5.98%	6.1%			
Stot		14.86%	17.2%			
H_2SO_4	220 g/L			25.9 g/L	0.264 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 22, 1994	leach residue
Cu : O	9.89	12.44
Cu : Stot	3.98	4.41
Stot : O	2.48	2.82

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		77.9	58.26%		0.91%	1.53%
Co	94.6%		7.51%	95.6%	1.38%	22.49%
Ni	94.8%		7.57%	94.7%	0.19%	2.50%
As	59.4%		0.68%	59.5%	0.00%	0.15%
Fe	95.2%		5.07%	96.1%	1.00%	24.46%
H_2SO_4		226.0				

AUTOCLAVE TEST WORKSHEET

test ID: #24
series ID: Pulp Density
date: Tuesday, August 23, 1994

temperature:	160 °C	320 °F
heat-up time to T:	55 min	
leaching time at T:	60 min	1 h
initial pressure:	6.2 bar	90 psig
final pressure:	6.2 bar	90 psig
stirring rate:	13.7 1/s	820 rpm
pulp density:	5.0% solids	

REAGENT BALANCE

Autoclave feed

IPC residue:	64.7 g
electrolyte:	126 mL
deionized water:	1074 mL

Autoclave products

leach residue:	59.2 g	residue ratio:	1.09 wt./wt.
leach filtrate:	1141 mL		
wash water:	314 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1455 mL		
repulp volume:	486 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	56 mV (SCE)	301 mV (SHE)
after:	slurry:	70 mV (SCE)	315 mV (SHE)
	supernatant:	104 mV (SCE)	349 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 22, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	59.17%	76.1%	0.78 g/L	0.012 M	0.242 g/L
Co		6.13%	0.36%	4.0 g/L	0.068 M	0.131 g/L
Ni		7.76%	0.45%	4.2 g/L	0.072 M	0.152 g/L
As		0.68%	0.32%	0.23 g/L	0.003 M	0.007 g/L
Fe		4.07%	0.25%	2.5 g/L	0.044 M	0.184 g/L
O		5.98%	4.0%			
Stot		14.86%	18.2%			
H2SO4	220 g/L			10.2 g/L	0.104 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 22, 1994	leach residue
Cu : O	9.89	19.03
Cu : Stot	3.98	4.18
Stot : O	2.48	4.55

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		73.9	62.24%		3.07%	5.19%
Co	94.6%		7.40%	95.5%	1.27%	20.76%
Ni	94.7%		7.90%	94.8%	0.14%	1.83%
As	57.3%		0.70%	58.6%	0.02%	2.96%
Fe	94.4%		4.55%	95.0%	0.48%	11.74%
H2SO4		247.8				

AUTOCLAVE TEST WORKSHEET

test ID: #23
series ID: Pulp Density
date: Friday, August 19, 1994

temperature:	160 °C	320 °F
heat-up time to T:	52 min	
leaching time at T:	60 min	1 h
initial pressure:	6.1 bar	88 psig
final pressure:	6.1 bar	88 psig
stirring rate:	13.7 1/s	820 rpm
pulp density:	20.9% solids	

REAGENT BALANCE

Autoclave feed

IPC residue:	360.0 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	308.9 g
leach filtrate:	984 mL
wash water:	756 mL
total filtrate:	1740 mL
repulp volume:	470 mL

residue ratio:	1.17 wt./wt.
wash acidity:	0 g/L H2SO4

POTENTIAL MEASUREMENTS

before:	slurry:	74 mV (SCE)	319 mV (SHE)
after:	slurry:	68 mV (SCE)	313 mV (SHE)
	supernatant:	140 mV (SCE)	385 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 22, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	59.17%	77.0%	3.00 g/L	0.047 M	0.240 g/L
Co		6.13%	0.33%	22.2 g/L	0.376 M	0.127 g/L
Ni		7.76%	0.42%	19.2 g/L	0.327 M	0.149 g/L
As		0.68%	0.38%	1.19 g/L	0.016 M	0.006 g/L
Fe		4.07%	0.24%	15.6 g/L	0.279 M	0.187 g/L
O		5.98%	5.4%			
Stot		14.86%	17.6%			
H2SO4	220 g/L			79.6 g/L	0.812 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 22, 1994	leach residue
Cu : O	9.89	14.26
Cu : Stot	3.98	4.38
Stot : O	2.48	3.26

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		79.3	58.14%		1.03%	1.74%
Co	95.3%		6.34%	95.5%	0.21%	3.50%
Ni	95.4%		5.60%	93.6%	2.16%	27.86%
As	52.3%		0.65%	50.0%	0.03%	4.56%
Fe	94.9%		4.47%	95.4%	0.40%	9.73%
H2SO4		210.1				

AUTOCLAVE TEST WORKSHEET

test ID: #22
series ID: Agitation
date: Thursday, August 18, 1994

temperature:	160 °C	320 °F
heat-up time to T:	51 min	
leaching time at T:	60 min	1 h
initial pressure:	5.9 bar	85 psig
final pressure:	5.9 bar	85 psig
stirring rate:	10.4 1/s	625 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	297 g	residue ratio:	1.21 wt./wt.
leach filtrate:	979 mL		
wash water:	527 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1506 mL		
repulp volume:	661 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	70 mV (SCE)	315 mV (SHE)
after:	supernatant ?:	228 mV (SCE)	473 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 18, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.80%	74.8%	0.48 g/L	0.008 M	0.706 g/L
Co		7.47%	0.89%	26.6 g/L	0.451 M	0.520 g/L
Ni		8.98%	0.63%	30.1 g/L	0.512 M	0.119 g/L
As		0.77%	0.74%	0.24 g/L	0.003 M	0.056 g/L
Fe		4.84%	0.36%	18.8 g/L	0.337 M	0.458 g/L
O		6.60%	4.3%			
Stot		14.51%	17.5%			
H2SO4	220 g/L			66.8 g/L	0.681 M	1 g/L

element ratio (wt./wt.)	IPC residue of May 18, 1994	leach residue
Cu : O	8.30	17.40
Cu : Stot	3.78	4.27
Stot : O	2.20	4.07

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		86.2	53.09%		1.71%	3.12%
Co	90.1%		7.97%	90.7%	0.50%	6.63%
Ni	94.2%		8.70%	94.0%	0.28%	3.13%
As	21.0%		0.67%	9.6%	0.10%	12.64%
Fe	93.8%		5.41%	94.5%	0.57%	11.78%
H2SO4		246.1				

AUTOCLAVE TEST WORKSHEET

test ID: #21
series ID: Agitation
date: Wednesday, August 17, 1994

temperature:	160 °C	320 °F
heat-up time to T:	50 min	
leaching time at T:	60 min	1 h
initial pressure:	5.9 bar	85 psig
final pressure:	5.9 bar	85 psig
stirring rate:	16.7 1/s	1000 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	307 g	residue ratio:	1.17 wt./wt.
leach filtrate:	974 mL		
wash water:	666 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1640 mL		
repulp volume:	702 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	74 mV (SCE)	319 mV (SHE)
after:	supernatant ?:	157 mV (SCE)	402 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 18, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.80%	73.8%	0.45 g/L	0.007 M	0.625 g/L
Co		7.47%	0.90%	27.1 g/L	0.459 M	0.391 g/L
Ni		8.98%	0.78%	30.1 g/L	0.514 M	0.003 g/L
As		0.77%	0.81%	0.01 g/L	0.000 M	0.004 g/L
Fe		4.84%	0.40%	19.9 g/L	0.356 M	0.368 g/L
O		6.60%	5.4%			
Stot		14.51%	17.8%			
H2SO4	220 g/L			64.1 g/L	0.653 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 18, 1994	leach residue
Cu : O	8.30	13.67
Cu : Stot	3.78	4.15
Stot : O	2.20	3.30

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		86.3	54.31%		0.49%	0.90%
Co	89.7%		8.09%	90.5%	0.62%	8.26%
Ni	92.6%		8.82%	92.5%	0.16%	1.80%
As	9.8%		0.70%	0.4%	0.07%	9.51%
Fe	93.0%		5.72%	94.1%	0.88%	18.10%
H2SO4		254.5				

AUTOCLAVE TEST WORKSHEET

test ID: #20
series ID: Agitation
date: Tuesday, August 16, 1994

temperature:	160 °C	320 °F
heat-up time to T:	50 min	
leaching time at T:	60 min	1 h
initial pressure:	5.9 bar	85 psig
final pressure:	5.9 bar	85 psig
stirring rate:	14.6 1/s	875 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	298 g	residue ratio:	1.21 wt./wt.
leach filtrate:	976 mL		
wash water:	872 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1848 mL		
repulp volume:	452 mL		

POTENTIAL MEASUREMENTS

before: slurry: 76 mV (SCE)   321 mV (SHE)

after: supernatant ?:   197 mV (SCE)   442 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 18, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.80%	74.2%	0.68 g/L	0.011 M	0.371 g/L
Co		7.47%	0.91%	24.3 g/L	0.413 M	0.238 g/L
Ni		8.98%	0.64%	30.4 g/L	0.517 M	0.142 g/L
As		0.77%	0.44%	1.50 g/L	0.020 M	0.011 g/L
Fe		4.84%	0.43%	19.6 g/L	0.350 M	0.206 g/L
O		6.60%	5.4%			
Stot		14.51%	17.3%			
H2SO4	220 g/L			70.5 g/L	0.719 M	1 g/L

element ratio (wt./wt.)	IPC residue of May 18, 1994	leach residue
Cu : O	8.30	13.74
Cu : Stot	3.78	4.29
Stot : O	2.20	3.20

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		85.7	52.85%		1.95%	3.55%
Co	89.9%		7.35%	89.7%	0.12%	1.54%
Ni	94.1%		8.76%	94.0%	0.22%	2.48%
As	53.2%		0.77%	53.1%	0.00%	0.39%
Fe	92.7%		5.66%	93.8%	0.82%	16.88%
H2SO4		236.6				

AUTOCLAVE TEST WORKSHEET

test ID: #19
series ID: Agitation
date: Friday, August 12, 1994

temperature:	160 °C	320 °F
heat-up time to T:	54 min	
leaching time at T:	60 min	1 h
initial pressure:	5.9 bar	85 psig
final pressure:	5.9 bar	85 psig
stirring rate:	12.5 1/s	750 rpm

REAGENT BALANCE

Autoclave feed

		Autoclave products			
IPC residue:	360 g	leach residue:	295 g	residue ratio:	1.22 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL	leach filtrate:	827 mL		
		wash water:	1063 mL	wash acidity:	0 g/L H2SO4
		total filtrate:	1890 mL		
		repulp volume:	670 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	94 mV (SCE)	339 mV (SHE)
after:	supernatant ?:	177 mV (SCE)	422 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 18, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.80%	75.4%	0.17 g/L	0.003 M	0.125 g/L
Co		7.47%	0.84%	30.4 g/L	0.516 M	0.290 g/L
Ni		8.98%	0.61%	33.3 g/L	0.567 M	0.470 g/L
As		0.77%	0.69%	0.30 g/L	0.004 M	0.030 g/L
Fe		4.84%	0.41%	22.1 g/L	0.396 M	0.133 g/L
O		6.60%	3.2%			
Stot		14.51%	18.0%			
H2SO4	220 g/L			77.7 g/L	0.792 M	0 g/L

element ratio (wt./wt.)	IPC residue of May 18, 1994	leach residue
Cu : O	8.30	23.56
Cu : Stot	3.78	4.19
Stot : O	2.20	5.63

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		87.1	53.08%		1.72%	3.15%
Co	90.8%		7.67%	91.0%	0.20%	2.72%
Ni	94.5%		8.14%	93.9%	0.84%	9.30%
As	26.3%		0.64%	10.8%	0.13%	17.34%
Fe	93.0%		5.42%	93.8%	0.58%	12.04%
H2SO4		249.3				

AUTOCLAVE TEST WORKSHEET

test ID: #18
series ID: Acid
date: Thursday, August 11, 1994

temperature:	160 °C	320 °F
heat-up time to T:	52 min	
leaching time at T:	60 min	1 h
initial pressure:	5.9 bar	85 psig
final pressure:	5.9 bar	85 psig
stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	303 g	residue ratio:	1.19 wt./wt.
leach filtrate:	973 mL		
wash water:	796 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1769 mL		
repulp volume:	548 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	69 mV (SCE)	314 mV (SHE)
after:	slurry:	132 mV (SCE)	377 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 9, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.94%	74.0%	0.1 g/L	0.002 M	0.207 g/L
Co		6.76%	0.39%	25.2 g/L	0.428 M	0.028 g/L
Ni		9.54%	1.06%	31.8 g/L	0.542 M	0 g/L
As		0.71%	0.83%	0.01 g/L	0.000 M	0.001 g/L
Fe		4.11%	0.21%	17.5 g/L	0.313 M	0.119 g/L
O		7.94%	2.8%			
Stot		15.38%	18.2%			
H2SO4	220 g/L			69.1 g/L	0.705 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 9, 1994	leach residue
Cu : O	6.92	26.43
Cu : Stot	3.57	4.07
Stot : O	1.94	6.50

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		87.2	53.56%		1.38%	2.50%
Co	95.2%		7.14%	95.4%	0.38%	5.58%
Ni	90.6%		9.49%	90.6%	0.05%	0.51%
As	1.8%		0.70%	0.4%	0.01%	1.48%
Fe	95.7%		4.90%	96.4%	0.79%	19.14%
H2SO4		240.9				

AUTOCLAVE TEST WORKSHEET

test ID: #17
series ID: Acid
date: Wednesday, August 10, 1994

temperature:	160 °C	320 °F
heat-up time to T:	51 min	
leaching time at T:	60 min	1 h

initial pressure:	5.9 bar	85 psig
final pressure:	5.9 bar	85 psig

stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

Autoclave products

IPC residue:	360 g	leach residue:	306 g	residue ratio:	1.18 wt./wt.
electrolyte:	700 mL				
deionized water:	500 mL	leach filtrate:	981 mL		
		wash water:	869 mL	wash acidity:	0 g/L H2SO4
		total filtrate:	1850 mL		
		repulp volume:	445 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	69 mV (SCE)	314 mV (SHE)
after:	slurry:	50 mV (SCE)	295 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 9, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.94%	74.5%	0.2 g/L	0.003 M	0.363 g/L
Co		6.76%	0.42%	25.8 g/L	0.437 M	0.121 g/L
Ni		9.54%	1.13%	29.6 g/L	0.504 M	0 g/L
As		0.71%	0.81%	0.01 g/L	0.000 M	0.002 g/L
Fe		4.11%	0.25%	16.2 g/L	0.291 M	0.164 g/L
O		7.94%	3.0%			
Stot		15.38%	18.0%			
H2SO4	150 g/L			22.7 g/L	0.231 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 9, 1994	leach residue
Cu : O	6.92	24.83
Cu : Stot	3.57	4.14
Stot : O	1.94	6.00

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		87.0	54.62%		0.32%	0.58%
Co	94.8%		7.37%	95.2%	0.61%	9.05%
Ni	89.9%		9.03%	89.4%	0.51%	5.36%
As	3.1%		0.69%	0.3%	0.02%	2.82%
Fe	94.7%		4.64%	95.3%	0.53%	12.90%
H2SO4		229.9				

AUTOCLAVE TEST WORKSHEET

test ID: #16
series ID: Acid
date: Tuesday, August 9, 1994

temperature:	160 °C	320 °F	
heat-up time to T:	51 min		
leaching time at T:	60 min	1 h	
initial pressure:	6.2 bar	90 psig	
final pressure:	6.2 bar	90 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	319 g	residue ratio:	1.13 wt./wt.
leach filtrate:	956 mL		
wash water:	604 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1560 mL		
repulp volume:	530 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	64 mV (SCE)	309 mV (SHE)
after:	slurry:	78 mV (SCE)	323 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 9, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.94%	74.5%	0.1 g/L	0.001 M	0.127 g/L
Co		6.76%	0.51%	26.6 g/L	0.452 M	0.942 g/L
Ni		9.54%	2.01%	27.6 g/L	0.470 M	0 g/L
As		0.71%	0.85%	0.01 g/L	0.000 M	0.001 g/L
Fe		4.11%	0.50%	15.3 g/L	0.274 M	0.590 g/L
O		7.94%	2.7%			
Stot		15.38%	18.1%			
H2SO4	100 g/L			0.2 g/L	0.002 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 9, 1994	leach residue
Cu : O	6.92	27.59
Cu : Stot	3.57	4.12
Stot : O	1.94	6.70

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		87.3	57.28%		2.34%	4.27%
Co	93.3%		7.53%	93.9%	0.77%	11.35%
Ni	81.3%		9.10%	80.4%	0.44%	4.57%
As	-6.0%		0.75%	0.3%	0.04%	6.28%
Fe	89.3%		4.51%	90.3%	0.40%	9.70%
H2SO4		193.9				

AUTOCLAVE TEST WORKSHEET

test ID: #15
series ID: Acid
date: Friday, August 5, 1994

temperature: 160 °C   320 °F
heat-up time to T: 53 min
leaching time at T: 60 min   1 h

initial pressure: 6.2 bar   90 psig
final pressure: 6.2 bar   90 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue: 360 g
electrolyte: 700 mL
deionized water: 500 mL

Autoclave products

leach residue: 344 g   residue ratio: 1.05 wt./wt.

leach filtrate: 995 mL
wash water: 757 mL   wash acidity: 0 g/L H2SO4
total filtrate: 1752 mL

repulp volume: 557 mL

POTENTIAL MEASUREMENTS

before: slurry: 60 mV (SCE)   305 mV (SHE)

after: slurry: -317 mV (SCE)   -72 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 9, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.94%	67.0%	0.1 g/L	0.001 M	0.111 g/L
Co		6.76%	1.13%	22.1 g/L	0.374 M	1.270 g/L
Ni		9.54%	5.81%	15.6 g/L	0.265 M	0.001 g/L
As		0.71%	0.76%	0 g/L	0 M	0.002 g/L
Fe		4.11%	1.51%	9.6 g/L	0.171 M	0.580 g/L
O		7.94%	5.9%			
Stot		15.38%	17.0%			
H2SO4	50 g/L			0.7 g/L	0.008 M	1 g/L

element ratio (wt./wt.)	IPC residue of May 9, 1994	leach residue
Cu : O	6.92	11.36
Cu : Stot	3.57	3.94
Stot : O	1.94	2.88

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		87.3	55.29%		0.35%	0.64%
Co	84.0%		7.18%	85.0%	0.42%	6.21%
Ni	41.8%		9.85%	43.7%	0.31%	3.29%
As	-2.8%		0.73%	0.2%	0.02%	3.00%
Fe	64.9%		4.08%	64.7%	0.03%	0.66%
H2SO4		95.2				

AUTOCLAVE TEST WORKSHEET

test ID: #14
series ID: Acid
date: Thursday, August 4, 1994

temperature:	160 °C	320 °F
heat-up time to T:	52 min	
leaching time at T:	60 min	1 h
initial pressure:	6.2 bar	90 psig
final pressure:	6.2 bar	90 psig
stirring rate:	13.7 1/s	820 rpm

REAGENT BALANCE

Autoclave feed

IPC residue:	360 g
electrolyte:	700 mL
deionized water:	500 mL

Autoclave products

leach residue:	376 g	residue ratio:	0.96 wt./wt.
leach filtrate:	962 mL		
wash water:	678 mL	wash acidity:	0 g/L H2SO4
total filtrate:	1640 mL		
repulp volume:	592 mL		

POTENTIAL MEASUREMENTS

before:	slurry:	61 mV (SCE)	306 mV (SHE)
after:	slurry:	-473 mV (SCE)	-228 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 9, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	54.94%	60.7%	0 g/L	0 M	0.001 g/L
Co		6.76%	1.90%	20.1 g/L	0.342 M	0.175 g/L
Ni		9.54%	8.43%	3.1 g/L	0.052 M	0.104 g/L
As		0.71%	0.69%	0 g/L	0 M	0.002 g/L
Fe		4.11%	2.89%	4.1 g/L	0.073 M	0.008 g/L
O		7.94%	8.1%			
Stot		15.38%	15.5%			
H2SO4	0 g/L			0.2 g/L	0.002 M	0.1 g/L

element ratio (wt./wt.)	IPC residue of May 9, 1994	leach residue
Cu : O	6.92	7.49
Cu : Stot	3.57	3.92
Stot : O	1.94	1.91

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		87.5	54.65%		0.29%	0.53%
Co	70.6%		7.37%	73.1%	0.61%	8.96%
Ni	7.7%		9.62%	8.5%	0.08%	0.88%
As	-1.4%		0.72%	0.2%	0.01%	1.53%
Fe	26.6%		4.11%	26.6%	0.00%	0.08%
H2SO4		-0.6				

AUTOCLAVE TEST WORKSHEET

test ID: #12
series ID: Copper
date: Wednesday, May 25, 1994

temperature:	160 °C	320 °F	
heat-up time to T:	54 min		
leaching time at T:	60 min	1 h	
initial pressure:	5.5 bar	80 psig	
final pressure:	16.5 bar	240 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g		leach residue:	290 g	residue ratio:
electrolyte:	700 mL				
distilled water:	500 mL		leach filtrate:	1007 mL	
			wash water:	873 mL	wash acidity:
			total filtrate:	1880 mL	
			repulp volume:	760 mL	

residue ratio: 1.24 wt./wt.

wash acidity: 0 g/L H2SO4

POTENTIAL MEASUREMENTS

before: supernatant ?:   88 mV (SCE)   333 mV (SHE)

after: supernatant ?:   -197 mV (SCE)   48 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 20, 1994	leach residue	leach filtrate		repulp filtrate
Cu	15 g/L	55.35%	72.78%	0 g/L	0 M	0 g/L
Co		7.09%	1.31%	24.2 g/L	0.410 M	0.017 g/L
Ni		9.13%	2.16%	29.5 g/L	0.503 M	0.153 g/L
As		0.76%	0.95%	0 g/L	0 M	0 g/L
Fe		5.04%	0.50%	18.4 g/L	0.329 M	0 g/L
O		6.23%	2.60%			
Stot		14.72%	17.75%			
H2SO4	220 g/L			52.3 g/L	0.533 M	0 g/L

element ratio (wt./wt.)	IPC residue of May 20, 1994	leach residue
Cu : O	8.88	27.99
Cu : Stot	3.76	4.10
Stot : O	2.36	6.83

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		29.2	55.71%		0.36%	0.65%
Co	85.1%		7.81%	86.5%	0.72%	10.16%
Ni	80.9%		9.99%	82.6%	0.86%	9.47%
As	-0.7%		0.77%	0.0%	0.01%	0.69%
Fe	92.0%		5.54%	92.7%	0.50%	9.89%
H2SO4		281.6				

AUTOCLAVE TEST WORKSHEET

test ID: #11
series ID: Copper
date: Monday, May 23, 1994

temperature:	160 °C	320 °F	
heat-up time to T:	114 min		heating and agitation problems
leaching time at T:	60 min	1 h	
initial pressure:	5.5 bar	80 psig	
final pressure:	7.2 bar	105 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed

Autoclave products

IPC residue:	360 g	leach residue:	294 g	residue ratio:	1.22 wt./wt.
electrolyte:	700 mL				
distilled water:	500 mL	leach filtrate:	1020 mL		
		wash water:	1010 mL	wash acidity:	0 g/L H2SO4
		total filtrate:	2030 mL		
		repulp volume:	516 mL		

POTENTIAL MEASUREMENTS

before: supernatant ?:   101 mV (SCE)   346 mV (SHE)

after: supernatant ?:   -189 mV (SCE)   56 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 20, 1994	leach residue	leach filtrate		repulp filtrate
Cu	30 g/L	55.35%	74.15%	0 g/L	0 M	0 g/L
Co		7.09%	1.03%	24.5 g/L	0.415 M	0.056 g/L
Ni		9.13%	1.79%	29.7 g/L	0.507 M	0.226 g/L
As		0.76%	0.92%	0 g/L	0 M	0 g/L
Fe		5.04%	0.42%	18.3 g/L	0.328 M	0 g/L
O		6.23%	2.58%			
Stot		14.72%	17.95%			
H2SO4	220 g/L			61.7 g/L	0.629 M	0 g/L

element ratio (wt./wt.)	IPC residue of May 20, 1994	leach residue
Cu : O	8.88	28.74
Cu : Stot	3.76	4.13
Stot : O	2.36	6.96

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		58.3	54.72%		0.63%	1.13%
Co	88.1%		7.77%	89.2%	0.68%	9.60%
Ni	84.0%		9.89%	85.2%	0.76%	8.27%
As	1.1%		0.75%	0.0%	0.01%	1.14%
Fe	93.2%		5.53%	93.8%	0.49%	9.75%
H2SO4		253.0				

AUTOCLAVE TEST WORKSHEET

test ID: #10
series ID: Copper
date: Sunday, May 22, 1994

temperature:	160 °C	320 °F	
heat-up time to T:	65 min		
leaching time at T:	60 min	1 h	
initial pressure:	5.5 bar	80 psig	
final pressure:	5.5 bar	80 psig	
stirring rate:	13.7 1/s	820 rpm	

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g	leach residue:	299 g	residue ratio:	1.20 wt./wt.
electrolyte:	700 mL				
distilled water:	500 mL	leach filtrate:	1018 mL		
		wash water:	1142 mL	wash acidity:	0 g/L H2SO4
		total filtrate:	2160 mL		
		repulp volume:	794 mL		

POTENTIAL MEASUREMENTS

before:	supernatant ?:	106 mV (SCE)	351 mV (SHE)
after:	supernatant ?:	73 mV (SCE)	318 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 20, 1994	leach residue	leach filtrate		repulp filtrate
Cu	45 g/L	55.35%	76.68%	0.32 g/L	0.005 M	0.247 g/L
Co		7.09%	0.83%	22.6 g/L	0.383 M	0.496 g/L
Ni		9.13%	0.57%	30.6 g/L	0.521 M	0.664 g/L
As		0.76%	0.49%	1.26 g/L	0.017 M	0.021 g/L
Fe		5.04%	0.39%	16.7 g/L	0.299 M	0.309 g/L
O		6.23%	2.55%			
Stot		14.72%	17.50%			
H2SO4	220 g/L			69.0 g/L	0.703 M	0 g/L

element ratio (wt./wt.)	IPC residue of May 20, 1994	leach residue
Cu : O	8.88	30.07
Cu : Stot	3.76	4.38
Stot : O	2.36	6.86

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades) absolute	relative
Cu		86.6	55.03%		0.32%	0.58%
Co	90.3%		7.08%	90.3%	0.01%	0.14%
Ni	94.8%		9.12%	94.8%	0.01%	0.10%
As	46.5%		0.76%	46.7%	0.00%	0.41%
Fe	93.6%		5.04%	93.6%	0.00%	0.06%
H2SO4		232.8				

AUTOCLAVE TEST WORKSHEET

test ID: #9
series ID: Copper
date: Saturday, May 21, 1994

temperature:	160 °C	320 °F
heat-up time to T:	64 min	
leaching time at T:	60 min	1 h

initial pressure:	5.5 bar	80 psig
final pressure:	5.5 bar	80 psig

stirring rate: 13.7 1/s   820 rpm

REAGENT BALANCE

Autoclave feed   Autoclave products

IPC residue:	360 g	leach residue:	301 g	residue ratio: 1.20 wt./wt.
electrolyte:	700 mL			
distilled water:	500 mL	leach filtrate:	1012 mL	
		wash water:	928 mL	wash acidity: 0 g/L H2SO4
		total filtrate:	1940 mL	
		repulp volume:	516 mL	

POTENTIAL MEASUREMENTS

before: supernatant ?:   105 mV (SCE)   350 mV (SHE)

after: supernatant ?:   107 mV (SCE)   352 mV (SHE)

ASSAYS

component	electrolyte	IPC residue of May 20, 1994	leach residue	leach filtrate		repulp filtrate
Cu	60 g/L	55.35%	77.20%	8.18 g/L	0.129 M	0.126 g/L
Co		7.09%	0.82%	21.8 g/L	0.369 M	0.083 g/L
Ni		9.13%	0.56%	29.6 g/L	0.504 M	0.108 g/L
As		0.76%	0.43%	1.41 g/L	0.019 M	0.002 g/L
Fe		5.04%	0.33%	16.0 g/L	0.287 M	0.024 g/L
O		6.23%	2.13%			
Stot		14.72%	17.77%			
H2SO4	220 g/L			73.8 g/L	0.752 M	0 g/L

element ratio (wt./wt.)	IPC residue of May 20, 1994	leach residue
Cu : O	8.88	36.24
Cu : Stot	3.76	4.34
Stot : O	2.36	8.34

METALLURGICAL BALANCE

component	assay head extraction	consumption kg/t IPC residue	calc'd head grade	calc'd head extraction	balance errors (w.r.t. head grades)	
					absolute	relative
Cu		93.7	55.18%		0.17%	0.30%
Co	90.3%		6.81%	89.9%	0.28%	4.00%
Ni	94.9%		8.78%	94.7%	0.35%	3.78%
As	52.7%		0.76%	52.4%	0.00%	0.53%
Fe	94.5%		4.77%	94.2%	0.27%	5.27%
H2SO4		220.3				

APPENDIX D

AIR DISCHARGE CALCULATIONS

INCO's preliminary calculations [62] have shown that, in order to discharge a 6000 US gallon First-Stage Leach (FSL) batch in 45 minutes, an air flow of 107 scfm at 115 psig (8 kg/cm^2) and 320°F would be required. At the same flow rate it would take roughly 7 minutes to prepressurize the autoclave from 80 psig (5.5 kg/cm^2) to the air discharge pressure.

The molar volume at 8 bar and 160°C is:

$$V_M = 0.0224 \times \frac{1}{8} \times \frac{433}{273} = 4.44 \times 10^{-3} \ m^3/mole \tag{D-1}$$

From Appendix B it follows that a typical FSL batch has a volume of 23150 L. Knowing that the FSL autoclaves are operated at about 15% freeboard, the volume of the plenum above such a batch can be calculated according to:

$$V_{plenum} = \frac{23150}{0.85} - 23150 = 4085 \ L \tag{D-2}$$

Consequently, the total number of moles of gas present in the reactor freeboard at the beginning of the air discharge process would amount to:

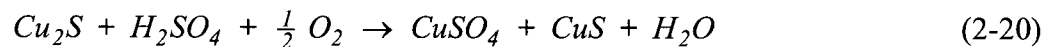$$N = \frac{4.085}{4.44 \times 10^{-3}} = 920 \ mole \tag{D-3}$$

The partial air pressure within the plenum at the initiation of the discharge operation would be 2.5 bar, so that:

$$n_{air} = \frac{2.5}{8} \times 920 = 287.5 \ mole \tag{D-4}$$

Approximating the composition of air as 21% (vol.) O_2 and 79% (vol.) N_2 gives:

$$n_{oxygen} = 0.21 \times 287.5 = 60.4 \ mole \tag{D-5}$$

Consider the oxidation reaction:

$$Cu_2S + H_2SO_4 + \tfrac{1}{2} O_2 \rightarrow CuSO_4 + CuS + H_2O \tag{2-20}$$

The stoichiometry of the above reaction dictates that two moles of $CuSO_4$ pass into solution for every mole of O_2 that reacts. Furthermore, reaction (2-20) is kinetically fast; the cuprous sulfide slurry can be expected to react with any oxygen introduced to the reactor almost instantaneously, whether it is stirred or not. Disregarding the hot O_2 consumed during prepressurization, at least 120.8 moles of cupric ion would be redissolved during air discharging of a FSL autoclave.

Hence, the minimal increase in copper concentration measured over the total volume of electrolyte and steam condensate (Appendix B) would be:

$$\Delta[Cu^{2+}] = \frac{120.8 \times 63.5}{21855} = 0.35 \ g/L \tag{D-6}$$

The actual increase in the copper content of the FSL solution would even be higher, since the discharge pressure would be maintained at 8 bar.