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**OXYGEN APPLICATION TO CHLORIDE
LEACHING OF COMPLEX SULFIDE
ORES**

**A
Thesis**

**Presented to the Faculty of the
University of Alaska in Partial Fulfillment
of the Requirements
for the Degree of**

MASTER OF SCIENCE

By

**KuoTung Chou, M.S.
Fairbanks, Alaska**

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ABSTRACT

The study investigates leaching of complex sulfide ores with simultaneous regeneration of the leaching solution and removal of dissolved iron to balance the iron concentration in the leaching process.

To minimize environmental pollution and obtain high metal extraction from the ores, leaching with a ferric chloride solution is adapted to treat Delta sulfide ores. The

experimental results indicate that under high oxygen pressure leaching, oxidation of ferrous ion to ferric ion and partial precipitation of iron from solution can occur simultaneously. However, the findings also indicate that leaching the ores with simultaneous iron precipitation in one operation is difficult. It is better to precipitate excess iron in one stage; then leach the ores in another stage using the regenerated leaching solution.

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CHAPTER 1

INTRODUCTION

1.1 Background

Sulfide ores are the most important sources of nonferrous metals. In Alaska, a massive sulfide deposit has been discovered in the Delta district in east central Alaska (Nauman and Duke, 1986). The massive sulfide ores consist of pyrite with lesser amounts of sphalerite, galena, chalcopyrite, pyrrhotite, and arsenopyrite as well as precious metals. The valuable minerals in the ores occur mostly in the interstices within aggregated pyrite (Rao and Letowski, 1986; Bloodworth and Schmidt, 1982). Although the sulfide minerals can be liberated by fine grinding, fine pyrite particles are difficult to depress during the subsequent froth flotation process. To evaluate the economic feasibility of mining the ores, several attempts have been made to recover the metals by flotation (Lam and Wilson, 1977; Schmidt and Shaw, 1984), leaching of bulk flotation concentrates (Schmidt and Shaw, 1984), and direct leaching of ores (Letowski et al., 1986). Sufficient recovery of a satisfactory grade could not be achieved by differential or bulk flotation. By leaching of the bulk flotation concentrates, it was found that 95-98% of lead was extracted. However, only 36-47% of zinc recovery with 29-34% of grade was realized in the following flotation process (Schmidt and Shaw, 1984).

It has long been known that there are several advantages to a hydrometallurgical process, including: (1) the comparative absence of air pollution by sulfur dioxide and by dust generated in a pyrometallurgical method; (2) the possibility of treating low grade ores that could not be economically upgraded using conventional milling, concentrating and smelting methods; (3) the possibility of recovering value from residue; and (4) the ability to regenerate the leaching solution (Dutrizac and MacDonald, 1974).

It is well-known that Alaska has severe legal restrictions to protect the environment. Strict regulations regarding pollution, such as those concerning discharge of sulfur dioxide or waste water, restrict development of the mineral industry. The advantages of a hydrometallurgical process mentioned above indicate that this treatment method for sulfide ores appears to be an attractive alternative in Alaska, especially considering the low recovery obtained by flotation.

In recent years there has been great interest in the treatment of complex sulfide ores (Zunkel et al., 1985; Jones 1981). Hydrometallurgical processes, involving ferric chloride and cupric chloride leaching (Beattie et al., 1984; Schweitzer and Livingston, 1982; Peter et al., 1981; Andersen et al., 1981; McNamara et al. 1980; Demarthe and Georgeaux, 1978), have been used for processing complex sulfide ores or concentrates. In addition, leaching with flotation has been developed to treat the complex sulfide

ores (Letowski, 1986).

Monhemius (1981) described a number of attractive features of the chloride-based hydrometallurgical processes compared to the sulfate-based as follows:

- (1) Many metal chloride salts were considerably more soluble than the corresponding sulfate salts, thus allowing the use of more concentrated metal solutions;
- (2) Ferric and cupric chloride solutions were aggressive oxidizing agents for many sulfide minerals, enabling direct leaching of these materials;
- (3) The formation of metal chlorocomplex ions in solution enabled a number of important metal separations to be achieved much more readily in chloride solutions than in sulphate solutions;
- (4) Hydrochloric acid could usually be recovered readily from chloride solutions, thus allowing regeneration of chloride within the process.

Owing to such attractive features and wide uses of chloride-based solution, direct leaching of the Delta ores has been conducted with the ferric chloride to determine the fundamental characteristics of the ores (Letowski et al., 1986).

1.2 Objective

Since regeneration of leaching solution and removal of iron produced during leaching may be important to the overall process, tests have been carried out to examine leaching with simultaneous regeneration of the leaching solution in a glass reactor under atmospheric pressure.

The further objective of this study is to investigate the simultaneous processes of leaching with flotation and iron precipitation under elevated oxygen pressure. This process has been studied by the addition of sulfuric acid H_2SO_4 and calcium oxide (CaO) at 70-100°C in an oxygen stream (Letowski, 1983).

To fulfill the objective of this study, the following processes were investigated:

- (1) Leaching with and without solution regeneration under atmospheric pressure;
- (2) Leaching in the presence and absence of iron precipitation under oxygen pressure;
- (3) Regeneration of the leaching solution together with iron precipitation in the presence and absence of a neutralizer.

1.3 Literature Survey

In the treatment of base metal sulfides, many investigators were interested in using the ferric ion as a leaching reagent. A review by Dutrizac and MacDonald (1974) presented a good account of various processes using ferric sulfate and ferric chloride as a leachant. Due to the property of a strong oxidant in acid media and the ability to produce sulfur in the nonpolluting elemental form, ferric chloride, especially, has been extensively used in the leaching of chalcopyrite (Dutrizac, 1982, 1981, 1978; Kunda et al., 1976), sphalerite (Bobeck and Su, 1985; Su, 1981; Dutrizac and MacDonald, 1978), galena (Fuerstenau et al., 1986; Morin et al., 1985), and complex sulfide bulk concentrates (Lucas and Shimano, 1985).

Lucas and Shimano (1985) investigated the effects of ferric to ferrous ratio, temperature, and HCl on metal extractions in two-stage leaching of complex sulfide bulk concentrates. The results concluded that extractions of zinc and lead were relatively insensitive to the level of excess ferric chloride in two-stage leaching. With increasing temperature, ranging 103-108°C, a significant increase in the copper extraction, a small increase in the zinc extraction, and no effect in the lead extraction were observed. The HCl concentration had no effect on zinc and lead extractions. However, the copper extraction was observed to decrease with increased HCl concentration.

Bobeck and Su (1985) studied the kinetics of dissolution of sphalerite in the ferric chloride solution. Their results showed that the reaction rate increased significantly with temperature; the activation energy was 47 kJ/mole. The dissolution rate was also found to be proportional to the concentration of ferric ion below about 0.1 M, but was insensitive to the ferric ion concentration above the value. The process of dissolution followed the mixed-control model.

Morin et al. (1985) conducted studies on the leaching of galena by applying a constant ferric chloride concentration. They found that particle size and ferric concentration had the major effect on kinetics, while ferrous ion and chloride ion concentrations had little or no effect. The kinetics were controlled by both the diffusion of the ferric ion through the pores of the sulfur layer, and the chemical reaction of the ferric ion at the galena surface.

Dutrizac (1978) investigated the dissolution of chalcopyrite in the ferric chloride solution. He found that the leaching rate increased steadily with increase of the ferric ion concentration (over the range from 0.001 to 0.3 M). The rate was also found to increase with the chloride concentration, but became independent when it was greater than about

2 M. The insensitivities of the concentrations of hydrochloric acid and ferrous chloride were also observed. In addition, in 1981 he reported that the rate was directly proportional to surface area of the chalcopyrite, and independent of temperature over the range from 45 to 100°C.

The regeneration of ferric ion in the ferrous chloride solutions using oxygen is commonly encountered in many hydrometallurgical processes. Therefore, some investigators focused on the study of parameters governing the oxidation of acid ferrous chloride solutions.

Swaminathan et al. (1981) concluded that the oxidation rate increased with oxygen pressure and temperature. They observed no significant effect of pH on the oxidation rate. $\text{Fe}(\text{OH})_3$ was produced when pH was greater than 2. A higher degree of hydrolysis and precipitation of hydrated oxides was observed when the cupric ion was used as a catalyst. They found that about 60% of the ferrous ions were oxidized in the presence of the catalyst under 515 kPa pressure at 140-150°C and 5 ml/min flow rate. Oxidation was about 40% without the catalyst.

Haver et al. (1975) studied the regeneration of a leaching solution and indicated that the reaction rate increased as the temperature increased. Oxygen partial pressure and gas flow rate were also found to have a positive effect on the reaction rate.

In the study of oxidation of the ferrous chloride in hydrochloric acid, different results have been presented by different investigators. Yano et al. (1974) concluded that the reaction rate was independent of the concentrations of the hydrogen ion and the ferric chloride in the range of 0.2-0.8 M when the concentration of chloride ion was kept constant. However, the reaction rate was second order with respect to the concentration of the ferrous chloride, and proportional to the oxygen partial pressure. Iwas et al. (1979), however, reported that the reaction rate was proportional to the activities of the hydrogen ion and the chloride ion, and also proportional to the ferrous ion and the oxygen partial pressure.

Colborn and Nicol (1973) showed that the oxidation of the ferrous chloride by oxygen was second order with respect to the ferrous ion concentration and proportional to the oxygen concentration. The oxidation rate was also second order with respect to the total concentration of the ferrous chloride complexes. The dependence on chloride ion could be explained by the formation of the ferrous chloride complexes. They also stated that the catalytic effect of the cupric ion was very pronounced, and the oxidation rate was independent of hydrogen ion concentration.

Awakura et al. (1986) investigated oxidation of the

ferrous ion in hydrochloric acid with and without the presence of cupric ions. They found that oxidation without the cupric ion was proportional to the activities of the ferrous ion and the oxygen partial pressure. But they indicated that with the presence of cupric ions, the oxidation rate was second order with respect to the ferrous ion concentration; inversely proportional to the ferric ion concentration; and was proportional to the oxygen partial pressure.

Because of the use of scrap iron for the cementation of copper, and the unwanted dissolution of iron during leaching, removal of the iron from the pregnant solution may become necessary. Jarosite process (Arauco and Doyle, 1986), goethite process (Beutier et al. 1986) and hematite process (Von Ropenack, 1986) were the three main iron precipitation techniques. These iron removal processes have been extensively employed in the zinc industry. The goethite precipitate, here, is a collective term which may consist of α -FeOOH (goethite), β -FeOOH (akaganeite), γ -FeOOH (maghemite) and α -Fe₂O₃ as well as amorphous phases (Davey and Scott, 1976, 1975). The hydrolysis of ferric salts normally gave a precipitate of α -FeOOH. But in chloride medium it formed β -FeOOH instead due to the inhibition of nucleation of α -FeOOH (Davey and Scott, 1976, 1975; Collepari et al., 1972; Schmalz, 1959). In the study on Fe₂O₃ - H₂O system, Schmalz (1959) indicated that at temperature up to 70°C, goethite (FeOOH) appeared to be more stable than hematite (Fe₂O₃) in the saturated solution of halite.

Raudsepp and Beattie (1986) showed that when the acid ferric ion solution was neutralized, Fe(OH)₃ formed below 90°C and goethite predominated between 90 and 130°C while hematite formed above 130°C. These temperature limits were not absolute. The report also indicated that the formation of the ferric ion complexes would tend to suppress iron precipitation.

Dutrizac (1980) reported that the commercial precipitations were carried out in the pH range of 2-3.5 and temperature from 75 to 95°C. The higher temperature favored the formation of hematite. Dutrizac also depicted the following advantages of goethite precipitation:

- (1) Good iron precipitation, final concentration of ferric ion could be lowered to less than 1 g/l;
- (2) Excellent filtrating characteristics;
- (3) Stable precipitate;
- (4) No need for adding alkalis.

In the study of jarosite formation in chloride media, Dutrizac (1981) concluded that the possibility of lead

jarosite precipitation existed when the leaching of sulfide minerals was carried out in concentrated FeCl₃ solution. He found that in a FeCl₃ - LiCl solution β -FeOOH was the precipitated phase when sulfate concentration was less than 0.05 M. At higher sulfate concentration, lead jarosite was the predominant phase although traces of β -FeOOH or PbSO₄ were also observed. However, the concentration of HCl in excess of 0.1 M essentially suppressed the formation of jarosite.

Dutrizac (1983) investigated various factors affecting alkali jarosite precipitation, such as pH, temperature, alkali concentration, retention time, presence of seed, ionic strength and iron concentration of solution. Of these factors, temperature, time and solution acidity were the most significant. Increasing temperature considerably increased the extent of iron precipitation. At 97°C, the amount of product increased with prolonged retention time. The solution acidity had the major influence on the amount of product formed.

CHAPTER 2 PRINCIPLES

2.1 Dissolution of Oxygen

Oxygen is applied extensively in many hydrometallurgical processes, thus knowledge of oxygen solubility is important. Three main factors that affect the oxygen solubility are ionic strength, temperature and pressure.

(1) Effect of Ionic Strength

The saturation solubility of oxygen usually decreases with an increase in the solute concentration; this phenomenon is known as salting-out. The solubility of oxygen in an electrolytic solution can often be described by the Sechenov equation (Narita et al., 1983; Schumpe et al., 1978):

$$\log \left(\frac{S_0}{S} \right) = \sum_i H_i I_i \quad (2-1)$$

where S_0 : solubility of oxygen in pure water
 S : solubility of oxygen in the electrolytic solution
 H_i : constant for species i
 I_i : ionic strength of species i

(2) Effect of Temperature

Cramer (1980), in the study of oxygen in brines, indicated that the solubility of oxygen decreased with increasing

temperature, until it reached a minimum in the temperature range of 60-100°C depending on the brine. At higher temperature the solubility then increased with the increasing temperature. The effect of temperature on the solubility of oxygen could be expressed in terms of the Van't Hoff's equation (Habashi, 1969):

$$\ln \left(\frac{S_2}{S_1} \right) = \frac{\Delta H (T_2 - T_1)}{RT_1 T_2} \quad (2-2)$$

where S_1, S_2 : solubility of oxygen at various temperatures

T_1, T_2 : various temperatures

ΔH : enthalpy change of oxygen dissolution

R : gas constant

The equation showed that if enthalpy change was positive, that was for an endothermic reaction, the solubility increased with increasing temperature.

(3) Effect of Pressure

In accordance with Henry's law, increasing oxygen partial pressure would increase the solubility of oxygen in the solution. Zoss (1954) measured the solubility of oxygen in water at various temperatures and pressures and gave the following equation:

$$S_o = k_h P \quad (2-3)$$

and

$$k_h = 0.145 \times (1.818 \times 10^{-2} - 1.439 \times 10^{-4} T + 1.95 \times 10^{-7} T^2)$$

where S_o : solubility of oxygen in water

P : oxygen partial pressure in kPa

k_h : Henry's constant in $\text{kg/m}^3 - \text{kPa}$

T : temperature ($^{\circ}\text{K}$)

At 90°C and 207 kPa oxygen pressure, S_o was calculated as 0.05 kg/m^3 . For 2 liters of water, the total oxygen dissolved in the water was 0.1 g.

2.2 Leachability

2.2.1 Thermodynamic Feasibility

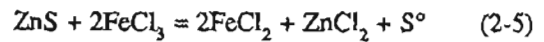
In most leaching systems of sulfide ores or concentrates, a strong oxidizing reagent might be used so that the free energy change for the dissolution reaction had a large negative value — the reaction was thermodynamically very favorable. A solution containing ferric chloride was a strong reagent with an associated oxidation potential of 0.77 volt. The dissolution reaction of a complex sulfide ore in this

acidified medium could be expressed as follows:

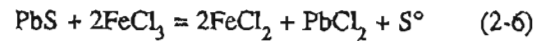
Chalcopyrite:



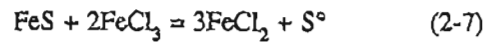
Sphalerite:



Galena:



Pyrrhotite:



The solubilities of CuCl and PbCl_2 were low in water. For the above reactions the standard free energy change, (ΔG°) and equilibrium constants ($^{\circ}\text{K}$) at 25°C could be calculated as:

$$\Delta G^{\circ} = -RT \ln K \quad (2-8)$$

where R : gas constant

T : temperature ($^{\circ}\text{K}$)

The calculated data without taking into account of the chlorocomplex effect are shown in Table 2.1 (Pankratz, 1984; Pankratz et al., 1984). The equilibrium constants indicate that the reactions are far to the right at 25°C. This means that the dissolution of these sulfide minerals in the ferric chloride solution occurs under the ambient condition.

Table 2.1 Thermodynamic data of reactions (kJ/mole)

| Reactions | ΔG° | K |
|-----------|--------------------|-----------------------|
| 2-4 | -70.83 | 2.61×10^{12} |
| 2-5 | -62.72 | 9.87×10^{10} |
| 2-6 | -111.04 | 2.92×10^{19} |
| 2-7 | -95.86 | 6.36×10^{16} |

2.2.2 Factors Affecting Reaction Process

Leaching is a heterogeneous reaction at the solid and liquid interface. The actual reaction rate may either be controlled by the rate of the chemical reaction itself or by the diffusion process.

The reaction process occurred using the following steps (Rosenqvist, 1983, Habashi, 1969):

- Transportation of liquid reactants from the bulk to the surface of solid reactants.
- Adsorption of reactants on the solid surface.
- Chemical reaction at the solid surface.

- (d) Desorption of products from the solid surface.
- (e) Diffusion of products from the solid surface to the bulk.

(1) Effect of Agitation

For the diffusion control the reaction rate followed the rate law (Habashi, 1969):

$$\text{Rate} = \frac{D}{\delta} AC \quad (2-9)$$

- where
- D : diffusion coefficient of reactant
 - δ : thickness of the boundary layer
 - A : surface area of solid
 - C : concentration of the reactants

The rate law showed that the rate of dissolution increased with a decrease in the thickness of the boundary layer as the stirring speed increased. In the chemical reaction control, the rate was independent of the speed of stirring.

(2) Effect of Temperature

In the case of diffusion control, the activation energy was usually less than 12 kJ/mole, therefore the effect of temperature on the reaction rate was much less. However, when the process was controlled by the chemical reaction the reaction rate increased rapidly with temperature. The activation energy was usually greater than 42 kJ/mole. The relationship was expressed by Arrhenius equation (Habashi, 1969):

$$k = A e^{-E/RT} \quad (2-10)$$

- where
- k : rate constant
 - A : frequency factor
 - E : activation energy
 - R : gas constant
 - T : temperature ($^{\circ}\text{K}$)

(3) Effect of Particle Size

Particle size usually imposed the major constraint in extraction rate. The finer the particle, the greater the extraction, since the smaller the particles, the larger the surface area per unit weight. As the leaching proceeded the particle surface area would be changing, the layer of insoluble product might be formed and the inner unreacted core of particle would decrease. Many mathematical models have been developed to describe the leaching rate of pure mineral in terms of the fraction reacted (Bobeck and Su, 1985; Su,

1981; Levenspiel, 1972). For the diffusion control through the porous sulfur layer, the rate could be expressed as:

$$1 - \frac{2}{3}R - (1 - R)^{2/3} = \frac{2bMDC_s}{r_o^2 \rho_p} t \quad (2-11)$$

where

- R : fraction reacted ($R = 1 - \left(\frac{r}{r_o}\right)^3$)
- b : stoichiometry factor
- M : molecule weight of mineral
- D : diffusion coefficient
- C_s : concentration of reactant at the mineral surface
- r_o : original radius
- r : radius of unreacted core
- ρ_p : density of particle

In the case of chemical control reaction, the rate could be represented by:

$$1 - (1-R)^{1/3} = \frac{bMK_c C_s}{r_o \rho_p} t \quad (2-12)$$

where K_c : chemical reaction rate constant

If neither the chemical reaction rate nor the diffusion rate controlled the overall process completely, both steps should be taken into consideration simultaneously in obtaining the expression for the overall rate. When both rates were of the same magnitude the combined rate could be expressed as follows:

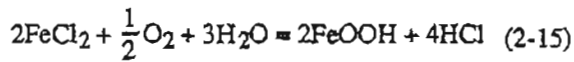
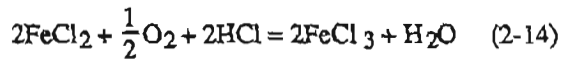
$$\frac{bMK_c DC_s}{r_o^2 \rho_p} t = \frac{K_c}{2} \left(1 - \frac{2}{3}R - (1 - R)^{2/3} \right) + \frac{D}{r_o} (1 - (1 - R)^{1/3}) \quad (2-13)$$

(4) Effect of Complex Ion

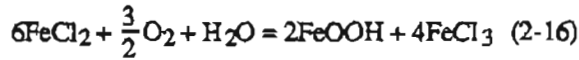
Generally, the solubility of an ion was less in a solution containing a common ion than in pure water. But if there was a formation of complex ion the solubility would increase. The increase in solubility was ascribed to the removal of the simple ions by the formation of complex ions.

2.3 Solution Regeneration and Iron Precipitation

The regeneration of leaching reagent with simultaneous removal of dissolved iron from the leaching solution could occur through oxidation of the ferrous ion by oxygen. Two steps were involved in this process. The reactions were as follows:



Reaction (2-14) was an oxidation step to reduce the excess acid by oxygen. Reaction (2-15) was a step of oxidation with hydrolysis to precipitate the dissolved iron as goethite and to produce acid. Therefore, the pH of the solution should initially increase to maximum, and then drop during precipitation. The overall reaction could be given as:



It could be seen that at the end of oxidation, one third of initial total ferrous ions were precipitated as goethite and two thirds were oxidized to ferric ions. In the reaction of precipitation without addition of seed, nuclei were generated during the induction period, and the nuclei then acted as seeds which accelerated the precipitation.

The main factors affecting the regeneration of solution and iron precipitation were: solution pH, oxygen pressure, temperature and iron concentration.

(1) Effect of pH

The pH of the solution was the main parameter controlling the solubility of hydrolyzed metal species. Figure 2-1 (Monhemius, 1981), a plot of activity of metal ion in solution vs solution pH, showed that the ferric ion was stable in the acid media but started to hydrolyze at pH of around 2 depending on the ferric ion activity in the solution. The ferrous ion, however, was stable in a rather wide range of pH up to about 8. This meant that the ferric ion precipitated-out easier than the ferrous ion, and the excess iron could be removed during regeneration of the leaching solution by controlling the solution pH.

(2) Effect of Oxygen Partial Pressure

The oxidation rate was usually dependent on oxygen partial pressure. Increasing oxygen partial pressure would usually increase the oxidation rate. According to Henry's law, with an increase in oxygen pressure the solubility of oxygen would increase.

(3) Effect of Temperature

Like all other equilibria, precipitation would be affected by temperature according to Van't Hoff's equation (see 2-2). Goethite was a stable precipitate and its solubility in acid solution decreased with increasing temperature. It was also known that temperature might determine the forms of precipitate. For example, the higher temperature favored the

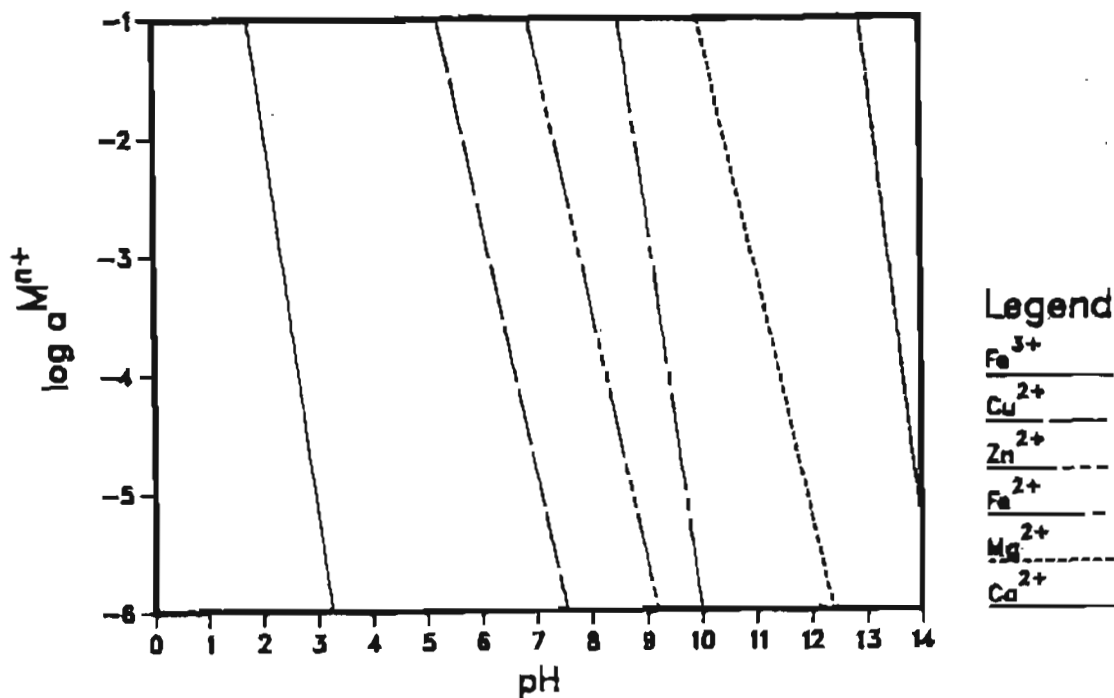
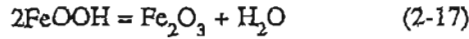


Figure 2.1 Precipitation diagram for metal hydroxide (Monhemius, 1981).

formation of hematite.



Since the standard free energy of above reaction was -4.02, -4.6 and -5.69 kJ/mole at 60, 80, 100°C, respectively, it appeared that this reaction favored thermodynamically at higher temperature (Collepari et al. 1972).

(4) Effect of Iron Concentration

The oxidation rate was a function of the concentration of ferrous ion, probably also of total iron depending on conditions. As far as iron precipitation was concerned, an increase in total iron increased the adsorption rate of the iron complexes onto the surface of the iron precipitate, resulting in an increase in the surface concentration of the reacting complexes.

2.4 Hydrodynamics in a Column Reactor

Columns were widely used industrially as absorbers, strippers and multiphase reactors because of their simple construction and operation, less maintenance, low operating cost and better mass transport of the system. However, they were difficult to design due to complicated flow characteristics and unknown behavior under different sets of design parameters such as diameter and height, etc. (Shah et al., 1982).

2.4.1 Physical Properties of Liquid

The kinematic behavior of a fluid was usually expressed in terms of the Reynolds number, which was defined as follows (McCabe et al., 1985):

$$N_{Re, l} = \frac{D_c U \rho_l}{\mu} \quad (2-18)$$

where $N_{Re, l}$: Reynolds number of liquid
 D_c : diameter of column
 U : average velocity of flow
 ρ_l : density of liquid
 μ : viscosity of liquid

Referring to the Reynolds number the types of flow were classified as either laminar or turbulent. Laminar flow commonly occurred at Reynolds numbers below 2,100, while above 4,000 turbulent flow was always encountered.

According to the relationship between shear stress and shear rate, the laminar flow could be classified as Newtonian or Non-Newtonian. As shear stress was proportional to the shear rate the fluid was a Newtonian one, and the propor-

tional constant was called viscosity. Inversely, the fluid which did not follow this relationship was characterized as a Non-Newtonian fluid. The viscosity of a liquid decreased significantly with increasing temperature, and increased slowly with increasing pressure when pressure was less than 4.0 MPa.

The viscosity of a liquid could be estimated approximately by Eyring equation (Szekely and Themelis, 1971; Bird et al., 1960):

$$\mu = \frac{4 \times 10^{-3}}{V_m} e^{3.8 T_b/T} \quad (2-19)$$

where T_b : normal boiling point (°K)
 T : temperature (°K)
 V_m : molar volume

2.4.2 Movement of Particles in Liquid

Based on the movement, density and diameter of particles, flow could be classified as either in the Stokes' or Newton's law range. To identify the range in which the flow lay, a Reynolds number was often applied:

$$N_{Re, p} = \frac{D_p U_t \rho_p}{\mu} \quad (2-20)$$

where $N_{Re, p}$: Reynolds number of particles
 D_p : diameter of particle
 U_t : terminal velocity
 ρ_p : density of particle

If the Reynolds number was less than 1, Stokes' law was employed. For a Reynolds number between 1,000 and 20,000 Newton's law was applied. The terminal velocity in Stokes' law range was expressed as:

$$U_t = \frac{g D_p^2 (\rho_p - \rho_l)}{18\mu} \quad (2-21)$$

where g : gravitational acceleration

2.4.3 Bubble Dynamics

(1) Bubble Diameter

At low gas flow rate ($N_{Re, o} < 500$) through a submerged orifice in a liquid, the bubble diameter was determined by the balance between the buoyancy and surface tension forces (Szekely and Themelis, 1971):

CHAPTER 3 EXPERIMENTAL WORK

$$D_b = \left(\frac{6D_o\sigma}{g(\rho_l - \rho_g)} \right)^{1/3} \quad (2-22)$$

where D_b, D_o : bubble and orifice diameters,
respectively

σ : surface tension

ρ_g : density of gas

(2) Rising Velocity of a Bubble

The rising velocity of a bubble was determined mainly by the buoyancy force that drove the bubble upwards and the viscous force that tended to decrease this motion. For small bubbles ($D_b < 0.2$ cm) that behaved like rigid spheres, the terminal rise velocity could be determined from Stokes' law:

$$U_r = \frac{gD_b^2(\rho_l - \rho_g)}{18\mu} \quad (2-23)$$

(3) Gas Holdup

Gas holdup was defined as the percentage by volume of the gas in the two or three phase mixtures in the column. It was often written as:

$$E_g = \frac{V_g}{V_s} \quad (2-24)$$

where E_g : gas holdup

V_g : volume of gas bubbles

V_s : volume of mixtures

The gas holdup depended principally on the superficial gas velocity and often was sensitive to the physical properties of the liquid.

Average bubble velocity could be related to the gas holdup and the superficial velocity by:

$$U_b = \frac{U_g}{E_g} \quad (2-25)$$

where U_b : average bubble velocity

U_g : superficial velocity

3.1 Chemical Experiments

In this study the following experiments were performed:

- (1) Leaching under atmospheric pressure of air in the glass reactor (see 3.3.1).
- (2) Leaching under atmospheric pressure of oxygen in the glass reactor (see 3.3.1).
- (3) Leaching under oxygen pressure of 1034 kPa in the autoclave (see 3.3.2).
- (4) Continuous leaching under 345 kPa oxygen pressure in the column reactor (see 3.3.3).
- (5) Continuous regeneration of solution with iron precipitation under oxygen pressure of 345 kPa in the column reactor (see 3.3.3).

General conditions of experiments are described below:

(1) In the One-Liter Glass Reactor

| | Leaching | Leaching with Oxygen |
|---------------------------------------|-------------|-------------------------|
| Sample ^a : | LPU, DDN | DDS |
| Particle size (mesh): | 60-400 | 325-400 |
| Sample weight (g): | 20-50 | 100 |
| Volume of solution (ml): | 600-700 | 660 |
| Temperature (°C): | 90 | 90 |
| Pressure: | atmospheric | atmospheric |
| Time (hrs): | 4 | 4 |
| Initial concentrations of ions (g/l): | | |
| Fe(I) | | 42 |
| Fe(III) | 20-80 | |
| Zn | 0-1.5 | 2.9 |
| Pb | 0-0.4 | 1.6 |
| Cu | 0-0.2 | 0.9 |
| Cl (M)** | 4-7 | 4 |
| HCl (g/l): | 14-50 | 38 |

under hydrodynamic steady state

* Metal contents in Table 3.2.

** Calculated as $MgCl_2 + CaCl_2$ only.

(2) In the Autoclave

| | Leaching with Oxygen |
|---------------------------------------|-------------------------|
| Sample [*] : | LPU |
| Particle size (mesh): | 150-270 |
| Sample weight (g): | 100 |
| Volume of solution (l): | 1.4 |
| Temperature (°C): | 90 |
| Oxygen pressure (kPa): | 1034 |
| Time (hrs): | 4 |
| Initial concentrations of ions (g/l): | |
| Fe(III) | 20-21 |
| Cl (M) ^{**} | 2.7 |
| HCl (g/l): | 3-22 |

under hydrodynamic steady state

(3) In the Column Reactor

| | Leaching with Oxygen | Oxidation with Precipitation |
|---------------------------------------|-------------------------|---------------------------------|
| Sample ^{***} : | LP 86 | — |
| Particle size (mesh): | -270 | — |
| Sample weight (g): | 600 | — |
| Volume of solution (l): | 2.0-2.8 | 1.85-2.2 |
| Temperature (°C): | 75-95 | 70-95 |
| Time (min): | 80-145 | 70-100 |
| Oxygen pressure (kPa): | | |
| Inlet | 45-379 | 345-379 |
| Outlet | 103-276 | 103-276 |
| Oxygen flowrate (ml/sec): | 5-30 | 5-25 |
| Feed flowrate (ml/min): | 160 | 160 |
| Initial concentrations of ions (g/l): | | |
| Fe(I) | 40-44 | 73-83 |
| Fe(III) | 33-40 | 11-16 |
| Fe(II) | 4-7 | 59-72 |
| Zn | 14-14.5 | 11-21.5 |
| Pb | 6.3-7.8 | 8-13.6 |
| Cu | 0.9-1.3 | 1.0-1.6 |
| Cl (M) ^{**} | 3.8-4.1 | 3.7-5.2 |

*** Metal contents refer to Figure 4.15.

3.2 Materials

(1) Characteristics of Ore Sample

Mineralogical and chemical analysis of the ores used in this study are shown in Tables 3.1 and 3.2 (Rao and Letowski, 1986). Table 3.1 indicated that pyrite was the main matrix mineral with minor amounts of sphalerite, galena, chalcopryrite and arsenopyrite, while quartz was the principal gangue mineral.

In the study of leachability of various sulfide minerals, in the ores with ferric chloride solution the dissolution rates were found to be $PbS > FeS \gg ZnS > CuFeS_2$. Pyrite was basically unattacked (Rao and Letowski, 1986).

(2) Preparation of Leaching Solution

The various test solutions were prepared from deionized distilled water and reagent grade chemicals such as hydrochloric acid, ferric chloride, calcium chloride and magnesium chloride. Two kinds of leaching solutions were applied in these experiments. The resulting pregnant solution from previous tests was used for the tests conducted in the column reactor, while a newly-prepared fresh solution was used in the autoclave. In the glass reactor both kinds of solution were used. The oxygen gas was supplied from a pressurized cylinder.

(3) Chemical Features of Leaching Solution and Conditions

Calcium chloride and magnesium chloride were added to increase the solubilities of metal ions, especially copper(I), lead, and silver, by forming complexes. The additives also elevate the boiling point of the solution and lower the pH. Hydrochloric acid was added mainly to prevent hydrolysis of the ferric ion, and to avoid the formation of sulfate. Oxygen in this study was applied to facilitate the regeneration of the ferric chloride and the rejection of the dissolved iron as goethite or jarosite. Media temperature around 90°C was used.

3.3 Apparatus and Procedure

Three kinds of reactors were used. Leaching under atmospheric pressure was carried out in the one-liter glass

Table 3.1 Mineralogical composition of the Delta ore samples

| | Sphalerite ZnS % | Galena PbS % | Chalco- pyrite CuFeS ₂ % | Arseno- tite FeAsS % | Pyrite FeS ₂ % | Pyrrho- FeS % |
|-----|------------------------|--------------------|--|-------------------------------|---------------------------------|---------------------|
| LPU | 11.0 | 4.2 | 1.0 | 0.5 | 67.4 | — |
| DDS | 6.3 | — | 4.4 | — | 49.6 | 38.5 |
| DDN | 17.1 | 0.06 | 4.6 | 0.07 | 1.07 | 64.1 |

Table 3.2 Elemental composition of the Delta ore samples

| | Zn % | Pb % | Cu % | Fe % |
|-----|---------|---------|---------|---------|
| LPU | 6.63 | 2.83 | 0.38 | 32.25 |
| DDS | 0.16 | 0.06 | 0.80 | 47.33 |
| DDN | 8.63 | 0.08 | 1.18 | 44.20 |

reactor. Those experiments of leaching and solution regeneration with iron precipitation under 345 kPa were conducted in the glass column reactor. The experiments under 1034 kPa were carried out in the autoclave with teflon lining.

3.3.1 One-Liter Glass Reactor

A. Apparatus

The whole assembly consists of a four-necked pyrex flask, a condenser, a sampling device, a thermometer, an oxygen dispersion tube and a stirrer. The reactor is heated by a mantle connected with adjustable powerstat. The stirring system is driven by a motor. A schematic diagram of the glass reactor is shown in Figure 3.1.

B. Procedure

1. A desired volume of leaching solution is placed in the reactor through one of the ports.
2. The heater and stirring system is turned on.
3. After temperature reached 90°C, a charge of the desired amount of sample.
4. Oxygen is introduced through a glass tube if necessary.
5. About 10 ml of sample for chemical analysis is collected periodically during the leaching.
6. At the end of the test, the heater, stirring system and oxygen supply is turned off.
7. The solid is separated from solution by filtration through the porcelaneous funnel. The residue is washed, dried and the filtrate collected.
8. The redox potential, pH value and chemical content are measured at room temperature.

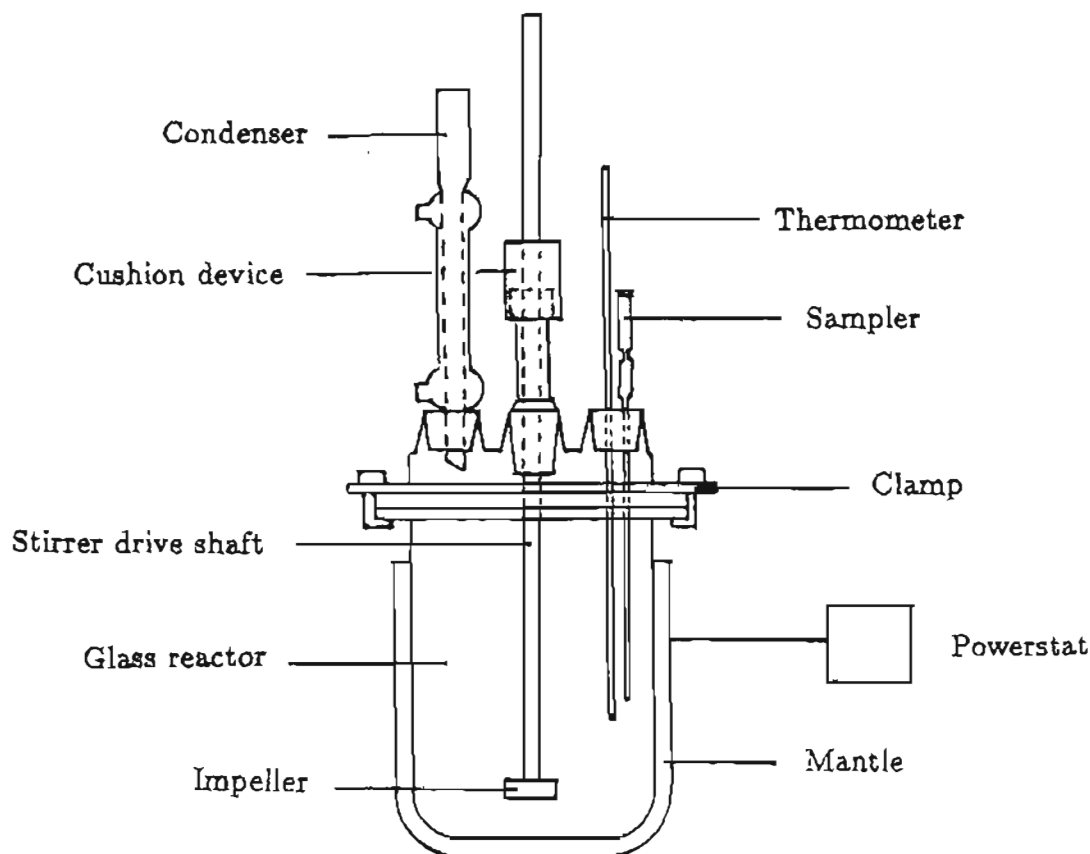


Figure 3.1 Schematic diagram of the one-liter glass reactor.

3.3.2 Two-Liter Autoclave

A. Apparatus

A reactor with the maximum working pressure of 1034 kPa was set up by Dr. F. Letowski. A schematic diagram of the autoclave assembly is shown in Figure 3.2.

The autoclave body and cover are made of steel with teflon lining to protect from corrosion from chloride solution. The stirring shaft with two impellers and the thermocouple well are made of titanium alloy. The sampling tube with sparger in the end and the gas inlet tube are made of teflon tube. The inside dimensions of the autoclave are 8.5 cm in diameter and 32.5 cm in height.

The motor driven stirring system is regulated by a speed controller and calibrated by a tachometer. The autoclave is heated with a heating tape wrapped around the body and covered with an insulator to prevent heat loss. A temperature controller is used to obtain the desired temperature. The total pressure in the system is indicated by a pressure gauge.

B. Procedure

1. A 1,400 ml volume of initial leaching solution is

added to the autoclave.

2. The autoclave is sealed and the heater is turned on.

3. After the solution heated up to the desired temperature, the autoclave is opened and a charge of 100 g of 150 x 270 mesh ore sample is added to the solution. The autoclave is tightly sealed again.

4. Oxygen is introduced and adjusted to 1034 kPa.

5. The stirring mechanism is turned on and adjusted to the desired speed.

6. Throughout the experiment, samples are collected periodically for chemical analysis. The following steps are taken to collect samples: (1) the agitating is stopped for 1 minute; (2) a 15 ml volume of solution is used to flush the sampling tube; (3) a 15 ml volume of solution is then collected; and (4) the agitation is started again.

7. At the end of the experiment, the stirring mechanism and the heater are turned off; the oxygen

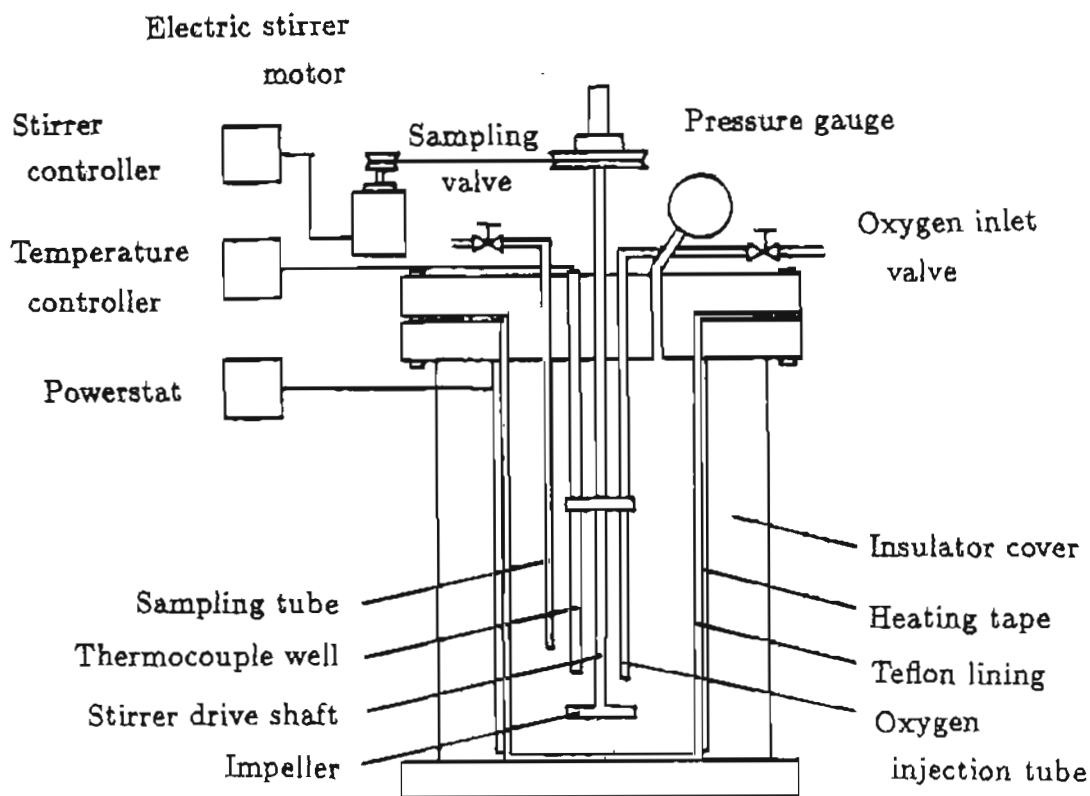


Figure 3.2 Schematic diagram of the two-liter autoclave.

valve is shut off, and oxygen overpressure is bled off through a vent valve.

8. The slurry is taken out of the autoclave. The solid is separated from the pregnant solution by vacuum filtration and then washed by deionized distilled water. The residue is dried and stored for another use. Samples from pregnant and washing solutions are also collected respectively.
9. The redox potential, pH value and chemical contents are measured at room temperature.

3.3.3 Column Reactor

A. Apparatus

The column reactor assembly, working under 345 kPa of maximum pressure, was designed and set up by Dr. F. Letowski. Except for the final pulp collection container made of steel with teflon lining, the column itself is made of glass. The tubes for the transportation of sample feed and gas are made of teflon. A schematic diagram of the column reactor is shown in Figure 3.3.

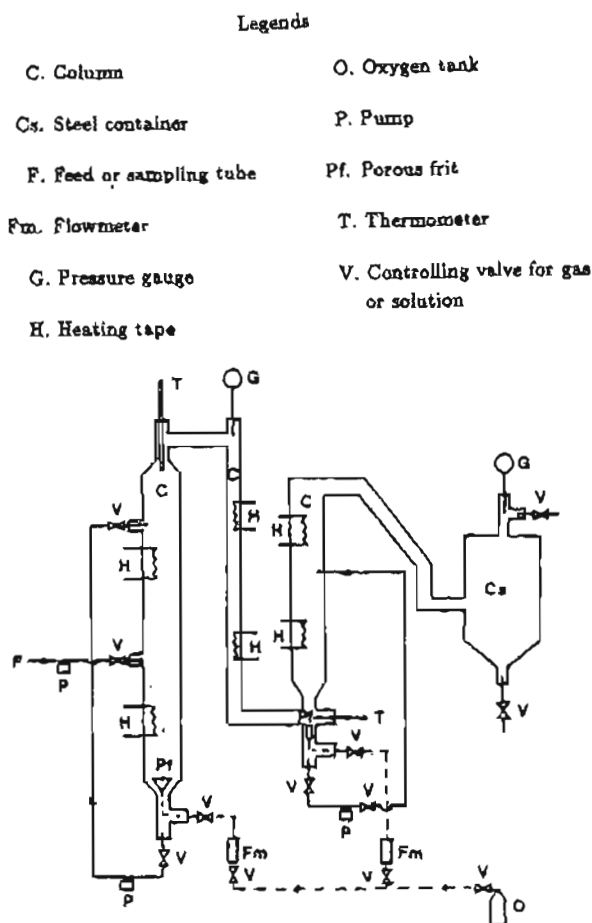


Figure 3.3 Schematic diagram of the column reactor.

The two main reactors and the final pulp container are connected by tubes with 2.54 centimeters inside diameter. The size of the first reactor is 5.08 centimeters in diameter and 1.27 meters in length while the second reactor is 5.08 centimeters in diameter and 0.85 meter in length. The capacity of the steel container is 2 liters.

Oxygen is introduced through the porous frit in the larger column reactor to suspend the solid in solution. The desired oxygen flowrate is obtained using a flowmeter connected to the porous frit. The reactor is heated with a heating tape connected to the adjustable powerstat. The insulator covers the columns and the tubes to prevent heat loss. The temperature is read by a thermometer inserted into each of the reactors. The total pressure in the system is monitored by two gauges. A closed circulating system is constructed with teflon tubes, controlling valves and pumps in each column reactor. The leaching solution is circulated through pumps at the desired flow rate from the bottom to the upper part of the column. The preheated pulp is fed through a pump into the first column reactor at the desired flow rate. Samples are drawn through the feed tube.

B. Procedure

1. A volume of leaching solution is pumped into the column(s).
2. All the heaters are turned on, and the gas is bubbled into the solution through a flowmeter at a certain flow rate. The pump is sometimes turned on to circulate the leaching solution and to equilibrate the temperature of the solution.
3. The pulp or solution to be introduced into the column during the experiment is preheated to the system temperature.
4. The preleached pulp or solution is pumped into the first column at a constant flow rate after the desired conditions are reached.
5. During the experiment, solution samples are collected periodically. The following procedures are taken to collect samples: (1) the pump is turned to the reverse direction; (2) a 15 ml volume of solution is used to flush the sampling tube; (3) a 15 ml volume of solution is then collected; and (4) the direction of the pump is reset. The solution or slurry is circulated through the closed circuit by a pump.
6. At the end of the experiment, the heater and the oxygen valve are turned off. The gas overpressure is bled off through a vent valve. The slurry is taken out of the column reactor by a valve. The solid

is separated from the pregnant solution by decantation or filtration. The residue from filtration is washed. Both pregnant and washing solutions are collected.

7. The redox potential, pH value and chemical contents are measured at room temperature.

C. Operations

(a) Pressure:

The continuous tests in a column are carried out under pressure permitted by this glass installation. The maximum working pressure is 345 kPa. To avoid stopping the transportation of oxygen it is necessary to keep a pressure drop between oxygen inlet and outlet of the column. The adjustment of pressure is made by the flowmeter and the outlet valve of oxygen. Oxygen inlet pressure of 345 kPa is kept in most cases while outlet pressure varies from 103 to 276 kPa.

(b) Flowrate of oxygen:

The oxygen flowrate applied in this study ranges from 5 to 30 ml/sec as required to produce a small bubble and suspend the solid in the solution. The flowrate decreases with decreasing pressure drop. The oxygen flowrate is controlled by the flowmeter or an oxygen outlet valve.

(c) Heating:

The solution is preheated to 70-90°C. The working temperature is maintained at 70-95°C.

(d) Feeding and sampling:

The solution or suspension is fed through a two-way feeding pump, while the sample is taken by the reverse pumping. The feed rate can be adjusted by the speed of the pump. The feed rate of 160 ml/min is usually used in this study.

(e) Circulation of Solution or Suspension:

Circulation of the solution or suspension from the bottom to the upper part of the column by a recycling pump is important to prevent the solid from settling to the bottom of the column. If necessary, a container can be connected to the bottom of the column to retain part of solid or iron precipitate. Through the circulation a uniform temperature of solution in the column can also be maintained.

3.4 Analysis Methods

3.4.1 Solution Analysis

All the concentration of metal elements, except for ferrous ion, are determined by the Perkin-Elmer model 603 Atomic Absorption Spectrometer (AAS). The concentration of ferrous ion is determined by titration with 0.01 N potassium permanganate (Snell and Etre, 1972). The

concentration of ferric ion is calculated by subtracting that of ferrous ion from total iron determined by AAS.

3.4.2 Solid Analysis

The procedures for analyzing the metal contents in the ore or the leaching residue are as follows: (1) a desired weight of dried sample is digested in 200 ml of aqua regia; (2) 15 ml of perchloric acid is then added; (3) the solution is boiled again for half hour and then cooled; (4) the cooled solution is filtered and the filtered residue is rinsed with distilled water until pH is greater than 4; and (5) the filtrate is made up to 200 ml and used for analysis of various metal ions by AAS.

The mineralogical composition of iron precipitate is determined by a Rigaku X-ray diffractometer and by chemical analysis. The procedures of chemical analysis are: (1) 1-3 g of dried sample are dissolved by 10% of HCl and H₂SO₄ in a beaker, respectively, at about 70°C for half hour; (2) the solution is cooled and filtered; and (3) the filtrate is made up to 100 ml for analysis of metal ions by ASS.

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Experiments in the Glass Reactor

(1) Effect of Chloride Ion

The effect of chloride ion concentration on leaching is shown in Table 4.1. Under constant ferric and chloride ion concentrations, the final extractions of Zn, Pb and Cu remain the same at different HCl concentrations (Tests #1 and #2). Under constant HCl concentration, tests #1 and #3 show that extractions of metal ions increase as the concentration of chloride ion increases.

(2) Effect of Solid/Liquid Ratio

Tables 4.2 and 4.3 present the effect of various solid/liquid ratios on extraction. Results in Table 4.2 show that metal extractions increase as the ratio of solid/liquid decreases. However, it is important to note that, from a practical point of view, building up a higher concentrations of valuable metals in the solution in a short time is favorable. Table 4.3 shows that higher concentration of Zn, Pb and Cu are obtained at higher solid/liquid ratio in 4 hours of leaching.

(3) Effect of Particle Size

Three leaching experiments were performed by using 60 x 150, 150 x 270, and 270 x 400 mesh DDN samples at 90°C for 4 hours. The solution initially contained 1.3-1.4 M of ferric ion, 0.39 M of HCl and 4.14 M of chloride ion with solid/liquid of 20 g/600 ml. Figure 4.1 shows that zinc extraction increases with a decrease in particle size. The

Table 4.1 Effect of chloride ion concentration on metal extractions of LPU sample.
(Conditions: S/L=20 g/700 ml; 270-325 mesh; 90°C; 4 hours.)

| Test No | Conditions (M) | | | Extraction (%) | | |
|---------|----------------|------|------|----------------|-------|-------|
| | Fe(III) | HCl | Cl* | Zn | Pb | Cu |
| 1 | 0.48 | 0.47 | 4.38 | 78.20 | 72.26 | 64.47 |
| 2 | 0.48 | 0.94 | 4.38 | 78.95 | 72.08 | 64.47 |
| 3 | 0.38 | 0.47 | 6.96 | 100.00 | 84.28 | 73.37 |

* Cl is calculated by MgCl₂ and CaCl₂ only.

Table 4.2 Effect of solid/liquid ratio on metal extractions of LPU sample.
(Conditions: 32 g/l Fe(III), 46 g/l Fe(T), 1.5 g/l Zn, 0.36 g/l Pb, 0.24 g/l Cu; 90°C; 4 hours.)

| Test No | S/L (g/l) | Zn (%) | Pb (%) | Cu (%) |
|---------|-----------|--------|--------|--------|
| 1 | 50/700 | 79.22 | 88.66 | 61.05 |
| 2 | 30/700 | 81.10 | 92.12 | 63.16 |
| 3 | 20/700 | 88.72 | 97.48 | 71.05 |

Table 4.3 Effect of solid/liquid ratio on metal concentrations in solution.
(Conditions are the same as Table 4.2.)

| Test No | S/L (g/ml) | Zn (g/l) | Pb (g/l) | Cu (g/l) |
|---------|------------|----------|----------|----------|
| * | — | 1.50 | 0.36 | 0.24 |
| 1 | 50/700 | 5.20 | 2.40 | 0.44 |
| 2 | 30/700 | 3.84 | 1.74 | 0.38 |
| 3 | 20/700 | 2.68 | 1.12 | 0.30 |

* initial concentration.

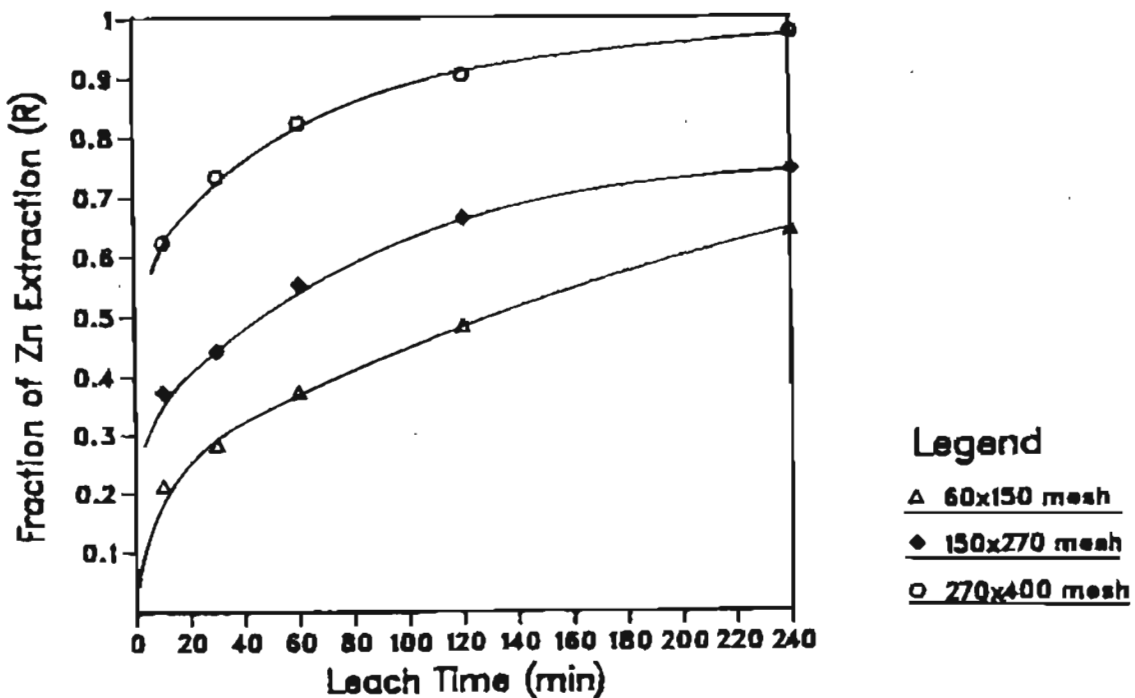


Figure 4.1 The effect of particle size on leaching rate. (Conditions: DDN sample; S/L = 20 g/600 ml; 1.3 M Fe(III), 4 M Cl, 0.4 M HCl; 90°C.)

linear relationship of $1 - \frac{2}{3}R - (1 - R)^{2/3}$ vs time shown in Figure 4.2 suggests that porous product layer diffusion is likely to be the rate-limiting step. According to equation 2.11, the slope in Figure 4.2 should be proportional to r_0^{-2} to fit the pore diffusional model. The result in Figure 4.3, a plot of the slope vs d_0^{-2} ($d_0 = 2r_0$ in equation), confirms this relationship.

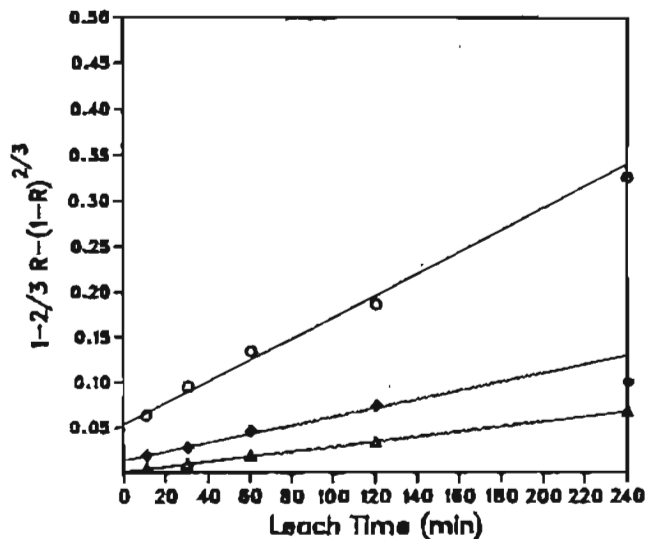


Figure 4.2 Plots for $1 - \frac{2}{3}R - (1 - R)^{2/3}$, product layer diffusion control, vs leaching time,

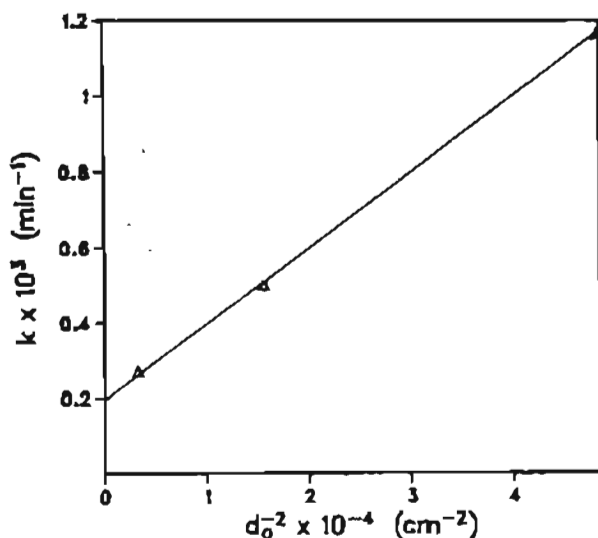


Figure 4.3 Plot for rate constant dependence on particle size.

(4) Leaching with Solution Regeneration under Atmospheric Pressure

In this test, leaching was carried out with 325-400 mesh DDS sample in solution containing 0.75 M Fe(T), 0.05 M Zn, 0.004 M Pb, 0.01 M Cu, 1.08 M HCl and 4 M Cl at 90°C for 4 hours with solid/liquid of 100 g/660 ml. Figure 4.4 shows that the oxidation potential drops initially and then increases slowly. The total iron concentration increases with time, while only minor increases in zinc and lead are observed. This may be because of a high percentage of pyrrhotite and a low percentage of sphalerite and galena in the ores.

4.2 Tests in the Autoclave

(1) Effect of Acidity

Two tests with concentrations of 3.2 g/l and 21.6 g/l HCl, respectively, were carried out with 150-270 mesh LPU sample in 20 g/l Fe(III) and 96 g/l Cl solution at 90°C under 1034 kPa of oxygen pressure. Figures 4.5 and 4.6 give the effect of acidity on iron precipitation. It is obvious that iron precipitation occurs at the lower acidity (Figure 4.5), but not at the higher acidity (Figure 4.6).

(2) Effect of Precipitation on Leaching

The effect of precipitation on leaching is presented in Figures 4.5 and 4.6. The results show that in 4 hours of leaching, higher metal extractions are obtained without iron precipitation (Figure 4.6) than with precipitation (Figure 4.5). Figure 4.5 also shows that prolongation of leaching time causes the decrease in metal extraction. However, 96% of zinc extraction is still achieved when leaching time is as short as 110 minutes. The simultaneous decrease in extractions of Pb and Fe shown in Figure 4.5 implies that lead together with iron is precipitated.

(3) Effect of Oxygen Pressure

Figures 4.6 and 4.7 show the effect of oxygen pressure under conditions shown in Table 4.4. The results show that under atmospheric pressure nearly the same metal extraction as that under 1034 kPa oxygen pressure is obtained. However, it has to be achieved at higher ferric ion concentration using a two-stage leaching in 8 hours. A lower ferric ion is needed in a single stage leaching under high oxygen pressure, in which the reduced ferric ion can be regenerated simultaneously during leaching with oxygen.

(4) Composition of Iron Precipitate

Iron compounds precipitated from the solution under oxygen pressure are identified by X-ray powder diffraction as lead jarosite. Calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is also found in the product.

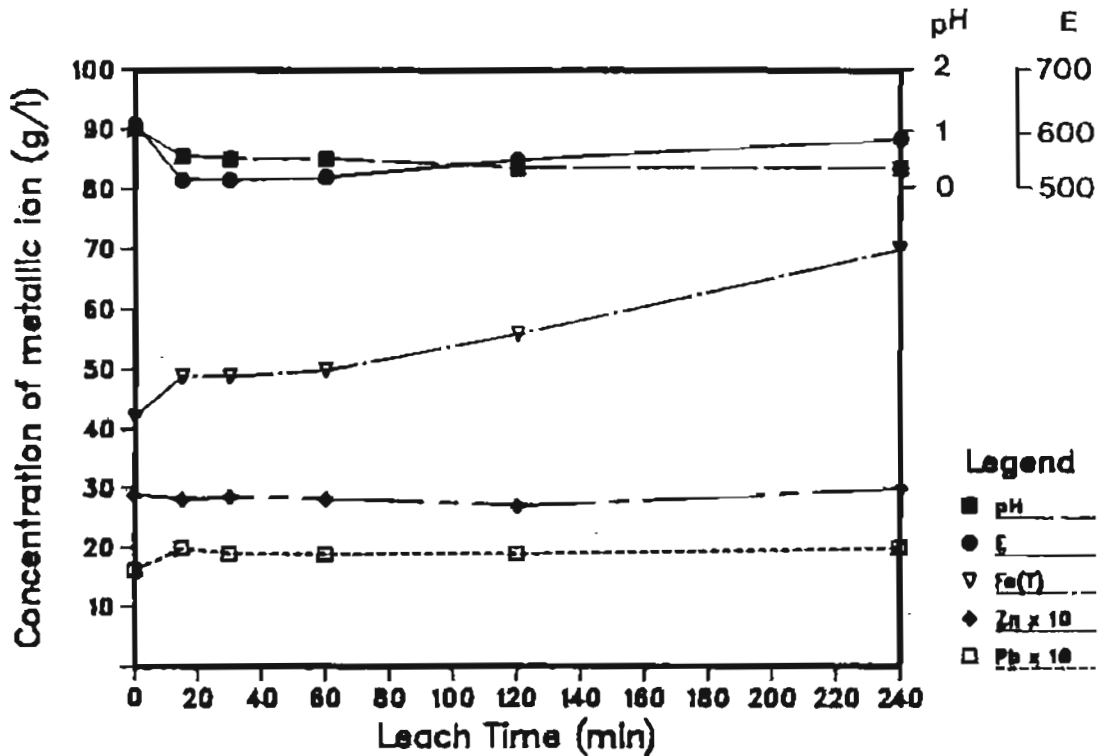


Figure 4.4 Leaching under atmospheric pressure of oxygen in the one-liter glass reactor. (Conditions: DDS sample; 325-400 mesh; S/L = 100 g/660 ml; 0.75 M Fe(T), 0.04 M Zn, 0.008 M Pb, 0.014 Cu(T), 4 M Cl, 1.04 M HCl; 90°C.)

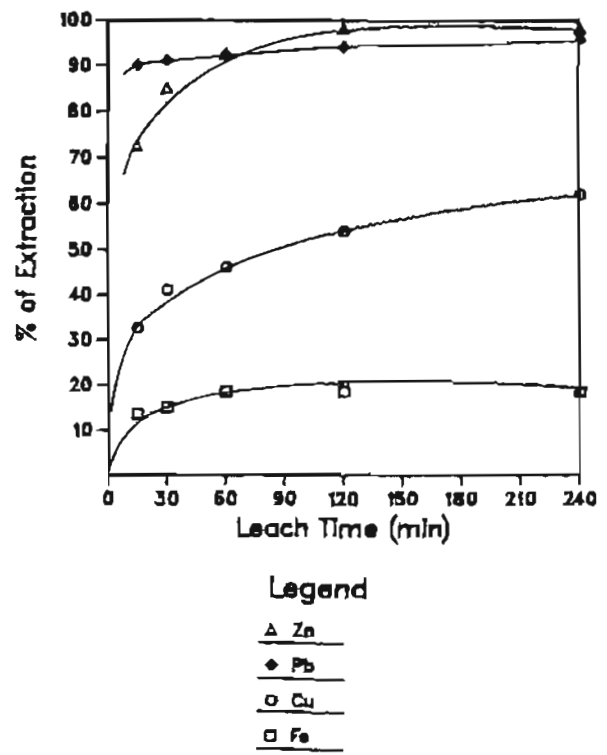
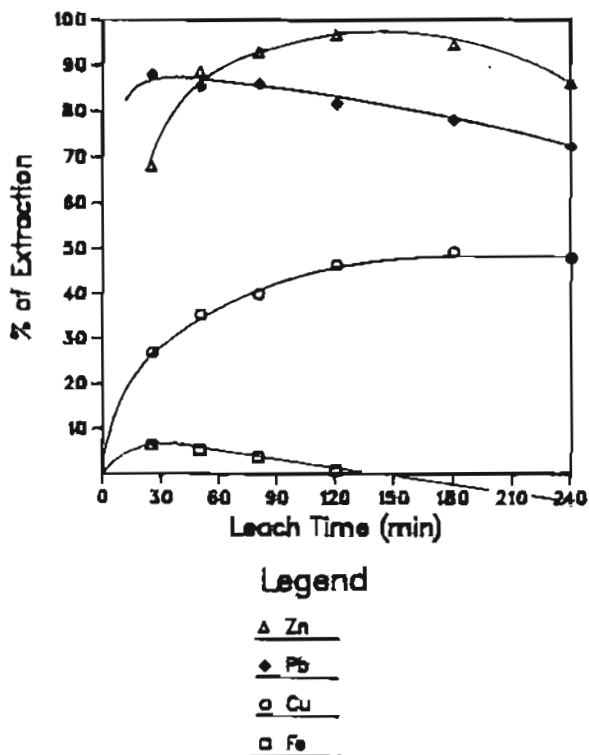


Figure 4.5 Plots for leaching rate with precipitation in the autoclave. (Conditions: LPU sample; 150-270 mesh; S/L = 100 g/1.4 L; 0.36 M Fe(III), 2.7 M Cl, 0.09 M HCl; 90°C; 1034 kPa oxygen pressure.)

Figure 4.6 Plots for leaching rate in the autoclave. (Conditions: LPU sample; 150-270 mesh; S/L = 100 g/1.4 L; 0.36 M Fe(III), 2.7 M Cl, 0.59 M HCl; 90°C; 1034 kPa oxygen pressure.)

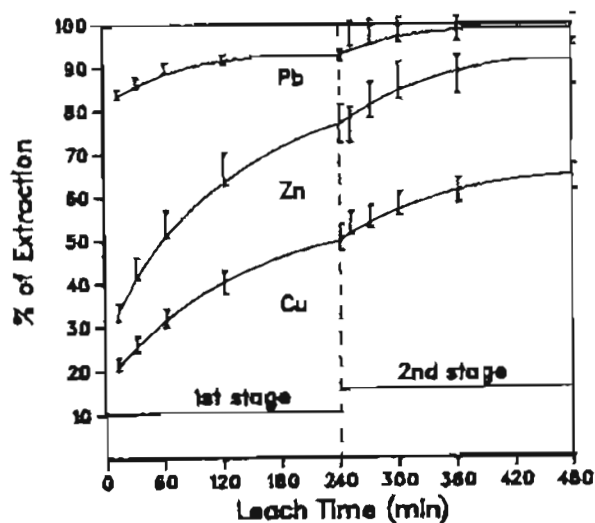


Figure 4.7 Plots for leaching rate with two-stage leaching in the glass reactor. (Conditions: 1.79 M (1st stage), 1.45 M (2nd stage) Fe(III), 2.7 M Cl, 0.01 M HCl; 80°C; atmospheric pressure (Letowski et al., 1986).)

4.3 Continuous Leaching, Solution Regeneration and Iron Precipitation Tests in the Column Reactor

The experimental conditions conducted in the column reactor are described in Table 4.5.

(1) Effect of Oxygen Pressure

Figure 4.8 indicates that the rate of ferrous ion oxidation with precipitation, under atmospheric pressure of oxygen, is rather slow. A relatively faster rate is observed under 138-276 kPa oxygen pressure (Figure 4.9). The faster oxidation rate, as mentioned previously, is due to the higher oxygen solubility in solution under pressure.

(2) Effect of Acidity

The effect of acidity on iron oxidation and precipitation is presented in Figures 4.9 and 4.10. Figure 4.9 shows that the oxidation and the precipitation appear to be equilibrated within about 25 minutes. However, Figure 4.10 shows that with the addition of CaO, the oxidation almost finishes within about 50 minutes and thereafter only precipitation occurs. The pH of solution in Figure 4.10 should decrease since precipitation produces acid, however the result indicates a slight increase in pH. This is because an additional

Table 4.4 Conditions of leaching of 150-270 mesh LPU sample under atmospheric and elevated oxygen pressure.

| Test No | Fe(III) (M) | HCl (M) | Cl (M) | S/L (g/l) | Pres. (kPa) | Temp. (°C) | Time (hrs) | Remark (Figure) |
|---------|-------------|---------|--------|-----------|-------------|------------|------------|-----------------|
| 1 | 0.37 | 0.59 | 2.7 | 100/1.4 | 1034 | 90 | 4 | 4.6 |
| 2 | 1.15-1.79 | 0.01 | 2.7 | 75/0.6 | 101 | 80 | 4 | 4.7 |

Table 4.5 Experimental conditions in the column reactor.

| Test No | Fe(I) (g/l) | Fe(III) (g/l) | Fe(II) (g/l) | Zn (g/l) | Pb (g/l) | Cu (g/l) | Cl (M) | S/L (g/l) | Time (min) | Remark (Figure) |
|---------|-------------|---------------|--------------|----------|----------|----------|--------|-----------|------------|-----------------|
| 1 | 52.2 | 46.5 | 5.7 | 15.8 | 8.7 | 1.2 | — | 0/2.0 | 100 | 4.5 |
| 2 | 76.4 | 16.3 | 60.1 | 21.5 | 8.7 | 1.6 | 3.7 | 0/2.0 | 70 | 4.6 |
| 3 | 72.9 | 14.3 | 58.6 | 21.0 | 7.8 | 1.0 | 5.2 | 0/1.85 | 100 | 4.11 |
| 4 | 43.7 | 39.5 | 4.2 | 14.5 | 7.8 | 1.2 | 3.8 | 600/2.0 | 80 | 4.8 & 4.12 |
| 5 | 83.0 | 10.7 | 72.3 | 11.2 | 13.6 | 1.5 | — | 0/2.2 | 70 | 4.9 |
| 6 | 39.8 | 32.8 | 7.0 | 14.0 | 6.3 | 0.9 | 4.1 | 600/2.8 | 145 | 4.10 |

Fraction in tests #4 and #6 are -400 and 270-325 mesh, respectively.

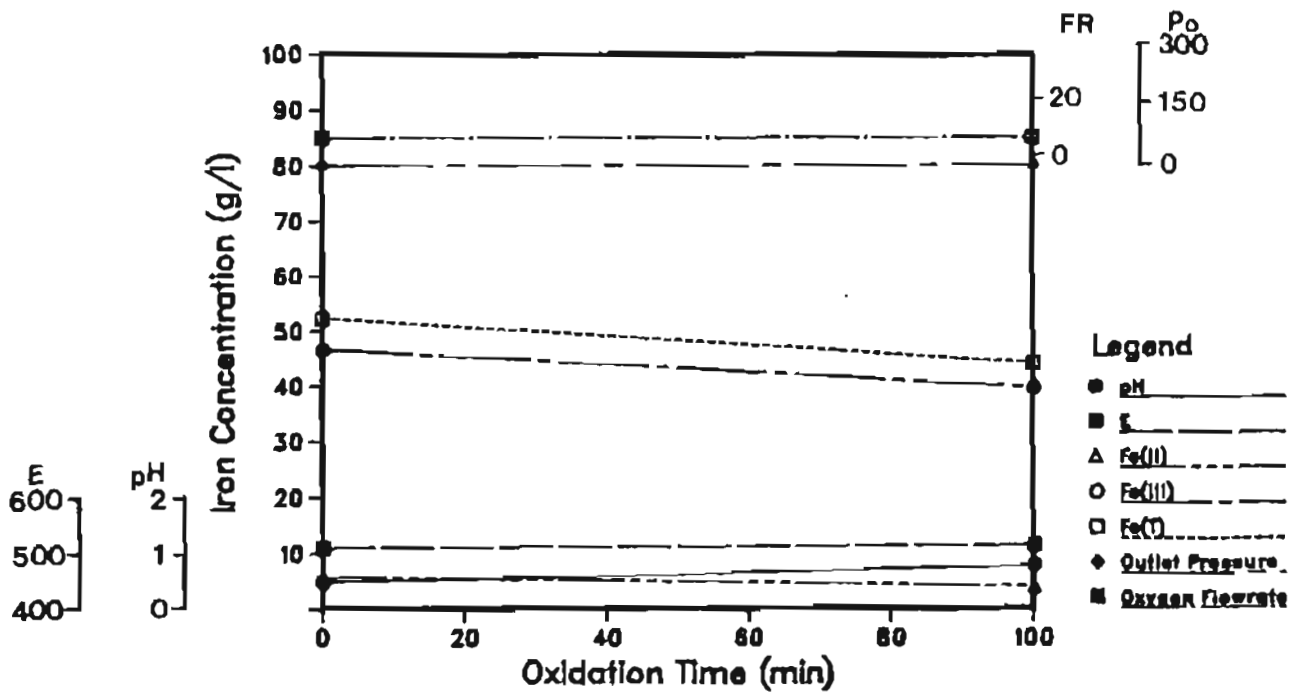


Figure 4.8 Solution regeneration and iron precipitation under atmospheric pressure of oxygen in the column reactor (Conditions: see Table 4.5).

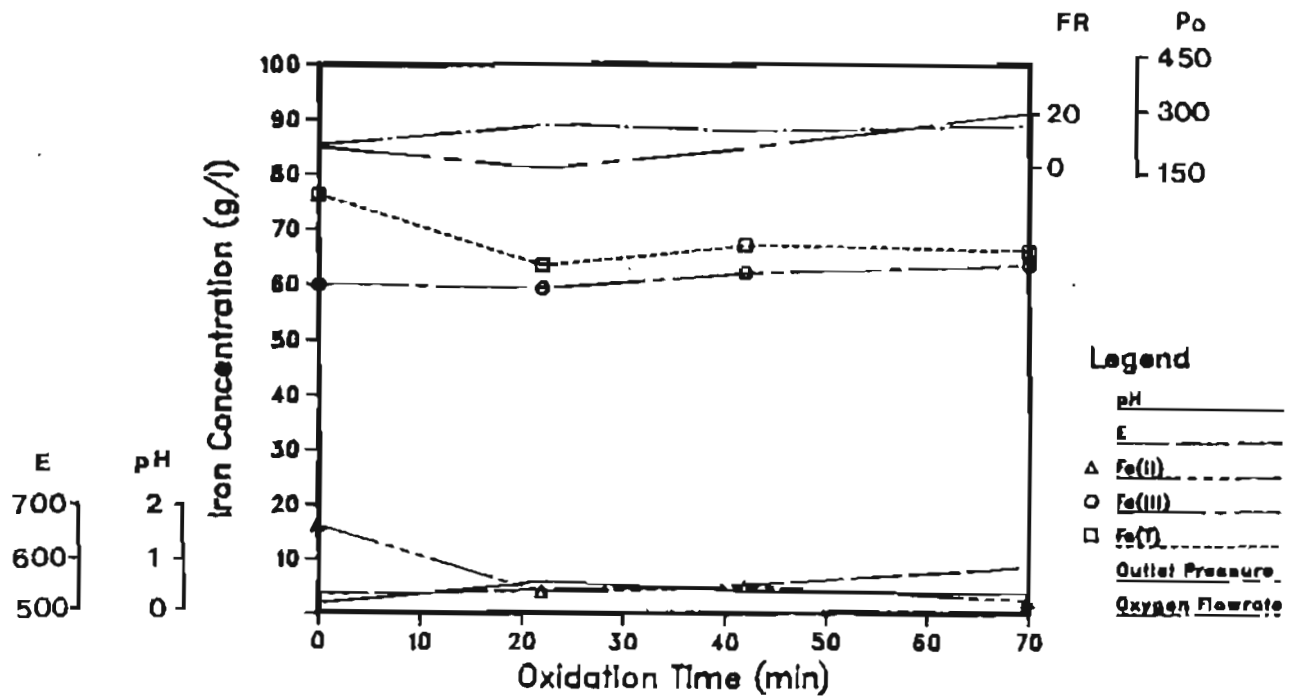


Figure 4.9 Solution regeneration and iron precipitation under 138-276 kPa oxygen pressure in the column reactor (Conditions: see Table 4.5).

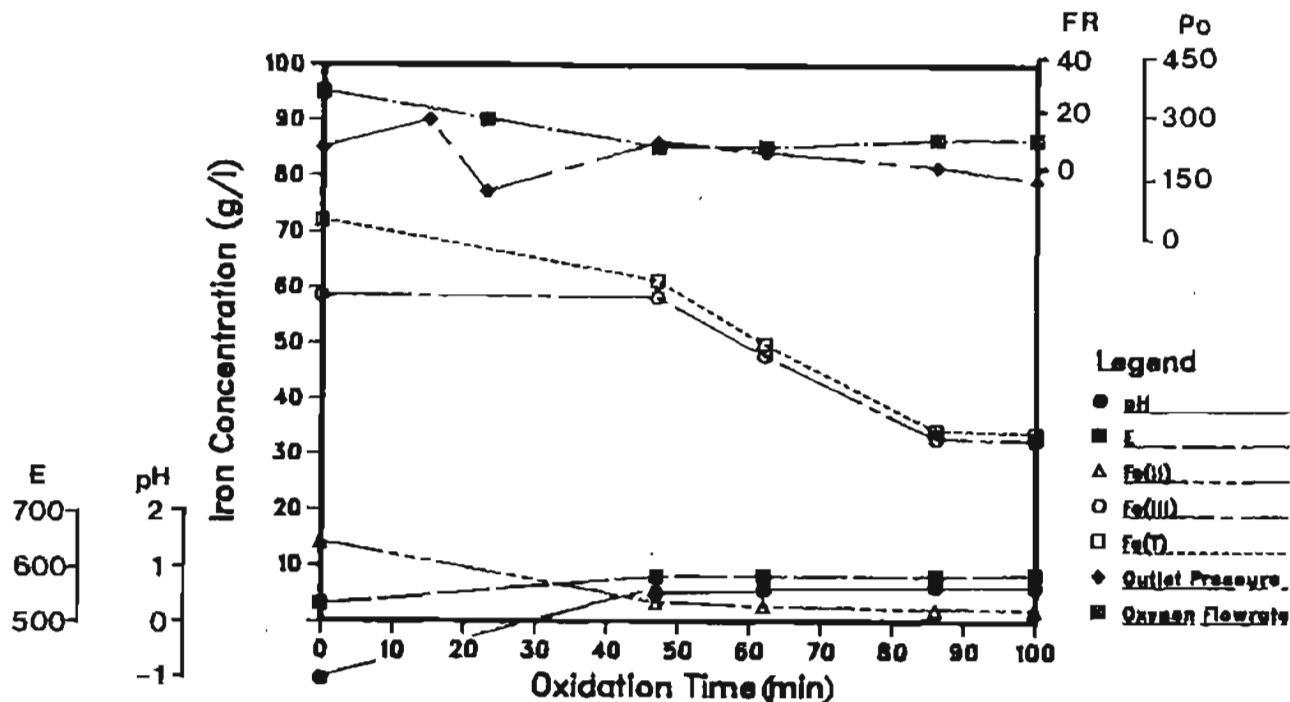


Figure 4.10 Solution regeneration and iron precipitation under 103-276 kPa oxygen pressure with CaO as a neutralizer in the column reactor (Conditions: see Table 4.5).

neutralizer is added during the solution regeneration in this case.

(3) Leaching with Solution Regeneration and Iron Precipitation

Figure 4.11 shows that leaching occurs with simultaneous solution regeneration and iron precipitation. The increase in the ferrous ion concentration is due to reduction from ferric ion or dissolution from ores during leaching. The increase in pH value results from consumption of acid during oxidation. The decrease in the total iron concentration suggests that iron precipitation occurs during leaching. However, the results shown in Figure 4.15 show that a low zinc extraction and an unsatisfactory lead extraction are obtained.

(4) Typical Characteristics of Ferrous Chloride Oxidation

Figure 4.12 shows the kinetics of ferrous chloride oxidation with partial precipitation of iron. The initial concentrations of Fe(II) and Fe(III) in solution are 73 g/l and 10 g/l, respectively. The results show that 12% of the iron is precipitated in 70 minutes, and the ferric ion percentage increases from 13% to 43%. The final concentrations of Fe(II) and Fe(III) are 37.1 g/l and 27.9 g/l, respectively.

(5) Composition of Iron Precipitate

The iron precipitate formed in the column reactor is determined by X-ray powder diffraction as akaganeite (β -FeOOH). No calcium sulfate or jarosite is observed in the

X-ray diffraction pattern. Chemical analysis of the solution resulting from digestion of this iron precipitate in 10% of HCl and H_2SO_4 , respectively, confirms that no calcium is present in the precipitate. It suggests that sulfate ion concentration in solution is not enough to form calcium sulfate.

(6) Typical Mass Balance in Various Processes

Figure 4.13 shows the mass balance of leaching with solution regeneration. The results indicate that 74.84% Zn, 91.43% Pb and 46.57% Cu are obtained, and part of the iron may be precipitated in 145 minutes. The mass balance of solution regeneration with iron precipitation is shown in Figure 4.14. With addition of CaO as a neutralizer, a 24.38% iron precipitate is obtained, but only 0.28% Zn and 1.55% Pb are coprecipitated. Based on the assumption that the iron precipitate is pure FeOOH, 36.9% of the Fe is obtained by calculation compared to 24.38% obtained by chemical analysis of the residue. Figure 4.15 presents the balance of leaching and solution regeneration with iron precipitation. In this case 39.98% Zn, 85.31% Pb and 22.62% Cu are extracted in 80 minutes.

(7) Flotation during Leaching

Elemental sulfur is produced in the acid solution during leaching. Since the sulfur exhibits native flotability and is stable at a low pH, a good flotability of particles is observed. However, in leaching with simultaneous solution regeneration, the pH value is changed by oxidation associated with the iron precipitation. The pH change causes a difference

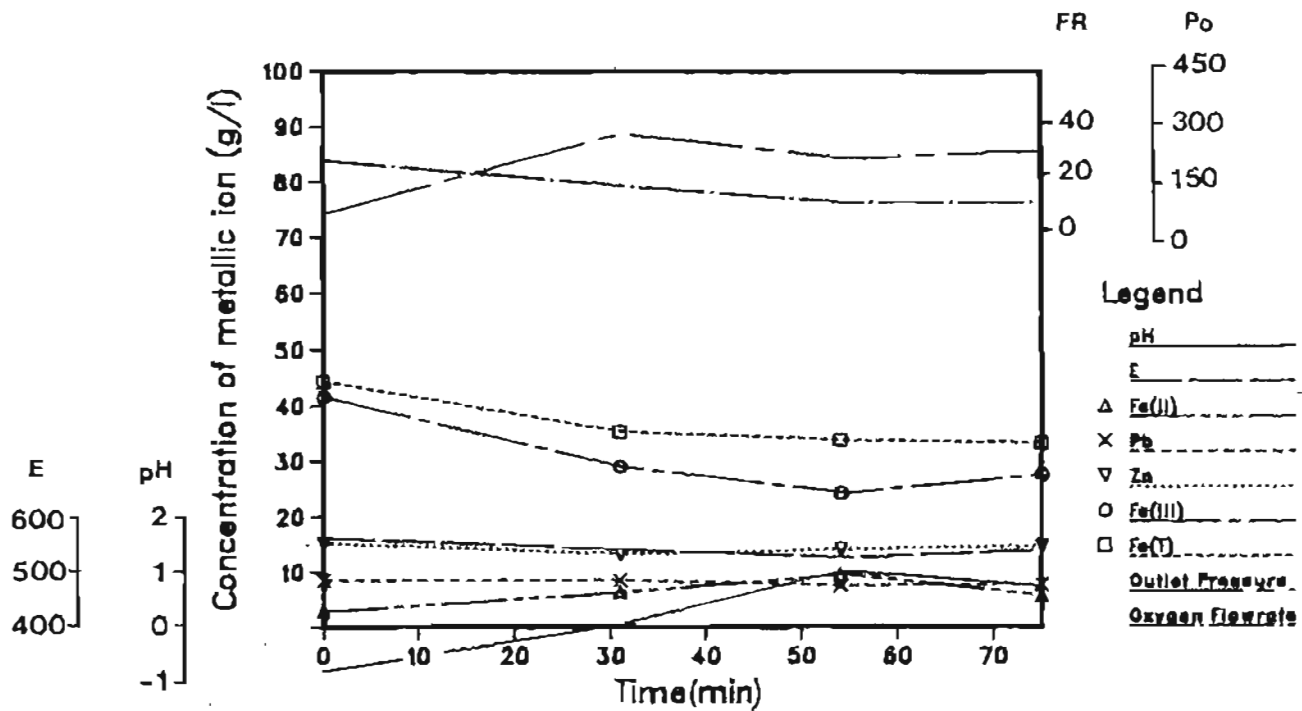


Figure 4.11 Leaching, solution regeneration and iron precipitation under 103-276 kPa oxygen pressure in the column reactor (Conditions: see Table 4.5).

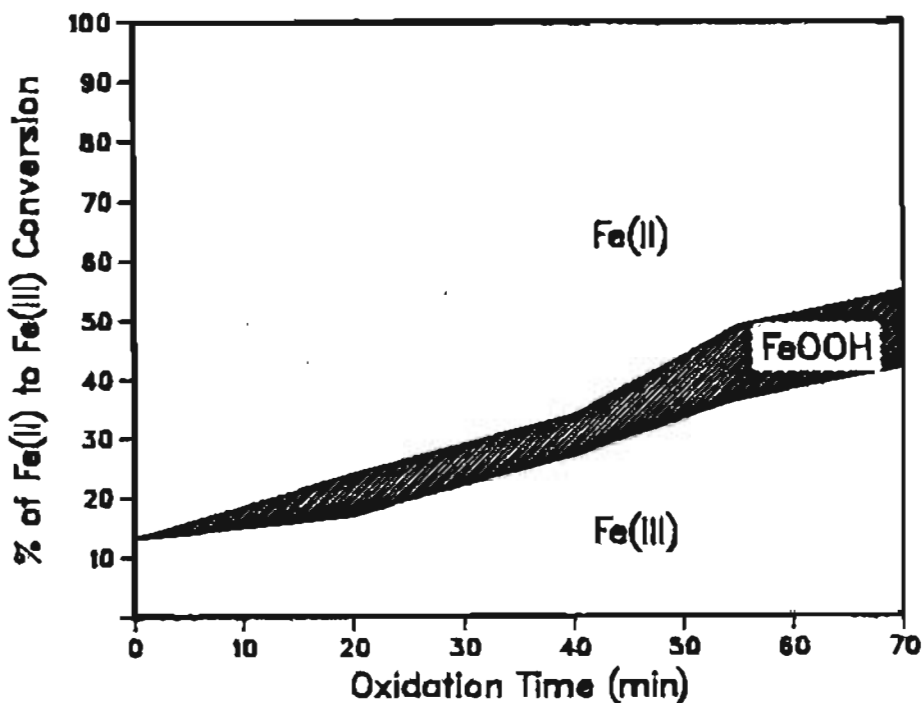


Figure 4.12 Kinetics of ferrous chloride oxidation by oxygen with partial precipitation of FeOOH under 172-310 kPa oxygen pressure in the column reactor (Conditions: see Table 4.5).

| | | | | | |
|--|-------|--------|-----------|------------------|------------------|
| | % | g | | | |
| | Fe | 30.17 | 181.02 | | |
| | Zn | 5.22 | 31.32 | | |
| | Pb | 2.78 | 16.68 | | |
| | Cu | 0.34 | 2.04 | | |
| | 600 g | | | | |
| | ↓ | | | | |
| | g/l | g | | g | |
| | Fe | 39.78 | 159.12 | | Fe 172.22 |
| | Zn | 13.98 | 55.92 | 4.0 L | Leaching & 3.2 L |
| | Pb | 6.32 | 25.28 | → Regeneration → | |
| | Cu | 0.87 | 3.49 | | Zn 73.68 |
| | | | | | Pb 37.73 |
| | | | | | Cu 4.83 |
| | ↓ | | | | |
| | 466 g | | | | |
| | | g* | Yield(%)* | | |
| | Fe | 191.97 | -6.5 | | |
| | Zn | 7.88 | 74.84 | | |
| | Pb | 1.43 | 91.43 | | |
| | Cu | 1.09 | 46.57 | | |

* Based on residue analysis.

Figure 4.13 Typical mass balance of leaching and solution regeneration in the column reactor (Conditions: see Table 4.5).

| | | | | | |
|--|----------|-------|-----------|-------------------|-----------------------|
| | 1 L | | | | |
| | CaO Pulp | | | | |
| | ↓ | | | | |
| | g/l | g | | g/l | g |
| | Fe | 72.88 | 134.83 | | Fe 34.50 90.39 |
| | Zn | 20.96 | 38.78 | 1.85 L | Regeneration & 2.82 L |
| | Pb | 7.76 | 14.38 | → Precipitation → | |
| | | | | | Pb 4.48 11.74 |
| | ↓ | | | | |
| | 79 g | | | | |
| | | g* | Yield(%)* | | |
| | Fe | 32.88 | 24.38 | | |
| | Zn | 0.11 | 0.28 | | |
| | Pb | 0.23 | 1.55 | | |

* Based on precipitate analysis.

Figure 4.14 Typical mass balance of solution regeneration and iron precipitation by CaO in the column reactor (Conditions: see Table 4.5).

| | | | | | | |
|--|-----|--------|-------------------------|-------|----------------|-----------|
| | % | g | | | | |
| | Fe | 31.72 | 180.32 | | | |
| | Zn | 7.45 | 44.70 | | | |
| | Pb | 1.77 | 10.62 | | | |
| | Cu | 0.42 | 2.52 | | | |
| | | | 600 g | | | |
| | | | 0.9 L CaCl ₂ | | | |
| | | | ↓ | | | |
| | g/l | g | | | | g |
| | Fe | 46.26 | 111.02 | 2.4 L | - Leaching, | 2.9 L |
| | Zn | 15.78 | 37.78 | → | Regeneration & | → |
| | Pb | 8.68 | 20.83 | | Precipitation | |
| | Cu | 1.19 | 2.87 | | | |
| | | | | | | Fe 104.17 |
| | | | | | | Zn 53.59 |
| | | | | | | Pb 26.00 |
| | | | | | | Cu 2.29 |
| | | | | | | |
| | | | | ↓ | | |
| | | | | 524 g | | |
| | | | | g* | Yield(%)* | |
| | Fe | 161.26 | 15.27 | | | |
| | Zn | 26.83 | 39.98 | | | |
| | Pb | 1.56 | 85.31 | | | |
| | Cu | 1.95 | 22.62 | | | |

* Based on residue analysis.

Figure 4.15 Typical mass balance of leaching, solution regeneration and iron precipitation in the column reactor (Conditions: see Table 4.5).

in particle flotability. This makes it difficult to separate particles from precipitate by flotation without adding a flotation reagent.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. A slow oxidation rate under atmospheric pressure makes leaching with solution regeneration unfavorable. A higher concentration of oxidant is necessary for good extraction.
2. Leaching and simultaneous regeneration of the solution with partial precipitation of iron can be achieved under elevated oxygen pressure, however, coprecipitation of metal with iron precipitation also occurs. This makes extraction lower in leaching with iron precipitation than it is with leaching alone.

3. In this work high dissolution of 98% Zn and 96% Pb is attained with 4 hours retention time under 1034 kPa oxygen pressure in the autoclave. In addition, 75% Zn and 91% Pb are obtained in about 2.5 hours under 138-276 kPa oxygen pressure in the column. After some modifications of the residue collecting device in the column, 97% Pb has been recovered by Letowski (1987).
4. Oxidation with simultaneous iron precipitation is possible as long as the pH value is proper. Addition of a neutralizer causes excessive precipitation of iron.
5. The iron precipitate formed at 90°C under 138-276 kPa in the column reactor is mainly β -goethite, while lead jarosite is the main product at 90°C under 1034 kPa in the autoclave.
6. Good leaching and simultaneous precipitation in one operation were difficult to achieve in this study. It is better to precipitate excess iron in one stage, and then use the regenerated solution to

leach the ores in another stage.

- 7 Leaching in oxygen causes flotation by which separation of floatable and nonfloatable minerals can be achieved. The flotability of particles is dependent on the solution pH. Flotation is favored by a low pH in which iron precipitation does not occur.

5.2 Recommendations

- 1 A more systematic investigation on leaching, or leaching with solution regeneration, is necessary to find the optimum conditions.
- 2 Continued study of the engineering characteristics of the column reactor is necessary to understand the effect of various parameters on the process.

REFERENCES

- Andersen E., Boe G. H., Dam Nielsen T. D. and Finne P. M., Production of base metals from complex sulfide concentrates by the ferric chloride route in a small, continuous pilot plant, in *Complex Sulfide Ore*, edited by Jones M. J., IMM, 1981, pp 86-192.
- Arauco H. and Doyle F. M., Hydrolysis and precipitation of iron during first stage pressure leaching of zinc sulfide concentrates, in *Iron Control in Hydrometallurgy*, edited by Dutrizac J. E. and Monhemius A. J., John Wiley and Sons Inc., 1986, pp 409-430.
- Awakura Y., Iwai M. and Majima H., Oxidation of Fe(II) in HCl and H₂SO₄ solutions with dissolved molecular oxygen in the presence and absence of a cupric catalyst, in *Iron Control in Hydrometallurgy*, edited by Dutrizac J. E. and Monhemius A. J., John Wiley and Sons Inc., 1986, pp 202-222.
- Beattie M. J. V., Craigan W. J. S. and Sarkar R. M., The Great Central Mines hydrometallurgical copper process, 14th annual CIM hydrometallurgical meeting, Ontario, Oct., 1984, pp 1-25.
- Beutier D., Burzynski J. P. and Torre Y., Iron elimination by oxygen in acid cuprous chloride solutions: the case of the Minemet process, in *Iron Control in Hydrometallurgy*, edited by Dutrizac J. E. and Monhemius A. J., John Wiley and Sons Inc., 1986, pp 640-656.
- Bird R. B., Stewart W. E. and Lightfoot E. N., *Transport Phenomena* John Wiley and Sons Inc., 1960, pp 27-29.
- Bloodworth R. and Schmidt R., Mineralogical investigation of massive sulfide pyrite cores sample, 1982, pp 1-37. (Nerco report)
- Bobeck G. E. and Su H., The kinetics of solution of sphalerite in ferric chloride solution, *Metallurgical Transactions B*, vol 16B, 1985, pp 413-424.
- Colborn R. P. and Nicol M. J., An investigation into the kinetics and mechanism of the oxidation of iron(II) by oxygen in aqueous chloride solutions, *Journal of the South African IMM*, April 1973, pp 281-289.
- Collepari M., Massida L. and Rossi G., Aging of iron oxide gels, *Transactions of IMM*, 1972, C43-C46.
- Cramer S. D., The solubility of oxygen in brines from 0 to 300°C, *Ind. Eng. Chem. Processes Res. Dev.*, vol 19, no 2, 1980, pp 300-305.
- Davey P. T. and Scott T. R., Removal of iron from leach liquors by the goethite process, *Hydrometallurgy*, no 2, 1976, pp 25-33.
- Davey P. T. and Scott T. R., Formation of β-FeOOH and α-Fe₂O₃ in goethite process, *Transactions of IMM*, 1975, C83-C86.
- Demarthe J. M. and Georgeaux A., Hydrometallurgical treatment of complex sulfides, in *Complex Metallurgy '78*, IMM, 1978, pp 113-120.
- Dutrizac J. E., The kinetics of dissolution of chalcopryrite in ferric ion media, *Metallurgical Transactions B*, vol 9B, 1978, pp 431-439.
- Dutrizac J. E., The physical chemistry of iron precipitation in zinc industry, in *Lead-Zinc-Tin '80*, TMS-AIME, 1980, pp 532-564.
- Dutrizac J. E., The dissolution of chalcopryrite in ferric sulfate and ferric chloride media, *Metallurgical Transactions B*, vol 12B, 1981, pp 371-378.
- Dutrizac J. E., Jarosite formation in chloride media, *Proceeding of Australasia of IMM*, no 278, 1981, pp 23-32.
- Dutrizac J. E., Ferric ion leaching of chalcopryrite from different localities, *Metallurgical Transactions B*, vol 13B, 1982, pp 303-309.
- Dutrizac J. E., Factors affecting alkali jarosite precipitation, *Metallurgical Transactions B*, vol 14B, 1983, pp 531-539.

- Dutrizac J. E. and MacDonald R. J. C., Ferric ion as a leaching medium, *Mineral Science and Engineering*, vol 6, no 2, 1974, pp 59-100.
- Dutrizac J. E. and MacDonald R. J. C., The dissolution of sphalerite in ferric chloride solutions, *Metallurgical Transactions B*, vol 9B, 1978, pp 543-551.
- Fuerstenau M. C., Kinetics of galena dissolution in ferric chloride solutions, *Metallurgical Transactions B*, vol 17B, 1986, pp 415-423.
- Habashi F., *Principle of Extractive Metallurgy*, Gordon and Breach Science Publishers, vol 1, 1969, pp 289-299, 111-169.
- Haver F. P., Baker R. D. and Wong M. M., Improvement on ferric chloride leaching of chalcopyrite concentrate, *BuMines RI 8007*, 1975, pp 1-16.
- Iwai M., Majima H. and Izaki T., A kinetic study on the oxidation of ferrous ion with dissolved molecular oxygen, *Denki Kagaku*, no 7, 1979, pp 409-414.
- Jones M. J., *Complex Sulfide Ores*, IMM, Rome, 1981.
- Kunda W., Hitesman R. and Veltman H., Treatment of sulfidic copper concentrate in chloride systems, in *Extractive Metallurgy of Copper*, edited by Yonopoulos Y. C. and Agarwal J. C., AIME, 1976, pp 793-813.
- Lam B. D. and Wilson B., Differential and bulk Cu-Pb-Zn flotation of Delta project ore sample, 1977, pp 1-27. (Nerco report)
- Letowski F., Personal communication, 1987.
- Letowski F., Leaching/flotation in recovery of the complex sulfide ores, presented at 88th annual meeting of CIM, Montreal, May 11-15, 1986 (To be published in CIM bulletin).
- Letowski F., Bloise R. and Barbery G., Hydrometallurgical methods for recovery of valuable elements, FR patent 2526045, Nov. 4, 1983 (Chemical Abstract 100:71897s).
- Letowski F., Chou K. T. and Rao P. D., Hydrometallurgy of the Delta sulfide ores, 1986, pp 1-62. (Nerco report)
- Levenspiel O., *Chemical Reaction Engineering*, 2nd edition, John Wiley and Sons Inc., 1972, pp 359-377.
- Lucas B. M. and Shimano D. Y., Two-stage ferric chloride leaching of CANMET bulk concentrate, in *Complex sulfide*, edited by Zunkel A. D., Boorman R. S., Mooris A. E. and Wesely R. J., AIME, 1985, p 395.
- McCabe W. C., Smith J. C. and Harriott P., *Unit Process of Chemical Engineering*, McGraw Hill Co., 1985, pp 37-55, 239-241.
- McNamara J. M., Ahrens W. A. and Franek J. E., A hydrometallurgical process for the extraction of copper, *CIM Bulletin*, March, 1980, pp 201-204.
- Monhemius J., Hydrometallurgical processing of complex minerals, *Chemistry and Industry*, June, 1981, pp 410-420.
- Morin D., Gaunand A. and Renon H., Representation of the kinetics of leaching of galena by ferric chloride in concentrated sodium chloride solutions by a modified mixed kinetics model, *Metallurgical Transactions B*, vol 16B, 1985, pp 31-39.
- Narita E., Lawson F. and Han K. N., Solubility of oxygen in aqueous electrolyte solutions, *Hydrometallurgy*, vol 10, 1983, pp 21-37.
- Nauman C. R. and Duke N. A., Alteration accompanying massive sulfide mineralization in the Delta district, east central Alaska: Implication for exploration, *Journal of Geochemical Exploration*, vol 25, no 1/2, 1986, p 254.
- Pankratz L. B., Thermodynamic properties of halides, *BuMines Bulletin 674*, 1984.
- Pankratz L. B., Stuve J. M. and Gokcen N. A., Thermodynamic data for mineral technology, *BuMines Bulletin 677*, 1984.
- Peters E., Swinkels G. M. and Vizsolyi A., Copper recovery from sulfide concentrates by the UBC-Cominco ferric leach route, in *Process and Fundamental Considerations of Selected Hydrometallurgical Systems*, edited by Kuhn M. C., AIME, New York, 1981, pp 72-81.
- Rao P. D. and Letowski F., Research grant proposal for Nerco Minerals Co, MURL, UAF, Jan., 1986.
- Raudsepp R. B., Beattie M. J. V., Iron control in chloride system in *Iron Control in Hydrometallurgy*, edited by Dutrizac J. E. and Monhemius A. J., John Wiley and Sons Inc., 1986, pp 163-182.

- Rosenqvist T., Principle of Extractive Metallurgy, McGraw Hill Co., 2nd edition, 1983, pp 101-134.
- Schmalz R., A note on the system $\text{Fe}_2\text{O}_3 - \text{H}_2\text{O}$, Journal of Geophysical Research, vol 6, no 5, 1959, pp 575-579.
- Schmidt R. and Shaw D. R., Delta complex sulfide ores, metallurgical and mineralogical studies, 1984, pp 1-35. (Nerco report)
- Schumpe A., Adler I. and Deckwer W. D., Solubility of oxygen in electrolyte solution, Biotechnology and Bioengineering, vol 20, 1978, pp 145-150.
- Schweitzer F. W. and Livingston R. W., Duval's clear hydrometallurgy process, in Chloride Electrometallurgy, edited by Parker P. D., AIME, New York, 1982, pp 221-227.
- Shah V. T., Kelkar B. G., Godbole S. P. and Deckwer W. D., Design parameters estimation for bubble column reactors, AIChE, vol. 28, no. 3, 1982, pp 353-379.
- Snell F. D. and Etre L. S., Encyclopedia of Industrial Chemical Analysis, vol 15, 1972, pp 37-38.
- Su H., Dissolution of sphalerite in ferric chloride solutions, U. S. Geology Survey OFR NO 81-609, 1981, Washington D. C. 20240.
- Swaminathan K., Subramanian C. and Rao C. S., The pressure oxidation of acidic ferrous chloride solution with oxygen, Hydrometallurgy, vol 6, 1981, pp 339-346.
- Szekely J. and Themelis N. J., Rate Phenomena in Process Metallurgy, John Wiley and Sons Inc., 1971, pp 14-20, 684-709.
- Von Ropenack, A., Hematite - the solution to a disposal problem - an example from the zinc industry, in Iron Control in Hydrometallurgy, edited by Dutrizac J. E. and Monhemius A. J., John Wiley and Sons Inc., 1986, pp 730-741.
- Yano T., Suetaka T. and Umehura I., Kinetics of oxidation of iron(II) chloride in HCl with oxygen, Nippon Kagaku Kaishi, no 8, 1974, pp 1375-1379.
- Zoss L. M., Sucin S. N. and Sibbitt W. L., Solubility of oxygen in water, Transactions, AIME, 76, 1954, pp 69-71.
- Zunkel A. D., Boorman R. S., Morris A. E. and Wesely R. J., Complex Sulfide, proceeding of ores, concentrates and by-products, AIME, 1985.

APPENDIX

Abbreviations

| | |
|------------|----------------------------|
| Cu(T) | Total copper concentration |
| DDN | Sample symbol |
| DDS | Sample symbol |
| E | Oxidation potential |
| Fe(T) | Total iron concentration |
| Fe(III) | Ferric ion concentration |
| Fe(II) | Ferrous ion concentration |
| FR | Oxygen flowrate |
| L | Liter |
| LPU | Sample symbol |
| LP 86 | Sample symbol |
| M | Molarity |
| N | Normality |
| a^{Mn^+} | Activity of metal ions |
| Po | Outlet oxygen pressure |
| pH | Acidity in logarithm |
| Pres. | Pressure |
| Temp. | Temperature |