Kinetics of Leaching Galena Concentrates with Ferric Fluosilicate Solution

by

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Abstract

A new hydrometallurgical leaching process, which dissolves galena concentrates with acidified ferric fluosilicate solution, has been investigated for the selective extraction of lead and zinc from the galena concentrates. The process of leaching galena concentrates avoids the generation of sulfur dioxide and lead dust emissions and is capable of treating complex sulfide and low-grade flotation concentrates.

The leaching of Pine Point galena concentrates by ferric fluosilicate solutions was studied under various experimental conditions in the temperature range 20 to 95°C. Temperature had a pronounced effect on the dissolution of the concentrates. The rates of lead leaching are very rapid over the temperature range 38 to 95°C. The reaction rates for the dissolution of galena were found to be controlled by surface chemical reaction. The apparent activation energy of the leaching reaction was calculated to be equal to 62.1 kJ/mole which is consistent with a chemical reaction control mechanism.

The SEM micrographs show that the elemental sulfur reaction product formed in the leaching of the galena concentrate is fairly rough and appears to be quite porous on the particle surface. It is a non-protective product layer.

The fluosilicate lixiviant may dissociate at high temperatures. Some white precipitates were found in the leached residue which were generated in the course of reactions at above 65°C.
The initial contents of Pb²⁺, H⁺, and Fe³⁺ in the lixiviant do not have a significant effect on the lead extraction under the experimental conditions in the study. The insensitivity of the leaching rates to the leaching variables probably arises from an electrochemical mechanism involving adsorption of ferric ions on cathodic sites, isolated from anodic sites where the leaching takes place.

During the course of the galena leaching, zinc extraction is much lower than lead extraction, especially at temperatures below 65°C. Separation of lead and zinc by selective leaching seems to be feasible and effective. Therefore, the ferric fluosilicate leaching system appears to have great potential to treat both conventional lead sulfide concentrates and complex sulfide concentrates, such as the McArthur River concentrates.

The solubility of lead salt in fluosilicate medium is relatively high, and easily meets the concentration requirement for the subsequent aqueous electrolysis operation.
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CHAPTER 1 Introduction

Lead is among one of the most ancient metals known to mankind. The relatively simple extraction methods for lead from its ores made it one of the few metals used extensively since earliest times. Lead was in common usage in Ancient Egypt for ornamental objects and solder, but the most extensive use of lead by the Ancient Romans was in the manufacture of water pipes based on its malleable and ductile properties.

The most important ore of lead is galena (PbS) which is widely distributed throughout the world. The main sources of lead ores currently worked are in the USA, Australia, Mexico, Canada and the former USSR. In the earth's crust lead is estimated to be present at 16 ppm by weight, and to be in sea water at a concentration of 0.004 ppm[1].

So far, only pyrometallurgical smelting methods are practised in the commercial extraction of lead from its ores. However, the release of SO$_2$ and particulate lead emissions which are usually generated in pyrometallurgical smelting processes have resulted in severe pollution problems. Another drawback of conventional smelting processes for lead is that the process is not well suited for treating complex sulfides as well as low grade ores. As the high grade lead sulfide ores are gradually being depleted, this problem is becoming more severe.

Under the current pressure of strict environmental legislation and regulations, lead producers are seeking more efficient ways to produce lead. Hydrometallurgical leaching
of galena concentrates avoids the generation of sulfur dioxide and lead dust emissions and is capable of treating complex sulfide and low grade flotation concentrates. A number of solvents have been tested as lixiviants for galena leaching.

The ferric chloride leaching of galena concentrate has received considerable attention in the past decades. Some processes have been piloted. For example, (a) the U.S. Bureau of Mines ferric chloride leach process which recovers lead via the molten salt electrolysis of PbCl₂[2] and (b) the Minemet Recherche ferric chloride leach process which recovers lead from chloride leach solutions using aqueous electrolysis[3]. However, none of these processes has been commercialized yet. There are some disadvantages still remaining in these processes: (1) low solubility of lead in chloride medium which leads to large plant size and high capital costs, (2) molten salt electrolysis has some technical difficulties associated with product purity, and (3) corrosive chlorine gas must be handled and used to regenerate the ferric oxidant. On the other hand, aqueous solutions of fluosilicic acid and lead fluosilicate have been used advantageously in lead electrorefining for a long time because of the high solubility of lead in these solutions. The fluosilicate medium has therefore been selected as a promising lixiviant on which to base the development of a lead leaching process. The ferric fluosilicate leaching of lead has the potential to overcome the problems met in the ferric chloride leaching system.

The purpose of this investigation was:
(1) To investigate whether lead can be selectively recovered from galena concentrates by dissolution in an aqueous ferric fluosilicate solution.
(2) To study the effect of time, stirring speed, temperature, concentration of Pb⁺², Fe⁺³ and acidity on the dissolution of lead from galena concentrates.
(3) To propose a flowsheet for the ferric fluosilicate treatment of galena containing concentrate.

(4) To test the suitability of this leaching system for different galena concentrates.
2.1 The Extractive Metallurgy of Lead

Lead, which required the simplest treatment for its extraction from its mineral compounds (galena, in particular), was assumed to have started the evolution of metallurgy about 10,000 years ago. Since then about 200 million tons of lead has been produced and, on average, 3 million tons per year are being produced at present. About 95% of lead bullion is produced in the traditional roast-reduction tandem 'sintering machine' and 'blast-furnace'.[4]

Over the past decades, there has been a great deal of progress in the extractive metallurgy of lead, and extraction efficiencies have improved greatly. Nowadays the lead extraction process can be conveniently simplified in the two-step flowsheet shown in Fig.1. The first step involves bullion production from the lead sulfide concentrate and the second step is the refining of bullion to the lead market products.

The conventional route for bullion production requires sintering of the concentrate to produce a lead oxide containing product, which is then reduced in a blast furnace with metallurgical coke to produce lead bullion. The blast-furnace (a continuous countercurrent reactor) has undergone essential structural and process modifications since 1900. The lead blast furnace is now being challenged by direct smelting processes. In the last ten years in the lead smelting field, commercial scale smelting using new furnace technology has started. The KIVCET flash smelting
process has been commercially proven and could become a major competitor to the sinter-blast furnace process. The KIVCET process consists of a single flash furnace that treats concentrates and secondary lead materials (e.g., zinc residues), and reduces both the costs of lead smelting and the environmental impact.

Fig. 1 Flowsheet for lead extraction from sulphide concentrates.
The KIVCET process replaces the sintering/blast furnace operations with an oxygen flash smelting step combined with the electrothermic reduction of the metal oxide bearing slag. In this process, lead sulfide is oxidized to lead bullion and sulfur dioxide in a stream of oxygen. In a second step, the bullion and slag flow under a weir to an electrically heated settling hearth where coke breeze or coal is added to reduce the residual lead oxide in the slag and produce a final bullion as well as a low-lead slag[4,5].

An alternate but yet unproven technology is the QSL process. The QSL process is carried out in a long, horizontal reactor. The reactor is lined with fused chrome-magnesite bricks. Bottom-blowing injectors for oxygen and coal are used to ensure intensive local mixing and to maintain separate zones for oxidation, reduction and settling. Lead concentrates, fluxes and flue dust are mixed and pelletized and continuously injected near one end into the molten, oxygen-saturated bath containing lead bullion, lead oxide-containing slag, and lead sulfide matte. Oxygen is blown into the bath in the feed injection and lead bullion discharge zone where it ultimately oxidizes sulfide sulfur to sulfur dioxide gas. Slag is tapped from the far end of the reactor after passing through a zone where reducing coal-air mixtures or natural gas are injected through tuyeres to lower its lead oxide content[6-8].

Since lead bullion contains numerous impurities derived from the ore, flux and refractories, prior to marketing lead products, the refining of lead bullion to remove impurities must be carried out by either a pyro-refining route or an electrolytic refining route. The criterion for choosing between pyro-refining and electrolytic refining is the degree of bismuth elimination required. Comparison of these two treatments shows that the pyro-refining route is usually used when ores with low bismuth content
are treated. For lead derived from high bismuth ores, the electrolytic refining (Betts process) route is usually carried out in a fluosilicic acid electrolyte and produces a high quality lead cathode product. A generalized flowsheet for the conventional pyrometallurgical/electrometallurgical refining of lead is shown in Fig.2.

Hydrometallurgical processes that entirely avoid smelting and its attendant gas and dust treatment systems and associated environmental risks have been investigated over the past few decades. They have been proposed to replace the current lead production technology, but an industrial application has not yet been reported.

A review on the development of hydrometallurgical processes for lead has been given by Flett[9]. It was concluded that at present hydrometallurgical processing for lead is likely to be used only in operations at small deposits that are remote from a smelter complex.
Fig. 2 A generalized flowsheet for the pyrometallurgical/electrometallurgical refining of lead.
2.2 Previous Studies on Lead Leaching

Many potential hydrometallurgical systems have been found that can solubilize lead, and in principle, can be the basis of a lead process. A number of proposals have been made for the recovery of lead from galena by aqueous treatment but none is presently in commercial use. These include leaching with alkali, acids, sulfate, nitrate, chloride as well as fluosilicate media. These processes are discussed below.

2.2.1 The Eh - pH Diagram for the Pb - S - H₂O System

The thermodynamics of the lead sulfide (galena) concentrates leaching system can be discussed in terms of the Eh-pH diagram for the Pb-S-H₂O system.

The Eh - pH diagram[12] shown in Fig.3 defines the leaching opportunities of galena under conditions of extended stability for reduced sulfur species such as elemental sulfur. The arrows shown in Fig.3 represent possible methods for the extraction of lead from galena, and correspond to the leaching reactions expressed by equations (1) to (3), respectively.
Fig. 3  Schematic Eh-pH diagram for the Pb-S-H$_2$O system at 25°C.
(Pb$^{2+}$=10$^{-3}$M, 1.0M total chloride)

\[ PbS + 2H^+ + 2e \leftrightarrow Pb + H_2S \]  \hspace{1cm} (1)

\[ PbS + 2H^+ \leftrightarrow Pb^{2+} + H_2S \]  \hspace{1cm} (2)

\[ PbS \leftrightarrow Pb^{2+} + S^0 + 2e \]  \hspace{1cm} (3)
The direct reduction process is represented by equation (1). Although this process is conceptually very simple, contamination of the lead product with various impurity elements (As, Bi, Cu, Ag, etc.) present in the concentrate is inevitable, and consequently, only a few studies have been reported on this option [10, 11]. Equation (2) shows the condition for non-oxidative leaching which dissolves lead with the concomitant evolution of hydrogen sulfide gas. The third arrow in Fig. 3 represents the process of oxidative leaching, whereby sulfur is oxidized to the elemental form and lead reports to the leach solution as divalent lead ions. Thermodynamically, sulfur in PbS will be oxidized to sulfate or bisulfate under moderately oxidizing conditions even at low pH values. In practice, however, elemental sulfur forms during the atmospheric leaching of galena in acidic media, and the sulfur product does not oxidize significantly under these conditions. Despite the observed formation of small quantities of oxidized sulfur species during galena leaching, the region of sulfur metastability expands to the right-hand side of Fig. 3 as suggested by the broken line. The extent of the sulfur metastability zone is not well defined, and depends on the anions present, pH, temperature, etc. In any event, the oxidative leaching reaction under a broad range of Eh - pH conditions can be expressed by equation (3) [12].

2.2.2 Alkali Leaching of Lead

Previous work on the leaching of galena in the presence of oxygen (5 atm) and sodium hydroxide was carried out by Anderson, Halpern and Samis [13]. The reaction is shown below:
\[
PbS + 2O_2 + 3OH^- \Rightarrow Pb(OH)_3^- + SO_4^{2-}
\]

The leaching rate is dependent on the partial pressure of oxygen. It was also found that the formation of insoluble lead sulfate can be prevented by maintaining the leaching solution at a high pH value at which \( Pb(OH)_3^- \) is stable.

Seraphim and Samis [14] also found that galena can be dissolved with oxygen in neutral solution by forming acetate complexes as shown below:

\[
PbS + \frac{1}{2}O_2 + 2NH_4^+ + 2Ac^- \Rightarrow PbAc_2 + S^0 + 2NH_3 + H_2O
\]

In this reaction elemental sulfur forms as a product on the particle surface. It was postulated that transport of reactants through the sulfur product layer limits the leaching reaction.

The late Professor Forward and co-workers [15] proposed a process whereby lead sulfide concentrates would be leached with alkyl amines and lead carbonate would be precipitated by passing \( CO_2 \) through the resulting solution of lead ammine.

Vizsolyi et al [41] investigated the possibility of recovering lead from a commercial lead concentrate by leaching with solutions of ammonia or its sulfate salt. When the concentrate was leached in the presence of 3 moles of \( NH_3 \) per mole of lead at a temperature of 120\(^\circ\)C and \( O_2 \) pressure of 137.9 kPa, 96.5\% lead conversion could be achieved within 4 hours. Increase of \( NH_3 \) concentration to 6 moles per mole of lead resulted in almost quantitative conversion of lead in 1 hour. The following reaction series was proposed to explain the leaching behavior:
2PbS + 4O₂ + 2NH₃ + 4H₂O

⇒ 2Pb(OH)₂ + 2H₂SO₄ + 2NH₃

⇒ PbOH⁺ + OH⁻ + PbSO₄↓ + 2H₂O + (NH₄)₂SO₄

⇒ PbO · PbSO₄↓ + 3H₂O + (NH₄)₂SO₄

### 2.2.3 Acidic Nonoxidative Leaching of Lead

Nonoxidative leaching of lead sulfide ore and concentrate in acidic solution, releasing hydrogen sulfide, has been repeatedly studied in laboratories.

The rate of nonoxidative leaching galena is very slow in sulfuric acid solutions. During leaching, a considerable amount of hydrogen sulfide is produced, which prevents further reaction unless removed from the leaching vessel[43].

Nunez et al[38,39] carried out several kinetic studies on the nonoxidative leaching of galena with solutions of hydrobromic and perchloric acid, as well as hydrochloric acid with or without a metal chloride salt. They found that the apparent order of reaction for the mean ionic activity of perchloric acid is one. For hydrochloric acid the order of reaction over a wide range of concentrations is 3/2 in the absence of a metal chloride salt and for hydrobromic acid, whose
anion has greater complex-forming power for lead than HCl, the order of reaction is 2. The addition of soluble metallic chloride to a HCl solution only increases the leaching rate of the galena by augmenting the mean ionic activity of the acid, but it does not change the leaching reaction order.

Awakura et al[19] conducted a kinetic study of the nonoxidative dissolution of natural galena in hydrochloric acid and perchloric acid solutions with and without the addition of sodium chloride. In this study, the dissolution rates were reported to be controlled by a chemical reaction on the surface of the galena sample. The galena dissolution rate is first order with respect to chloride ion activity in hydrochloric acid and perchloric acid solutions. The addition of sodium chloride to the acid solutions greatly enhanced the dissolution rate. The beneficial effect of sodium chloride has two possible interpretations: First, it may be explained by an increase in the hydrogen ion activity. Second, the enhancement of the dissolution rate observable at high sodium chloride concentration may be due to the specific adsorption of chloride ions or the surface complexing of chloride ions on the galena surface.

Both nonoxidizing and oxidizing HCl leaching have been studied for the processing of galena and complex sulfide concentrates on a laboratory scale. Muir et al[36] reported that it is possible to extract lead, zinc and silver from the McArthur River zinc-lead sulfide concentrate using both HCl and HCl-O₂ leaching techniques. The leaching reaction proceeded with vigorous evolution of H₂S and the formation of froth. Addition of NaCl to the leaching reagent was found essential to dissolve lead as its complex PbCl₄²⁻ anion.
2.2.4 Nitrate Leaching of Lead

In the area of galena leaching with a nitrate medium, only a few studies have been reported.

The mineral galena (PbS) can be leached with a solution of cold, moderate strength nitric acid (1 to 4 M) [25]. If the leaching temperature is maintained below 40°C, lead nitrate and elemental sulfur can be produced according to the following reaction:

\[ 3\text{PbS} + 8\text{HNO}_3 \Rightarrow 3\text{Pb(NO}_3)_2 + 2\text{NO(g)} + 4\text{H}_2\text{O} + 3\text{S}^\circ \]

The leaching process, however, becomes too slow to be useful at about 10 to 20 g/l free acid concentration, but the addition of a small excess of PbO₂ with fresh concentrate will lead to rapid neutralization at room temperature as in the following equation:

\[ \text{PbS} + \text{PbO}_2 + 4\text{H}^+ \Rightarrow 2\text{Pb}^{2+} + 2\text{H}_2\text{O} + \text{S}^\circ \]

This leaching chemistry was studied by Peters and Vizsolyi [34] on a bench scale. If this leach were to be used as the basic leach for a lead process, it would need a purification step (mainly to remove iron and zinc, but also to remove residual nitrite (\text{NO}_2) which would interfere in electrowinning). Such a purification would be achievable with PbO to neutralize acid and hydrolyze iron and copper, and any excess zinc, and with PbO₂ to oxidize reduced forms of nitrogen. For final pure lead production, electrowinning can be used. Although the process is quite energy efficient, it is known to be associated with serious unsolved problems [35].
Fuerstenau et al [16] studied the kinetics of leaching galena with ferric nitrate as oxidant and indicated that the rate of galena dissolution is controlled by surface chemical reaction. The rate is proportional to the square root of the concentration of ferric ion. The addition of more than one mole/liter sodium nitrate decreased the reaction rate. An activation energy of 47 kJ/mol was measured, and the rate has found to be proportional to the surface area of the galena particles. These results were explained in terms of mixed electrochemical control. The anodic reaction involves the oxidation of galena to lead ion and elemental sulfur, and the cathodic reaction involves the reduction of ferric ion to ferrous ion.

2.2.5 Chloride Leaching of Lead

Chloride solvents generally have been selected as the leaching agent for lead sulfide concentrates because of their low cost and because lead chloride is moderately soluble in concentrated chloride media. In this regard, the chloride media leaching of galena concentrates has received considerable attention in recent years and many studies have been published on the hydrometallurgical treatment of lead sulfide concentrates in chloride media.

Naito and Habashi [37] studied aqueous oxidation of lead sulfide concentrate in hydrochloric acid in the temperature range 80-140°C in the HCl concentration range 0.5-3 N. The following reactions were reported:
\[ \text{PbS} + 2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{PbCl}_2 + \text{S}^0 + \text{H}_2\text{O} \]

\[ 2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \]

In this work, lead was found mainly in the residue mostly as PbCl\(_2\). The lead chloride can be extracted from the residue with the aid of 3 N ammonium acetate at 80°C.

Mizoguchi and Habashi\[40\] investigated pressure leaching of complex sulfides containing galena, sphalerite, chalcopyrite with 1 to 2 N HCl at 120°C using O\(_2\) pressure of 1000 kPa. It was found that >97% zinc and >95% copper dissolved, whereas 83% lead remained in the residue as PbCl\(_2\) and PbSO\(_4\). The recovery of elemental sulfur was nearly 100% with respect to ZnS, PbS and CuFeS\(_2\). The rate of leaching was reported to be diffusion controlled.

Galena can be easily oxidized by ferric chloride solution to form crystalline PbCl\(_2\) salt or, at high Cl\(^-\) activity, PbCl\(_{2-}\) ions. Early investigations on the ferric chloride leaching of galena were reported by Russian researchers.

Vasilve and Muratova\[20\] investigated the reaction between galena and acidified ferric chloride solutions and found that galena dissolved in FeCl\(_3\) solution according to the following reaction:

\[ \text{PbS} + 2\text{FeCl}_3 \Rightarrow \text{PbCl}_2 + 2\text{FeCl}_2 + \text{S}^0 \]
It was observed that complete dissolution of galena was difficult due to coating of the sulfide particles with elemental sulfur.

Volskii, Agracheva and Egorov[21-23] described a process based on the leaching of galena by ferric chloride solutions followed by the electrolysis to deposit lead at the cathode and to form ferric chloride at the anode. They succeeded in achieving 98 to 99% lead extraction by carrying out leaching with solutions containing 100 to 200 g/l Fe\(^{3+}\) at 80°C.

Tsef et al[24] also demonstrated the effectiveness of acidified ferric chloride solutions in dissolving galena concentrates. At a temperature of 100°C, 100% lead extraction was achieved by leaching the galena concentrate for 2 hours in solutions containing 28 to 147 g/l Fe\(^{3+}\).

About 20 years later, the kinetic studies on the chloride system for lead leaching have been extended. Murray[26] leached a disk of galena in a 0.5 mole/l solution of ferric chloride and measured dissolution rates for galena concentrate in acidified ferric chloride solutions without the addition of NaCl. Based on the apparent activation energy of 56.5 kJ/mole and the nonlinear kinetics observed, the rate-limiting step was suggested to be diffusion of the reactant or product species through the elemental sulfur layer. A similar conclusion has been achieved by Chen[28] through leaching a larger diameter particle(512 μm) in 0.1 M FeCl\(_3\) and 3.0 M NaCl solution. The apparent activation energy in this case was calculated to be 28 kJ/mol.
Vygoda[27] studied the kinetics of dissolution of galena particles in solutions containing 75 to 175 g/l of ferric ions. He found that the leaching reaction is first order with respect to the ferric concentration.

Demopoulos[29] has found that the rate is chemically controlled in 3.0 M FeCl₃. In addition, for lower ferric concentrations the rate also appears to be under chemical control at least initially, and this part of the dissolution process is extended as the ferric chloride concentration is increased. This would be in reasonable agreement with the relatively large activation energy of 56.6 kJ/mol observed in 3.0 M FeCl₃.

Arai et al[30] investigated the dissolution of galena crystals in dilute FeCl₃-HCl media (FeCl₃<0.1M) and observed linear kinetics with > 90% elemental sulfur formation. The rate was independent of HCl concentrations in the range 0.01 to 0.5 mole HCl/l and increased as the 1.0 power of the FeCl₃ concentration over the range 0.01 to 0.1 M FeCl₃. The activation energy was about 40 kJ/mole. These workers also concluded that the leaching rate depended on the electronic properties of the galena although only two samples were studied.

Kim and Kim[31] studied the dissolution of sized galena powders in 1 to 3 M FeCl₃ media, and observed parabolic kinetics with a rate directly proportional to the surface area of the galena. The rate increased as the 1.2 to 2.2 power of the FeCl₃ concentration in the range 0.03 to 0.125 M FeCl₃ although it should be noted that there was a significant depletion of FeCl₃ during their tests. The rate increased significantly as the NaCl concentration increased from 0 to 4 M NaCl,
but CaCl₂ had a slight and complex effect on the leaching rate. The activation energy found in the absence of NaCl was 53 kJ/mole whereas in the presence of 3 M NaCl it was 38 kJ/mole.

Morin et al[32] studied the leaching kinetics in 4 M NaCl at pH 2.4 and 75°C. They postulated that the overall kinetics were controlled by a mixed model where ferric chlorocomplex diffusion through the sulfur layer and chemical reaction at the core interface are responsible for the overall rate of dissolution.

Kim et al[51] studied the dissolution of sized galena powder in 0.15 to 0.6 M Fe³⁺ media with 4 M of NaCl at temperatures from 27 to 57°C. The dissolution was represented by a shrinking core model with a surface chemical reaction as the rate-controlling step. The rate dependency on ferric ion concentration was of the order 0.21, and activation energy was 72.1 kJ/mole. They indicated that the dissolution rate of galena is controlled by a surface chemical reaction under their experimental conditions, i.e., low temperature and small particle size and suggested that the reaction may be limited by diffusion at higher temperature and in the final part of the reaction.

Fuerstenau et al[52] investigated the leaching kinetics at temperatures of 50°C and 90°C and a NaCl concentration of 3 M. Up to 0.2 M of ferric concentration, the reaction rate was controlled by the diffusion of ferric ion through the product sulfur layer. At ferric concentrations higher than 0.2 M, the reaction rate remained independent of ferric ion concentration. The apparent activation energy was found to be 33.7 kJ/mol. They concluded that the solubility
of lead chlorocomplexes inside the pore probably is responsible for the low dissolution rates at low NaCl concentrations. As the solubility of lead increased with increasing NaCl concentration, the reaction rate also increased.

Dutrizac[50] studied the dissolution of galena at 80°C and at ferric concentrations higher than 0.1 M. He observed that the dissolution rate was controlled by the outward diffusion of reaction product PbCl₂. The effect of various alkali or alkali earth chloride salts also was studied.

Rath et al[33] examined the leaching of a sized galena concentrate containing 86.3% lead in 0.1 M Fe³⁺ and 0.5 M NaCl solution over the temperature range of 14 to 80°C. The simple shrinking core model was obeyed and the rate constant increased according to the 0.76 power of the Fe³⁺ concentration. It was concluded that the reaction was electrochemically controlled.

Sohn et al[54] formulated a mixed kinetic equation using the law of additive reaction times based on the published data. This mixed model rate equation assumed both diffusion of PbCl₂ through the product sulfur layer and a surface reaction in the shrinking core model. In the temperature range from 25 to 50°C and various particle sizes, the prediction by the mixed kinetics equation showed excellent agreement with the results from published data in the condition of galena dissolution containing FeCl₃ concentration of 0.15 M or higher.

Warren et al[53] studied the dissolution of sized galena concentrates containing 79 to 81% lead in 0.2 M FeCl₃ media and noted a series of rate-controlling steps. The initial stage of reaction was surface controlled, but as
PbCl₂ was generated, the rate-controlling step moved progressively to diffusion across the elemental sulfur product layer. The rate increased directly with the NaCl concentration over the range of 0 to 5 M NaCl.

Dutrizac and Chen[55] studied the dissolution of galena in 0.3 M FeCl₃-0.3 M HCl solutions containing 0 to 6 M LiCl at 80°C. Parabolic kinetics were observed at all LiCl concentrations. The leaching rate increases with increasing LiCl concentrations. They concluded that the dissolution of galena is controlled by the outward diffusion of the PbCl₂ reaction product through the constantly thickening layer of elemental sulfur formed during leaching.

Although most chloride leaching activity has focused on the FeCl₃-HCl system, a lesser amount of work also has been carried out using CuCl₂-HCl lixiviants[56,57]. Cupric, as an oxidant in chloride leaching galena, has been investigated using the rotating disk technique by Dutrizac. Rapid nonlinear kinetics were observed over the temperature range 45 to 90°C and for NaCl concentrations from 0 to 4.0 M. The experimental results showed that dissolution of galena is controlled by the outward diffusion of the PbCl₂ and CuCl reaction products through the solution trapped in the pores of the constantly thickening elemental sulfur layer.

Recently, Kobayashi et al[12] critically reviewed the extensive literature on the ferric chloride dissolution of galena and compared the various results on a consistent basis. There is a consensus that the leaching reaction is rapid and that elemental sulfur is the dominant reaction product. Although quantitative agreement among the various studies is lacking because of differences in galena purity, experimental procedures and methods, and data interpretation, the overall
trends indicate a shallow temperature dependence, a direct total chloride concentration effect and a modest influence of solution agitation. The experimental observations are consistent with rate control either by the outward diffusion of the PbCl$_2$ reaction product through the elemental sulfur layer or by the surface chemical reaction.

In addition to the above studies on the ferric chloride leaching of galena, various electrochemical investigations have also been carried out to try to elucidate the reactions occurring during galena dissolution.

Ghali and Dandapani\[58,59\] studied the electrochemical reaction of galena dissolution in chloride media. Elemental sulfur is formed at low or moderate potentials (E<1 V SHE) and this sulfur passivates the galena surface. The anodic dissolution reaction was shown to be impeded by both the elemental sulfur and PbCl$_2$ reaction products. The presence of high chloride concentrations (as HCl) reduced the passivation, presumably by increasing the solubility of the PbCl$_2$ reaction product. Studies on the electrowinning of lead directly from galena also have been done by a few other researchers\[11,61,62\].

The extensive investigations on the kinetics of the leaching of galena with ferric chloride resulted in several lead leaching processes being developed on bench or pilot scales. The United States Bureau of Mines ferric chloride leaching process\[2,47,48\] involves ferric chloride leaching of galena to produce lead chloride and fused-salt electrolysis of the lead chloride to produce lead and chlorine. The flowsheet of this process is shown in Fig.4.
The Minemet Recherche ferric leaching process[3] includes dissolution of lead in a brine of sodium chloride by means of ferric chloride and recovery of lead from chloride leach solutions using aqueous electrolysis. Both processes were studied on a pilot scale.

Royston et al[49] conducted a feasibility study on the selective chloride leach process for the McArthur River semi-bulk concentrates to separate lead from zinc in the mineral. The results indicated that this process has the potential
to increase significantly the recovery of zinc (as zinc concentrate) and lead (as lead metal) over conventional flotation methods which produce lead and zinc concentrates.

2.2.6 Sulfate Leaching of Lead

Galena (PbS) is readily attacked by ferric ion over a wide range of conditions. If the leaching is done in a chloride medium, moderately soluble lead chloride complexes are formed; if the attack is done by sulfate solutions, an insoluble lead sulfate is produced that is, however, moderately soluble in an excess of chloride ion. Both types of leaching medium have been advocated for various ores[46].

During oxygen pressure leaching in sulfuric acid solutions, galena will oxidize according to the following reaction:

\[ PbS + H_2SO_4 + \frac{1}{2}O_2 \rightarrow PbSO_4 \downarrow + S^0 + H_2O \]

The reaction rate is rapid and a considerable amount of sulphur is formed. If iron oxide is added to the suspension (about 10% of the weight of galena) the galena reacts more rapidly. The iron appears to act as an oxygen ‘carrier’. The following reactions may occur[43]

\[ Fe_2(SO_4)_3 + PbS \rightarrow 2FeSO_4 + PbSO_4 \downarrow + S^0 \]
Naito and Habashi carried out aqueous oxidation of lead sulfide concentrate with O₂ in sulfuric acid and compared this with the same oxidation in hydrochloric acid. It was found that the aqueous oxidation of galena in the temperature range 80-140°C is slower in H₂SO₄ than in HCl of the same normality in the range 0.5-3 N. Lead is found mainly in the residue mostly as PbSO₄ when H₂SO₄ is used. The lead sulfate can be extracted from the residue with the aid of 3 N ammonium acetate at 80°C[37].

Mizoguchi and Habashi[40] investigated the pressure leaching of complex sulfides containing galena, sphalerite and chalcopyrite in sulfuric acid at 120°C using O₂ pressure of 1000 kPa. Compared with the complex sulfide leaching in HCl, it was found that the leaching rate in H₂SO₄ is slower than in HCl at the same acid normality, and lead jarosite is mainly formed in the residue when H₂SO₄ is used as a leaching agent.

Mackiw and Veltman[44] and Bolton et al[45] reported a complex sulfide acid leaching process which was developed by Sherritt Gordon. In the Sherritt Gordon process, the concentrate is leached by H₂SO₄ and air under pressure at 150°C and 350 kPa oxygen partial pressure for one hour. Zinc and copper go into solution while lead is transformed into PbSO₄ and lead jarosite and is retained in the residue together with the pyrite, and any iron minerals that are attacked and reprecipitated. The reactions taking place may be represented as follows:

\[2\text{FeSO}_4 + \text{H}_2\text{SO}_4 + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{H}_2\text{O}\]


\[
\text{ZnS} + H_2SO_4 + \frac{1}{2}O_2 \Rightarrow \text{ZnSO}_4 + S^0 + H_2O
\]

\[
PbS + H_2SO_4 + \frac{1}{2}O_2 \Rightarrow PbSO_4 \downarrow + S^0 + H_2O
\]

\[
CuFeS_2 + H_2SO_4 + \frac{5}{4}O_2 \Rightarrow CuSO_4 + FeOOH \downarrow + 2S^0 + \frac{1}{2}H_2O
\]

After filtration, the solution is purified to remove copper, and then electrolyzed to recover the zinc, and the acid generated during electrolysis is recycled to the leaching step. Pyrite and elemental sulfur can be floated from the residue, but the recovery of lead from the jarosite poses a problem since lead in this form is insoluble in the commonly used reagents, e.g., NaCl or ammonium acetate solution.

The sulfidic source of lead, galena (PbS), shows fairly rapid dissolution in hot ferric sulfate solution and yields an insoluble PbSO₄, and a suitable solvent removes it from the residue. If galena is associated with other sulfides, it might be possible to apply ferric sulfate leaching to extract much of the impurity content while leaving lead as an insoluble precipitate for subsequent processing[25].

Kuzminkh and Yakhontova[42] studied leaching of galena-sphalerite concentrates with acidified ferric sulfate solution at temperatures between 80 to 100°C. The galena was attacked according to the following reaction:

\[
PbS + Fe_2(SO_4)_3 \Rightarrow PbSO_4 \downarrow + 2FeSO_4 + S^0
\]
The leaching process obeyed linear leaching kinetics. The rate was found to increase by a factor of 1.5 times as the temperature was taken from 80 to 100°C.

Haver et al of the U.S. Bureau of Mines[18] have reported a more detailed study on the ferric sulphate leaching of galena for the recovery of lead and sulfur. The galena concentrate was leached with a hot, aqueous solution of ferric sulfate to yield lead sulfate and elemental sulfur. The slurry was then filtered and the ferric sulfate solution regenerated by electrolysis in a diaphragm cell. The residue was treated with ammonium carbonate to convert the lead to an acid-soluble form and to obtain ammonium sulfate as a by-product:

\[
PbSO_4 + (NH_4)_2CO_3 \rightarrow PbCO_3 + (NH_4)_2SO_4
\]

The lead carbonate product from the above operation was dissolved in the hydrofluosilicic acid, and the solution was electrolyzed to recover 99.9% pure lead metal and to regenerate H₂SiF₆. The sulfur was removed from the acid leach residue with carbon disulfide using a Soxhlet extractor.

Investigations of a lead production process using ammoniacal ammonium sulfate solutions (AAS) to dissolve oxidized lead compounds were reported by Bratt and Pickering[17]. This process is based upon the solubility of certain oxidized lead compounds in aqueous ammoniacal ammonium sulfate solutions. Sulfidic ores, or concentrates are pretreated by roasting or by oxidation in aqueous suspension to convert lead sulfide to lead sulfate, lead monoxide, or a basic lead sulfate. The pretreated material is leached with an AAS solution, under ambient conditions to produce a pregnant liquor containing up to 100 g per liter lead and a barren residue. Lead in the pregnant liquor may be recovered by electrolysis or
precipitation. The experimental results demonstrated that ammoniacal ammonium sulfate solutions could dissolve lead sulfate yielding a highly concentrated lead solution. It was also shown that lead and lead compounds could be readily recovered from these AAS solutions.

2.2.7 Fluosilicate Leaching of Lead

A fluosilicic medium has been used advantageously for a long time by lead metal refiners, because the lead salts in these electrolytes are very soluble, and there is no difficulty in electrowinning lead at a current density of 200 A/m²[63]. The idea of using it for the direct attack of galena or complex ores and of certain scraps, has been explored by a number of research workers.

Stauter[64] proposed a lead production hydrometallurgical process which comprises the steps of (a) treating a lead sulfide feed stock with a fluorinating agent, (b) dissolving the resultant lead fluoride in hydrofluosilicic acid, and (c) electrolysis of clarified leach solution.

A study on fluosilicic media direct leaching of galena was first reported by Pinaev and Novinskii[65] in 1981. They conducted a feasibility study on the fluosilicate leaching of galena which indicated that lead production using the process of leaching galena with a ferric fluosilicate solution and aqueous electrolysis is simpler and cheaper than the ferric chloride process.
Noual et al.[66] investigated the possibility of using the fluosilicic medium as a leaching agent. In a typical experiment, 100 grams of concentrate was first reacted with 44 grams of Fe\(^{3+}\) in a solution of 80 grams of H\(_2\)SiF\(_6\) in a liter of H\(_2\)O at 80°C for three hours. The leaching reaction allows the dissolution of Cu, Zn and some Fe, at the same time producing sulfur and sulfates; lead and silver precipitate as sulfates. In the following slurry repulping step, lead sulfate precipitates are mixed with a solution of H\(_2\)SiF\(_6\) and CaCl\(_2\) and dissolve to give complex chlorides, while sulfate ions are eliminated by gypsum precipitation. The solution then goes to an electrolysis cell where electrowinning of lead is performed. Recovery of metals from complex sulfide ores or concentrates was found to be promising on both the bench and pilot scale. The process is easy to apply because it needs neither special materials and equipment, nor high energy requirements. It gives great flexibility in the treatment of complex sulfide ores.

The U.S. Bureau of Mines has done extensive work on hydrometallurgical lead production processes that leach lead sulfide concentrates with fluosilicic media. Cole et al.[67] developed a process which recovers lead from sulfide materials by leaching the galena with H\(_2\)SiF\(_6\) in the presence of an oxidizing agent (e.g. H\(_2\)O\(_2\) and PbO\(_2\)), forming S and PbSiF\(_6\) and then followed by an electrolysis of the resulting PbSiF\(_6\) solution to produce lead and H\(_2\)SiF\(_6\). On a bench scale, 200 g PbS concentrate was leached in a 2-liter beaker containing 1 liter H\(_2\)SiF\(_6\) solution which contained 236 g/l H\(_2\)SiF\(_6\), 50 ml 30% H\(_2\)O\(_2\) and 98.5 g PbO\(_2\) at 90°C for 2 hours. About 98% leaching extraction was reached. The following electrolysis in a 2-liter cell with a PbO\(_2\)-coated Ti anode gave 99.998% lead at 96% current efficiency. Based on the successful bench scale experiment, they[68] further scaled up the process to pilot scale. The testing on the pilot-scale
experiments demonstrated that the process is technically feasible. The piloted process consists of (1) Oxidative leaching with H₂O₂, PbO₂, to produce a residue containing elemental S, (2) electrowinning the PbSiF₆ solution at 35°C to produce 99.99% lead metal and H₂SiF₆, and (3) solvent extraction to recover S, leaving a residue containing Cu, Ag, and other metal values. Spent electrolyte was recycled repeatedly, with impurity buildup controlled by controlling the leach parameters.

A preliminary evaluation of this leaching-electrowinning method indicated that H₂O₂ is an expensive oxidant for producing Pb. Therefore, a modification on the process has been conducted recently[69]. Instead of H₂O₂ and PbO₂, cheaper high pressure O₂ was selected as leaching reaction oxidant. The effects of several catalysts, O₂ pressure, time, and acid concentration on leaching reaction were investigated. 93% lead extraction was achieved when galena was pressure leached in H₂SiF₆ at 95°C with 200-psig O₂ pressure for 40 minutes, using ferric nitrate (Fe(NO₃)₃) as a catalyst.

Additional investigations have been made on the electrodissolution of galena in different acidic media (fluoboric acid, fluosilicic acid and ammonium acetate) at room and higher temperatures. The results indicate that these media offer potential for electrowinning lead from its sulfide[60].

2.3 Discussion of Lead Leaching Mechanism

Leaching or dissolution is the first prerequisite of any hydrometallurgical
process. Leaching is the term applied to the process of recovering a metal from an ore or concentrate by a solvent or lixiviant, leaving behind a residue consisting of inert minerals originally present, plus insoluble decomposition products of the reacted mineral. The two fundamental parameters which can be used to control the behavior of metals in aqueous solutions are pH and the oxidation potential of the solution. The thermodynamic behavior of an aqueous system is determined by these two parameters, together with the concentrations or activities of the dissolved species. Besides the degree of selectivity, the important parameters for the kinetic behavior of the leaching process are the overall reaction rate, and the variation in rate with leaching time.

The overall reaction process in a hydrometallurgical leaching system treating individual mineral particles may be broken down into the following steps: (1) solution diffusion of reactant through a liquid boundary film; (2) diffusion through solid reaction products; (3) surface reaction; and (4) diffusion of products away through solid reaction products and liquid boundary film. Since back-reaction kinetics are rarely important in hydrometallurgical leaching reactions only the first three steps will be included in a general solution[73]. For spherical geometry as shown in Fig.5, the three kinetic processes in series are:
Fig. 5 Reaction of a mineral particle with shrinking core and liquid boundary diffusion.

\[ \frac{dn}{dt} = \frac{4\pi r^2 D_s (C - C_s)}{\sigma \delta} \]

Boundary Diffusion

\[ \frac{dn}{dt} = \frac{4\pi D' r' r_s (C_s - C'_s)}{\sigma (r_o - r)} \]

Diffusion through Products
Surface Reaction

\[ \frac{dn}{dt} = -4\pi r^2 C \cdot \frac{r}{k} \]

where \( D_s \) is the coefficient of diffusion for bulk solution diffusion, \( D' \) is the effective diffusion coefficient for diffusion through products of reaction, \( k' \) is the surface reaction rate constant, \( \sigma \) is the stoichiometry factor, and \( n \) is the number of moles of unreacted metal remaining in the core at any time \( t \).

Under the steady-state approximation the above rates in series are equal, resulting in the combined expression (neglecting back-reaction kinetics)

\[ \frac{dn}{dt} = -\frac{4\pi r^2 D_s C}{\sigma \delta \left[ 1 + \frac{r_o (r_o - r)}{\delta D'} + \frac{D_s r_o^2}{\sigma \delta k' r^2} \right]} \]

For constant concentration, the final equation describing the kinetics of reaction may be integrated giving

\[ \frac{\sigma \delta}{D_s} X + \frac{3\sigma r_o}{2D'} \left[ 1 - \frac{2}{3} X - (1 - X)^{2/3} \right] + \frac{1}{k'} [1 - (1 - X)^{1/3}] = \frac{3CVt}{r_o} \]

where \( V \) is the molar volume of a solid, \( X \) is the fraction reacted and is represented as follows:
The integrated equation is the sum of expression for boundary diffusion, diffusion through solid products, and the surface reaction. It is obvious that the slowest step in the three stages usually becomes the overall reaction control step.

Leaching of galena with ferric fluosilicate is assumed to follow the chemical reaction:

\[ \text{PbS}(s) + \text{Fe}_2(\text{SiF}_6)_{3(aq)} \rightarrow \text{PbSiF}_6(aq) + 2\text{FeSiF}_6(aq) + S(s) \]

In this reaction elemental sulfur forms as a reaction product on the surface of the galena particles. The reaction rate then might be controlled by chemical reaction on the particle surface or by the transport of the ferric ions through the elemental sulfur layer. If the sulfur layer were a non-porous solid, further reaction would not have proceeded because the reactant could not diffuse through the product layer. The leaching rate expression is determined by the slowest process which controls the whole leaching process.

If the diffusion of ferric through the sulfur layer is the rate-controlling step, simplifying the integrated equation, the diffusion controlled model can be derived as follow:

\[
X = 1 - \frac{r^3}{r_o^3}
\]

\[
1 - \frac{2}{3}X - (1-X)^{2/3} = k_p t
\]
where

\[ k_p = \frac{2D'CV}{\sigma r_o^2} \]

When the leaching process is controlled by a chemical reaction on the surface of the unreacted core, the reaction controlled equation can be expressed as follow:

\[ 1 - (1 - X)^{1/3} = k_r t \]

where

\[ k_r = \frac{3k_o' CV}{r_o} \]

These different controlling models can be used to explain experimental results.

2.4 The Chemistry of the Fluosilicic Acid System

Hydrofluosilicic acid solution is one of the products of the action of water upon silicon tetrafluoride, and is also formed by dissolving silica in hydrofluoric acid:

\[ SiO_2 + 6HF \Leftrightarrow H_2SiF_6 + H_2O \]
Upon dissociation, $H_2SiF_6$ behaves like a strong acid, its strength being close to that of $H_2SO_4$ solutions. By potentiometric titration of $H_2SiF_6$ solutions in water and in various organic solvents, the first and second dissociation constants of the acid can be determined:\[70\]:

\[
\begin{align*}
H_2SiF_6 & \quad \Leftrightarrow \quad HSiF_6^- + H^+ \quad pK_1 = -0.13 \\
HSiF_6^- & \quad \Leftrightarrow \quad SiF_6^{2-} + H^+ \quad pK_2 = 1.79 
\end{align*}
\]

Fluosilicic acid is a non-volatile acid, and as far as we know, exists only in water solution. It will decompose into $SiF_4$ and $H_2F_2$ the moment it passes out of liquid water, and is similar to carbonic and sulfurous acids in this respect. When the acid is thus decomposed, the silicon tetrafluoride formed may exist in the presence of water vapor without combining with it to precipitate fluosilicic acid and silicic acid or silicon dioxide. Whenever hydrofluoric acid reacts with silicon dioxide or glass in the presence of water, the $SiF_4$ first formed immediately reacts with water to form fluosilicic and silicic acids according to the equation:

\[
3SiF_4 + 4H_2O \quad \Leftrightarrow \quad 2H_2SiF_6 + H_4SiO_4 
\]

At room temperature, fluosilicic acid can be concentrated to approximately 61%, which is considered the maximum obtainable in aqueous solution at room temperature. At this concentration the solution has a distinct odor, due to the decomposition products of the acid. It has a sharp stinging taste which in dilute solution is suggestive of alum. The specific gravity of a 61% solution at 25°C was
found to be 1.46. In dilute water solution the acid is quite stable, since it may be kept in glass vessels for a long period of time without etching, and the etching that eventually takes place is found right above the surface of the liquid.

The wide use of H$_2$SiF$_6$ in lead electrorefining is due to its low cost. Fluosilicic acid is produced as a by-product of the treatment of phosphate rock in fertilizer manufacture. Fluoride and silica contained in phosphate rock form fluosilicate and are separated from the fertilizer product. Fluosilicic acid is also produced as a by-product during the dissolution of apatite with sulfuric acid. The acid develops significant vapour pressures through volatile decomposition products at high temperature according to the reaction:

$$H_2SiF_6 \leftrightarrow 2HF(g) + SiF_4(g)$$

Temperatures above 105°C will result in a breakdown of the acid. SiF$_4$ and HF are both corrosive and toxic and are removed from lead refining tankhouses by adequate ventilation.

The properties of H$_2$SiF$_6$ can be well described through the Eh-pH diagram for the F-Si-H$_2$O system. As can be seen in Fig.6, the stability region of $SiF_6^{2-}$ extends over a considerable pH range. At pH values larger than 6.75, $SiF_6^{2-}$ hydrolysis takes place according to the following reaction:
$SiF_6^{2-} + 3H_2O \rightleftharpoons H_2SiO_3 + 6F^- + 4H^+$

The equilibrium constant of the reaction is a function of the ionic strength. Moreover, it has been shown that in the presence of $F$ ([F$^-$] > 6[SiF$6^{2-}$]) the maximum thermodynamic stability of SiF$_6^{2-}$ occurs at a pH between 2.6 and 2.7. In dilute solutions, hydrolysis of the hexafluosilicate ion takes place in elementary steps which involve splitting of one F$^-$ and formation of $SiF_5 \cdot H_2O^-$. This compound loses its $F^-$ ion in a second step forming SiF$_4$ which subsequently undergoes hydrolysis towards $H_2SiO_3$.
\[
\text{SiF}_6^{2-} + 2H_2O \iff \text{SiF}_5 \cdot H_2O^- + F^- \\
\text{SiF}_5 \cdot H_2O^- + 2H_2O \iff \text{SiF}_4 + F^- + 2H_2O \\
\text{SiF}_4 + 3H_2O \iff H_2SiO_3 + 4HF
\]

In the acidic range (pH<1) formation of \( \text{SiF}_5 \cdot H_2O^- \) and \( \text{SiF}_4 \cdot 2H_2O \) takes place:

\[
\text{SiF}_6^{2-} + 2H_2O + H^+ \iff \text{SiF}_5 \cdot H_2O^- + HF \\
\text{SiF}_5 \cdot H_2O^- + 2H_2O + H^+ \iff \text{SiF}_4 \cdot 2H_2O + HF
\]

The fluorine to silica ratio in \( H_2SiF_6 \) solutions is not always equal to six. F/\( Si \) ratios larger than 6 are observed in solutions in which HF is present. Solutions with F/\( Si \) ratios lower than 6 are observed when the acid has an excess of \( SiO_2 \cdot nH_2O \). A large variety of compounds containing silica can be present under these conditions. Among these, conductometric and cryoscopic measurements have shown that the solubility of \( SiO_2 \) in \( H_2SiF_6 \) is due to the formation of \( \text{SiF}_4 \cdot 2H_2O \).

\[
2\text{SiF}_6^{2-} + \text{SiO}_2 + 4H_3O^+ \iff 3\text{SiF}_4 \cdot 2H_2O
\]

This compound behaves like a strong acid. The F/\( Si \) ratio depends on the
technique used to produce the acid. F/Si ratios can also be changed by dilution. In very dilute solution, $SiF_{6}^{2-}$ is completely dissociated. This has lead to the use of fluosilicates (i.e. $Na_2SiF_6$) for the fluoridation of water supplies.

The chemistry of the ferric fluosilicate leaching of lead is as follows:

$$Fe_2(SiF_6)_3 + PbS \Rightarrow PbSiF_6 + 2FeSiF_6 + S^o$$

Other sulfides such as ZnS, CuFeS$_2$, FeS$_2$ will leach according to similar reactions, albeit at different rates.

2.5 Summary

So far, pyrometallurgical smelting processes are the only lead extraction method applied in the industrial production of lead. However, these processes are associated with pollution problems including the emission of toxic lead-containing dusts and fume and sulfur dioxide gas to the environment and to the workplace. Although the historical processes have been modified and new techniques have been introduced (such as the KIVCET and QSL processes), environmental and technical problems still remain in the pyrometallurgical smelting operations. This should result in a renewed interest in the hydrometallurgical processing of lead sulfide and complex sulfide ores.
Since hydrometallurgical leaching processes are not based on roasting, neither lead-polluting fumes nor sulfurous gases are released, and therefore pyrometallurgical air pollutants will not appear in the hydrometallurgical leaching processes.

A number of lead leaching studies were investigated on various selected lixiviants and reaction conditions, including studies using alkali, acid, nitrate, sulfate, chloride and fluosilicate media. Since the dissolution of galena is subject to the formation of Pb$^{2+}$ bearing species, the less soluble the species, the more difficult it is to recover lead from galena. Therefore, in most leaching systems, conditions which favor the formation of soluble lead-bearing species are used to avoid the formation of insoluble lead salts. The leached PbCl$_2$ and PbSO$_4$ salts have a very limited solubility in aqueous solution which makes aqueous electrolysis difficult. Lead metal was recoverable from PbCl$_2$ by molten-salt electrolysis operated at 450°C. However, this process is associated with some problems of product purity. The fluosilicic medium seems to be one of the best choices for a lead-leaching lixiviant.

Fluosilicate solution has been widely used in lead electrorefining process for a very long time because of its high lead solubility and low cost (compared with sulfamate and fluoborate solutions). Complete leaching and electrowinning from these electrolytes is possible, in principle. Lee et al[68, 69] have done extensive work on a process that leaches lead concentrates with oxidants such as hydrogen peroxide or lead dioxide, as well as high pressure oxygen. In this study, we chose ferric as oxidant for the following reasons: (a) ferric leaching has a stable oxidizing potential which is easily controlled, (b) H$_2$O$_2$ is an expensive oxidant for producing Pb, (c) high pressure oxygen leaching is technically more complicated than atmospheric
leaching, and (d) ferric ion is easily regenerated in an electrowinning cell. Despite a few fluosilicic media-based processing studies carried out on the dissolution of lead sulfide concentrates, no reference has been found in the literature to kinetic studies on ferric fluosilicate leaching of galena or complex sulfide ores.

Preliminary tests at UBC indicated that the ferric fluosilicate system has great potential for the treatment of both conventional lead sulfide and complex sulfide concentrates[71].
CHAPTER 3 Experimental

3.1 Solution Preparation

3.1.1 Chemical Reagents

All chemicals used in the preparation of lixivants were reagent grade with the exception of fluosilicic acid which was technical grade supplied by Cominco Research Center. Distilled water was used in all experiments.

3.1.2 Techniques for the Analysis of $\text{H}_2\text{SiF}_6$ Solution

$\text{H}_2\text{SiF}_6$ is a complex acid. The chemical properties of $\text{H}_2\text{SiF}_6$ are much more complicated than those of commonly used acids, such as $\text{HCl}$, $\text{H}_2\text{SO}_4$. Therefore, the concentration of $\text{H}_2\text{SiF}_6$ can not be determined through the normal titration method which is often used to analyze normal acids and alkalis.

There are several methods reported for measuring the concentration of $\text{H}_2\text{SiF}_6$. The method applied here is involves the addition of LiF to $\text{H}_2\text{SiF}_6$ and titration against LiOH. Its reaction equations are as follows:

(a) addition of LiF and reaction of HF with SiO$_2$(if present)
\[ H_2SiF_6 + 2LiF \rightarrow Li_2SiF_6 + 2HF \]

\[ 6HF + SiO_2 \rightarrow H_2SiF_6 + 2H_2O \]

(b) first neutralization point pH=4.5-5.5

\[ HF + LiOH \rightarrow LiF + H_2O \]

recording the volume of LiOH spent as \( V_1 \) and obtaining the moles of LiOH required in this titration: \( m_1 = V_1 \times [LiOH] \).

(c) second neutralization point pH=7.3-8.0

\[ Li_2SiF_6 + 4LiOH \rightarrow 6LiF + H_2SiO_3 + H_2O \]

recording the volume of LiOH spent as \( V_2 \) and obtaining the moles of LiOH required in this titration: \( m_2 = V_2 \times [LiOH] \).

HF is present when: \( 2V_1 > V_2 \), calculating \([HF]\) and \([H_2SiF_6]\) as follows:

\[
[H_2SiF_6] = \frac{m_2}{V_{sample} \cdot 4}
\]

\[
[HF] = \frac{m_1}{V_{sample}} - 2 \cdot [H_2SiF_6]
\]

SiO\(_2\) is present when: \( 2V_1 < V_2 \), calculating \([SiO_2]\) and \([H_2SiF_6]\) as follows:
\[ [H_2SiF_6] = \frac{m_1 + m_2}{6 \cdot V_{sample}} \]

\[ [SiO_2] = \frac{2 \cdot [H_2SiF_6] - \frac{m_1}{V_{sample}}}{4} \]

There were three titrations conducted to determine the concentration of fluosilicic acid. Examples of the titration curves are shown in Appendix A. From comparison of the titration curves, it can be seen that the titration is reproducible and hence the titration method is reliable to measure the concentration of fluosilicic acid. The concentration of fluosilicic acid in the sample received from Cominco was equal to 1.86M.

### 3.1.3 Lixiviant Preparation

There were three ferric fluosilicate solution preparation methods tested in the experiments. These three types of preparation are Fe(OH)$_3$ reacted with H$_2$SiF$_6$, FeSiF$_6$ with H$_2$O$_2$ and Fe$_2$(SO$_4$)$_3$ with H$_2$SiF$_6$.

(a) Lixiviant prepared via the reaction of Fe(OH)$_3$ with H$_2$SiF$_6$.

The ferric hydroxide was freshly precipitated by the reaction of 14.8 M NH$_3$ with a ferric chloride (or nitrate) solution, followed by thorough washing with warm water to remove chloride (or nitrate) ion from the Fe(OH)$_3$ precipitate. The reaction of H$_2$SiF$_6$(1.86M) with Fe(OH)$_3$ (added to the acid all at once) was carried
out at 80 to 90°C with continuous stirring for three hours in a flask. A transparent pink colour ferric fluosilicate solution was obtained after filtering the reaction solution. The problem with this method was the difficulty of washing the ferric hydroxide precipitate. Chloride ions left in the fluosilicate solution react with lead ions to generate a precipitate of crystalline PbCl₂ in subsequent leaching experiments. The reactions in the preparation are as follows:

\[ \text{FeCl}_3 + 3\text{NH}_3 \cdot \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 \downarrow + 3\text{NH}_4\text{Cl} \]

\[ 3\text{H}_2\text{SiF}_6 + 2\text{Fe(OH)}_3 \rightarrow \text{Fe}_2(\text{SiF}_6)_3 + 6\text{H}_2\text{O} \]

(b) Lixiviant prepared via the reaction of FeSiF₆ with H₂O₂

Three reaction steps were carried out in this method. In the first step, PbSiF₆ was generated by the reaction of H₂SiF₆(1.86M) with litharge (PbO) in a stirred reactor. Then, the filtered PbSiF₆ solution was reacted with FeSO₄ generating ferrous fluosilicate which was then separated from the white precipitate of PbSO₄. The green coloured ferrous fluosilicate was gradually oxidized to pink ferric fluosilicate by the slow addition of oxidant H₂O₂ at about 60°C, some silica gel being formed. After decomposing the excess H₂O₂ by boiling, the silica was filtered off and separated from the ferric fluosilicate solution. The reactions can be expressed by the equations:

\[ \text{PbO} + \text{H}_2\text{SiF}_6 \rightarrow \text{PbSiF}_6 + \text{H}_2\text{O} \]

\[ \text{PbSiF}_6 + \text{FeSO}_4 \rightarrow \text{FeSiF}_6 + \text{PbSO}_4 \downarrow \]
\[2\text{FeSiF}_6 + \text{H}_2\text{SiF}_6 + \text{H}_2\text{O}_2 \rightarrow \text{Fe}_2(\text{SiF}_6)_3 + 2\text{H}_2\text{O}\]

(c) Lixiviant prepared via the reaction of \(\text{Fe}_2(\text{SO}_4)_3\) with \(\text{PbSiF}_6\)

The difference between this method and that from method (2) is that \(\text{Fe}_2(\text{SO}_4)_3\) reacted directly with fluosilicate. The \(\text{H}_2\text{O}_2\) oxidizing step was avoided in this method. This simplifies the lixiviant-making procedure, because of the elimination of a very slow oxidizing step, and prevents the existence of excess \(\text{H}_2\text{O}_2\) in the lixiviant which may interfere with the subsequent experiments. The preparation reactions take place according to the following equations:

\[\text{PbO} + \text{H}_2\text{SiF}_6 \rightarrow \text{PbSiF}_6 + \text{H}_2\text{O}\]

\[3\text{PbSiF}_6 + \text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{Fe}_2(\text{SiF}_6)_3 + 3\text{PbSO}_4\downarrow\]

After comparison of the 3 methods, method (3) was chosen to make up the lixiviant used in this study. After filtration to remove the \(\text{PbSO}_4\) precipitate, the supernatant pink solution was used in the leaching experiments as lixiviant. The solution contained \(\text{Fe}^{+3}=53\text{g/l}, \text{Pb}^{+2}=1.58\text{g/l}, \text{Free H}_2\text{SiF}_6=34\text{g/l}\).

### 3.2 Apparatus

The leaching apparatus that was used during this research provided controlled conditions for studies on galena dissolution. The leaching apparatus is shown in Fig.7.
The 500-ml reactor was constructed of teflon to prevent corrosion from the highly corrosive fluosilicic acid. Stirring was provided by a variable speed motor and a teflon impeller inserted through a central port in the reactor. A teflon-coated thermometer was used to measure the temperature of the lixiviant solution in the reactor. The sampling port, which was used to add galena powders and withdraw leachate samples, was covered by a plastic stopper. The thermostated water was heated by an immersion heater. A thermoregulator was used to measure and control the water temperature in the water bath. To maintain a uniform temperature, the water bath was stirred continuously by a constant speed motor. Plastic balls were used to cover the water surface to avoid the loss of heat and water vapour in the water bath.
Fig. 7 Schematic diagram of leaching apparatus
3.3 Materials and Experimental Procedure

3.3.1 Materials

For comparative purposes, three types of lead sulfide concentrates were used in this study. Two concentrates were from Cominco Pine Point Mines. A complex sulfide sample was from Cominco Red Dog Mines. All experiments were done using ground and sized galena powders which were prepared from galena flotation concentrates by means of crushing, grinding, and then wet screening into various mesh fractions. All of the desired sized particles were washed repeatedly to remove finer particles and air dried at room temperature to eliminate the moisture in the powder. The flotation concentrates were analyzed with the chemical composition given in Table 1.
Table 1 Chemical analysis of major metallic constituents of galena concentrates

<table>
<thead>
<tr>
<th>Weight %</th>
<th>Type 1</th>
<th>Type 2</th>
<th>Type 2</th>
<th>Type 2</th>
<th>Type 3</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pine Point Galena</td>
<td>Pine Point Galena</td>
<td>Pine Point Galena</td>
<td>Pine Point Galena</td>
<td>Red Dog Complex</td>
</tr>
<tr>
<td>(-150 +200mesh)</td>
<td>(-80 +100mesh)</td>
<td>(-170 +200mesh)</td>
<td>(-270 +325mesh)</td>
<td>(-170 +230mesh)</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
<td>75.26</td>
<td>75.95</td>
<td>77.08</td>
<td>78.73</td>
<td>23.02</td>
</tr>
<tr>
<td>Zn</td>
<td>2.07</td>
<td>1.56</td>
<td>1.76</td>
<td>1.63</td>
<td>34.22</td>
</tr>
<tr>
<td>Fe</td>
<td>5.46</td>
<td>1.82</td>
<td>2.05</td>
<td>1.96</td>
<td>4.17</td>
</tr>
<tr>
<td>Cu</td>
<td>0.0013</td>
<td>0.0022</td>
<td>0.0073</td>
<td>0.0046</td>
<td>0.12</td>
</tr>
</tbody>
</table>

3.3.2 Experimental Procedure

The experimental procedure consisted of the following steps:

(1) The thermostated water bath was filled with water and covered with plastic balls to avoid loss of heat and water vapour, the immersion heater turned on and the temperature controller set at the required temperature.

(2) 300 ml of lixiviant of the required concentration was measured and put into the 500-ml teflon reactor.
(3) When the thermostat temperature was close to the targeted value, the teflon reactor was lowered into the water bath, the stirrer motor turned on to drive the teflon stirrer inside the reactor to improve the heat transfer in the lixiviant solution.

(4) When the lixiviant solution temperature reached the required value, a weighed amount of galena concentrate was quickly added into the reactor through the sampling port. The leaching reaction was started at this time. The leaching reaction time was recorded by means of a stopwatch.

(5) Samples of about 1ml (0.3% of the initial solution volume), were taken through the sample port at selected times (at intervals of 5, 10, 20, 35, 60, 90 minutes - depending on the expected rate of dissolution) and collected in a sample tube which was immediately stoppered to prevent vapour loss during cooling.

(6) After cooling to room temperature, the samples were filtered through a Buchner funnel to separate the residue from the sample solution which is then diluted for chemical analysis.

(7) The diluted samples were analyzed for dissolved lead and zinc using an atomic absorption spectrophotometer.
CHAPTER 4 Results and Discussion

The results and discussion have been organized in the following manner. First, the results of the experiments on the leaching of Pine Point concentrates at various stirring speeds and temperatures are presented and discussed. Following this, the effect of a number of experimental variables on the rate of leaching are reported. Finally, a hydrometallurgical process flowsheet for the production of lead from galena concentrate, which includes the leaching of galena, is proposed.

Most of the results in this section are presented only in graphical form. Unless otherwise noted, the ferric fluosilicate leaching solutions contained 53g/l Fe\(^{3+}\), 1.58g/l Pb\(^{2+}\) and 34g/l free H\(_2\)SiF\(_6\), and the galena concentrate was Type 1 from Cominco Pine Point Mine with particle size range (-140 +200 mesh).

4.1 Effect of Stirring Speed

Stirring speeds in the reactor were varied from 500 to 800 rpm. Results from these experiments, shown in Fig.8, are expressed in terms of the fraction of lead extracted from a galena concentrate. Over this range of stirring speeds, no significant effect of stirring on the reaction rate was found. Based on these data a stirring speed of 550 rpm was chosen for all subsequent experiments.
Leaching of Pb from Galena Concentrate at Various Stirring Speeds

Fig. 8 Leaching results for various stirring speeds and 5g galena concentrate, 45°C, 300 ml lixiviant (Pb$^{2+}$=1.58g/l, Fe$^{3+}$=53g/l, free H$_2$SiF$_6$=34g/l).

4.2 Effect of Temperature

The kinetics of the leaching reaction were examined over the temperature range 20 to 95°C. The leaching results are presented in Figs. 9 and 10. As expected, a higher temperature resulted in a faster rate of dissolution for both lead and zinc from galena concentrate.
Fig. 9 shows the fractional lead extraction from galena concentrate as a function of time for experiments conducted at seven different temperatures. The rate of lead leaching increased dramatically with temperature. At 85 and 95°C, the rates were so fast that the lead leaching reaction was virtually complete in 5 minutes.
The results of zinc leaching are demonstrated in Fig. 10. At low temperature, very low leaching rates were observed. At 85 and 95°C, the reaction rates were significantly faster.

Fig. 10 Leaching of Zn for various temperatures and 5g galena concentrate, 550rpm, 300 ml lixiviant(Pb²⁺=1.58g/l, Fe³⁺=53g/l, free H₂SiF₆=34g/l).

Fig. 11 illustrates the reaction rate difference between lead extraction and zinc extraction during the course of the galena concentrate leaching. Lead leaching is easier and faster than zinc leaching. This could make it possible to selectively recover...
Comparison of Pb and Zn Extraction from Galena Concentrate

Fig. 11 Comparison of lead and zinc extraction at 30 and 45°C, and 5g galena concentrate, 550rpm, 300 ml lixiviant(Pb²⁺=1.58g/l, Fe³⁺=53g/l, free H₂SiF₆=34g/l).

lead and zinc from galena concentrate by dissolution in an aqueous ferric fluosilicate solution. Under this condition, lead would be leached into solution while zinc would be left in the solid leach residue.
Fig. 12 A plot of \(1 - (1 - X)^{\frac{1}{3}}\) vs. time to determine the intrinsic leaching kinetics.

The leaching data have been tested for the degree of fit to the linear leaching kinetics and parabolic leaching kinetics model. Fig. 12 and Fig. 13 show the linear kinetics plot of \(1 - (1 - X)^{\frac{1}{3}}\) vs time and the parabolic kinetics plot of \(1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}\) vs time respectively. These models were chosen based on reports by other authors on the ferric ion leaching of galena. The linear leaching model was used to test for rate control by a slow surface chemical reaction. The parabolic leaching kinetics
Fig. 13 A plot of $1 - \frac{2}{3}X - (1 - X)^{\frac{2}{3}}$ vs. time to determine the mass transfer kinetics.

model is used to test for mass transfer control through the elemental sulfur product layer. Comparing Figs. 12 and 13, it can be concluded that surface chemical reaction controls the galena leaching process under the experimental conditions.

The parameters of the linear leaching reaction kinetics, which were calculated based on linear kinetics equation $1 - (1 - X)^{\frac{1}{3}} = k_i t$, are presented in Table 2.
Table 2. The Linear Kinetic Parameters of Galena Concentrate Leaching

<table>
<thead>
<tr>
<th>Temperature</th>
<th>$k_i$(min$^{-1}$)</th>
<th>$k_{r_0}$(μm/min)</th>
<th>$1/T$</th>
<th>log $k_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20°C</td>
<td>0.002476</td>
<td>0.1108</td>
<td>0.003413</td>
<td>-2.606</td>
</tr>
<tr>
<td>30°C</td>
<td>0.005806</td>
<td>0.2598</td>
<td>0.003300</td>
<td>-2.236</td>
</tr>
<tr>
<td>38°C</td>
<td>0.01051</td>
<td>0.4703</td>
<td>0.003215</td>
<td>-1.978</td>
</tr>
<tr>
<td>45°C</td>
<td>0.01687</td>
<td>0.755</td>
<td>0.003145</td>
<td>-1.773</td>
</tr>
<tr>
<td>65°C</td>
<td>0.05448</td>
<td>2.438</td>
<td>0.003003</td>
<td>-1.264</td>
</tr>
</tbody>
</table>

The apparent reaction rates and rate constants were obtained from the linear responses of the dissolution of the galena concentrate shown in Fig. 12. The reaction rates were used to plot the leaching rates vs. temperature. These rate constants were used to plot an Arrhenius diagram.

Fig. 14 is the plot of lead leaching rates expressed in μm/min at various temperatures. The rates of lead dissolution in ferric fluosilicate solution are seen to increase with temperature. The retention time in the leaching of the galena concentrate can be calculated from the diagram. If the whole leaching process is controlled by the slow chemical reaction, the completion of the dissolution of a 50 μm particle of galena needs about 10 and 30 minutes at 65°C and 45°C respectively. This is an important parameter for process design and industrial operation.
Fig. 14 A plot of lead leaching rates vs. temperatures.

The Arrhenius plot for the dissolution of galena concentrate is demonstrated in Fig. 15. The apparent activation energy of lead leaching, which has been calculated based on the slope of straight line in the Arrhenius plot, is equal to 62.1 kJ/mol. This value is consistent with a surface chemical reaction control mechanism.

Careful examination and identification of the solid reaction products are important segments of the study of any heterogeneous reaction. Residues from several leaching experiments at various temperatures were examined using a scanning...
Fig. 15 Arrhenius plot for leaching of lead from galena concentrate

Figs. 16(a-f) show the scanning electron micrographs of unleached galena concentrate and its residues. Typical unreacted, sized, galena concentrate was depicted in Fig. 16a for comparison. Figs. 16(b-f) show galena leach residues which have been reacted at various temperatures (20 to 95°C). Fig. 16b is a low magnification micrograph, which shows that the residue surface is very rough and appears to be quite porous. Visual examination and comparison of the original galena concentrate...
and leached galena residues at 20°C and 45°C demonstrated that the surface was
covered with a mass of small particles of sulfur crystals. This kind of elemental sulfur
product layer is porous and, therefore, non-protective.

Fig. 16e and Fig. 16f show that white fluffy precipitates appeared in the residues
at temperatures of 65°C and 95°C. These silicon-bearing precipitates probably came
from the decomposition of the fluosilicate solution. As mentioned previously, there
is some excess SiO₂ in the hydrofluosilicic acid solution. When the solution
temperature increases to about 65°C, excess SiO₂ might start to precipitate. If the
temperature exceeds 105°C, the acid will break down. Hence, the leaching reaction
should be kept under 65°C to avoid precipitates.
Figs. 16a,b SEM micrographs of unreacted galena and leach residue at 20°C.
Figs. 16c,d  SEM micrographs of galena leach residues at 20°C and 45°C respectively.
Figs. 16e,f  SEM micrographs of galena leach residues at 65°C and 95°C respectively.
4.3 Effect of Particle Size

![Graph showing leaching of Pb at various particle size ranges](image)

Fig. 17 Leaching of lead for various particle size ranges of galena concentrate at 35°C.
The effect of particle diameter on the rate of lead extraction was examined by measuring the kinetics of reaction for four size fractions, shown in Fig.17. As expected, a smaller particle size results in a faster rate of dissolution, and the data when plotted according to equation $1 - (1 - X)^{1/3} = k_1 t$ are linear as shown in Fig.18. The slopes of each of the lines in Fig.18 are the apparent rate constants, $k_1$, given by equation $k_1 = \frac{3kCV}{r_e}$. Particle sizes and rate constants from Fig.18 were used to produce
Fig. 19 A plot of the apparent reaction rate constant as a function of $1/r_o$.

Fig. 19 which yields the linear relationship between $k_i$ and $1/r_o$. The straight line passes through the origin. These data further support the concept that the reaction rate is limited by a surface reaction during most of the extraction process.
4.4 Effect of $\text{H}_2\text{SiF}_6$ Concentration

Fig. 20 Leaching of lead from galena concentrate at various fluosilicic acid concentrations and 45°C, 300 ml lixiviant ($\text{Pb}^{2+}=1.06\text{g/l}$, $\text{Fe}^{3+}=35.3\text{g/l}$).

Fig. 20 shows lead extraction during galena concentrate leaching at different fluosilicic acid concentrations. Lead extractions in the initial and final stages at fluosilicic acid concentration in the range 45 to 112 g/l are relatively close to each other. This probably can be explained by the value $A (\alpha_{H^+}/\alpha_{F^{3+}})$, which is a ratio of
the experimentally measured initial activity of the hydrogen ion to that of the initial ferric ion activity. The galena leaching reactions may be considered as a competition between nonoxidative and oxidative dissolution as follows:

\[
PbS + 2H^+ \leftrightarrow Pb^{2+} + H_2S \quad \Delta G_{298K} = 41.06kJ
\]

\[
H_2S + 2Fe^{3+} \rightarrow 2Fe^{2+} + 2H^+ + S^0 \quad \Delta G_{298K} = -121.66kJ
\]

\[
PbS + 2Fe^{3+} \rightarrow 2Fe^{2+} + Pb^{2+} + S^0 \quad \Delta G_{298K} = -80.6kJ
\]

The two oxidative reactions are thermodynamically more favorable. The nonoxidative dissolution will become the predominant reaction only if the ratio of activities exceeds about 4.0 to 5.0. When this activity ratio is less than 4.0, the kinetics are governed by the oxidative process[51]. Because the value A in our experiments is less than three, the oxidative reaction is predominant in the dissolution of galena. This is consistent with the observation that no H$_2$S smell was detected in the course of the experiments. This result is also in agreement with the findings of other authors. Arai et al[30] previously demonstrated that acid concentrations of <0.5 M had no effect on the rate of galena dissolution in ferric ion media. Dutrizac[50] indicated that ferric ion attack dominates at acid concentrations <3 M, and that acid dissolution, in the presence of 0.3 M ferric ion, became significant only above 3 M acid concentration. Therefore, the change of acid concentration in the low A value range should have no or only a slight effect on the dissolution of galena in ferric solution.

Zinc extraction under the same leaching condition is much lower as shown in Fig.21. At 112 g/l H$_2$SiF$_6$, the zinc extraction is greater than in the two lower acid experiments.
Leaching of Pb from Galena Concentrate at Various Acid Strengths

![Graph showing leaching of lead from galena concentrate at various acid strengths.](image)

**Fig. 21** Leaching of zinc from galena concentrate at various fluosilicic acid concentrations and 45°C.

### 4.5 Effect of Oxidant Fe³⁺ Ion Concentration

Three experiments were performed to find out the dependence of the dissolution rate of lead leaching on the ferric ion concentration in solution. The results are plotted in Fig. 22, which shows lead extraction at ferric concentrations of 25g/l to 45g/l. It can be seen that there is no significant difference between the leaching curves. This
Fig. 22 Leaching of lead from galena concentrate at various Fe$^{3+}$ concentrations and 45°C.

Experimental result is similar to the work reported by Jin et al[74] and Kim et al[51]. Both of groups observed that the order of reaction in the ferric leaching of sulfide minerals was zero at high ferric concentration (roughly 0.6 M). Furthermore, Fuerstenau et al[52] observed that increasing Fe$^{3+}$ concentration resulted in a sharp increase in the rate constant up to about 0.2 M Fe$^{3+}$. Above this value, the rate constant becomes relatively independent of the Fe$^{3+}$ concentration. This observation suggests
that ferric ions play an important role in limiting the reaction rate only at the lower ferric ion concentrations (<0.2 M Fe$^{3+}$). In the more concentrated solutions that could be of commercial interest, the rate is essentially independent of the Fe$^{3+}$ concentration. The ferric ion concentrations of 0.45 to 0.81 M, which were used in this study, are more concentrated than 0.2 M. Therefore, the independence of the rate constant on the concentration of the ferric oxidant during the course of galena leaching in the present experiments is reasonable.

The insensitivity of the leaching reaction to higher concentrations of ferric ion may be attributed to an electrochemical mechanism. At lower concentrations of ferric ion (<0.2M), the oxidizing potential of Fe$^{3+}$/Fe$^{2+}$ increases as the concentration of ferric ion increases. When the concentration of ferric ion increases to a certain extent (about 0.2M), subsequent variation of ferric ion concentration no longer has a significant effect on the Fe$^{3+}$/Fe$^{2+}$ potential on the leaching reaction surface. Hence, the reaction rate due to an electrochemical reaction would be independent of the variation of ferric ion concentration in the leaching solution. An alternative explanation ascribes the results of the insensitivity to an electrochemical reaction involving adsorption of ferric ions[12,51,73]. It is considered likely, the surface sites of the mineral become saturated with ferric ions as the ferric concentration in the solution increases. Once all the active sites have been saturated the leaching rate no longer depends on the ferric concentration.
4.6 Effect of Pb$^{2+}$ Concentration

The initial Pb$^{2+}$ concentration has been considered as an experimental variable for two reasons:

1. The methods used to make ferric fluosilicate lixiviant in these studies include PbO and $SO_4^{2-}$. In order to eliminate $SO_4^{2-}$ from the lixiviant solution, some Pb$^{2+}$ has to be kept in the solution.

2. In closed circuit of commercial production, there would always be a certain amount of Pb$^{2+}$ in the lixiviant solution.

Figs. 23 and 24 indicate that there is almost no effect of initial Pb$^{2+}$ concentration, in the Pb$^{2+}$ concentration range 4.08 to 14.26g/l, in lixiviant, on the lead and zinc extraction during galena leaching with ferric fluosilicate solution. These results agree with Morin’s observation[32] in the experiment on the leaching of galena with a ferric oxidant. He indicated that the presence of lead in solution had no effect upon the reaction kinetics.
Fig. 23 Leaching of lead from galena concentrate at various initial Pb$^{2+}$ concentrations and 45°C, 300 ml lixiviant (Fe$^{3+}$=51.2 g/l, free H$_2$SiF$_6$=32.9 g/l).
4.7 Effect of Pulp Density at Constant Fe³⁺ Concentration

Experiments at various pulp densities have been carried out to find out how high a concentration of Pb²⁺ in the leachate can be reached.
Fig. 25 shows that lead extractions during galena leaching are relatively close for the addition of 5, 15 and 30g galena concentrate. The final lead extractions are all greater than 90%. While the same volume ferric lixiviant reacted with 40g galena concentrate under the same conditions, the lead extraction is lower and less than 90%. This is probably due to depletion of the ferric oxidant before completion of the leaching reaction. The results of zinc extraction are shown in Fig. 26. The zinc extraction expressed as a fractional extraction deceases with increasing pulp density. This may be advantageous with respect to the leaching of bulk concentrates.
Fig. 26 Leaching of zinc from galena concentrate for various pulp densities at 65°C.
Leaching of Pb from Galena Concentrate at Various Pulp Densities

Fig.27 Lead concentration in leachate for various pulp densities at 65°C.

Figs.27 and 28 are plots of concentration vs. time. Fig.27 demonstrates that the lead concentration in the leachate increases as the amount of galena concentrate added to the leaching solution increases. A lead concentration of 90 g/l can be generated by the addition of 40 g galena concentrate to the leach solution. This lead concentration is higher than the 67 g/l which was used in the conventional Betts process for lead electrorefining. It is easy to see that completion of the leaching reaction needs 10 minutes at 5 and 15 g galena concentrate, 20 minutes at 30 g galena concentrate. However, upon the addition of 40 g of galena concentrate the leaching
reaction was not completed in an hour's leaching time. The zinc concentration profile is shown in Fig.28. The greater the addition of galena concentrate, the higher was the zinc concentration in the leachate. The highest zinc concentration is about 0.23g/l, almost 400 times less than the lead concentration in the leachate. The slow zinc leaching reactions did not reach completion before the leaching experiments were terminated.
4.8 Effect of Concentrate Type

Lead concentrates obtained from different mines or even from the same mine at different times, usually have different chemical and/or physical properties. This could result in different leaching kinetics, even under the same leaching condition.

Fig. 29 Leaching of lead from Type 2 concentrate at 45°C.
The fractional lead extraction for Type 2 galena concentrate at three particle size is shown in Fig.29. The extractions of lead are less than 85% and lower than lead extraction for Type 1 galena concentrate. This is probably because there is some oxidized lead sulfate on the mineral surface which could reduce lead conversion. It indicates that different lead extractions during galena leaching could be achieved for different types of galena concentrates.

![Red Dog Concentrate Leaching Results](image)

Fig.30 Results for the leaching of Red Dog concentrate at 45 and 65°C, using 10g concentrate.
Fig. 30 shows Pb/Zn extraction in the Type 3 sulfide concentrate leaching experiment. The lead leaching reaction rate is much faster than that for zinc. The completion of the lead leaching reaction only took about 10 minutes, but the final lead extraction of the Red Dog sulfide concentrate is lower than that for the Pine Point galena concentrates. Type 3 mineral from the Red Dog Mine of Cominco actually is a complex sulfide concentrate. Its properties are closer to sphalerite than galena, because there is more Zn(34.22%) than Pb(23.02%) in the concentrate. Therefore, the leaching behavior of the Red Dog complex sulfide concentrate may be quite different from that of the Pine Point galena concentrates.

4.9 A Proposed Process for Galena Leaching

The results of the present work demonstrated that selective extraction of lead and zinc from the dissolution of lead sulfide concentrates with ferric fluosilicate lixiviant is feasible on a bench scale. The ferric fluosilicate leaching can extract lead rapidly from galena concentrates and has advantages over sulfate and chloride leaching of galena. Based on these findings, a commercial process based on the ferric fluosilicate leaching may be a viable option. A simplified flowsheet for lead production using this leaching approach for galena concentrate is proposed (Fig. 31).

The lead sulfide concentrate is first leached with a ferric fluosilicate solution. The leach slurry is then filtered through a thickener. The residue containing elemental
Fig. 31 A proposed flowsheet for the recovery of lead by the ferric fluosilicate leaching of a galena concentrate.
sulfur and precious metals from the ferric fluosilicate leach is sent for further treatment. The filtrate, which contains all of the dissolved lead and zinc, is purified by adding lead powder to cement Cu, Bi, and Sb from the leach solution.

The clarified leach solution is sent to an electrolytic cell for lead electrowinning. In the electrowinning step, the lead ion is reduced to lead metal on the cathode. The ferrous in the leach solution is oxidized on the anode to regenerate the ferric fluosilicate solution that is recycled for further treatment of the galena concentrate.

Zinc remains in the solution and becomes more and more concentrated with repeated leaching of the concentrate. After the concentration of zinc in the solution reaches a certain limit, in order to remove the zinc ion from the solution, purification of the leach solution is conducted by adding hydrogen sulfide to precipitate zinc sulfide. This process is a closed circuit operation thereby reducing the environmental impact.
CHAPTER 5  Conclusions and Recommendations

5.1 Conclusions

(1) The leaching of Pine Point galena concentrates by ferric fluosilicate solution was studied under various experimental conditions in the temperature range 20 to 95°C. Temperature had a pronounced effect on the rate of dissolution of the concentrates. Leaching of lead is very rapid over the temperature range 38 to 95°C. The reaction rates of the dissolution of galena were controlled by surface chemical reaction. The apparent activation energy of the leaching reaction was calculated to be equal to 62.1 kJ/mol which is consistent with chemical reaction control mechanism.

(2) The elemental sulfur reaction product formed in the leaching of galena concentrate is fairly rough and appears to be quite porous on the particle surface. This kind of non-protective product layer does not inhibit the reaction and results in linear reaction kinetics.

(3) The fluosilicate medium used for leaching may dissociate at high temperatures. There were some white precipitates generated in the course of reactions at above 65°C. This suggested that the operational temperature for the ferric fluosilicate leaching should be kept equal to or less than 65°C.

(4) The contents of Pb\(^{2+}\), H\(^+\), and Fe\(^{3+}\) in the lixiviant do not have a significant effect on the lead extraction under the experimental conditions in the study. These experimental results were also observed by a number of other researchers, working
in chloride and sulfide systems. The insensitivity of the leaching of galena concentrate to the leaching variables probably could be attributed to an electrochemical mechanism.

(5) During the course of the galena leaching, zinc extraction is much lower than lead extraction, especially at temperatures below 65°C. Separation of lead and zinc by a selective leach seems to be feasible and effective. Therefore, the ferric fluosilicate leaching system appears to have a great potential to treat both conventional lead sulfide concentrates and complex sulfide concentrates, such as the McArthur River concentrates in Australia.

(6) The solubility of lead salt in fluosilicate medium is relatively high, and easily meets the concentration requirement of lead for the subsequent aqueous electrowinning operation.

(7) Different lead sulfide ores result in different lead extractions. Any specific complex sulfide ore should be studied to optimize a proper extraction technology.

5.2 Recommendations for Further Work

(1) Fundamental kinetic studies should be conducted to elucidate the characteristics and the mechanism of the dissolution of galena concentrates in ferric fluosilicate lixiviant.
(2) The behavior of sulfide sulfur, which was oxidized mostly to elemental sulfur and partly to sulfate sulfur during the leaching, should be investigated because the sulfate reacts with lead ion generating white precipitates of lead sulfate. This precipitation results in lower lead extraction.

(3) A rotating disk study of the dissolution of crystalline galena should be helpful for obtaining SEM pictures to demonstrate the variation of the mineral surface morphology during the course of the leaching reaction.

(4) More detailed work should be pursued to study the effects of leaching variables of Fe$^{3+}$ and H$^+$ concentration on the ferric fluosilicate leaching of galena concentrates. The studies on the variation of ferric concentration might result in finding the critical point in the ferric concentration, beyond which the leaching rate is independent of the ferric concentration. This unique leaching behavior was observed by several previous researchers in the chloride leaching system. This finding should be studied further to determine the critical concentration (i.e. saturation concentration) of ferric ion in the ferric fluosilicate leaching system.

(5) Further work should be carried out on the dissolution of complex sulfide concentrates (such as complex concentrates from the Red Dog mine or from the McArthur River deposits). It may be possible to recover lead selectively from complex sulfide concentrates, leaving zinc in the leach residue.

(6) Based on the results of this investigation, it is strongly felt that the purification and electrowinning steps in the proposed lead production process, should be studied. Such a study would greatly assist in determining the commercial feasibility of the process.
REFERENCES


APPENDIX A. Examples of the Titration Curves

Figures 32(a,b,c) are examples of the titration curves in the analysis of hydrofluosilicic acid. These titration curves are reproducible. The results of the titrations are given in Table 3. The titrations were carried out according to the following procedure: 1 ml $\text{H}_2\text{SiF}_6$ at unknown concentration was diluted to 200 ml using deionized water, then approximate 0.5 g LiF was added to the solution. This solution was titrated against 0.979 M LiOH solution.

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<td>7.49</td>
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**H$_2$SiF$_6$ Titration against LiOH with addition of LiF**

![Graph](image)

**Fig.32a** $H_2SiF_6$ titration curves for sample 1.
Fig. 32b  $\text{H}_2\text{SiF}_6$ titration curves for sample 2.
Fig. 32c  \( \text{H}_2\text{SiF}_6 \) titration curves for sample 3.
APPENDIX B. Tables of Experimental Data

Table 4. The effect of stirring speeds on Pb extraction at 45°C.

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Table 5. The effect of temperature on Pb and Zn extraction at 20°C.

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Table 6. The effect of temperature on Pb and Zn extraction at 30°C.

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Table 7. The effect of temperature on Pb and Zn extraction at 38°C.

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Table 8. The effect of temperature on Pb and Zn extraction at 45°C.

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Table 9. The effect of temperature on Pb and Zn extraction at 65°C.

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Table 10. The effect of temperature on Pb and Zn extraction at 85°C.

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Table 11. The effect of temperature on Pb and Zn extraction at 95°C.

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Table 12. The effect of galena particle sizes on Pb extraction at 35°C.

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<td>Pb%(140x170)</td>
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Table 13. The effect of H₂SiF₆ on Pb and Zn extraction at initial free H₂SiF₆=45 g/l.

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Table 14. The effect of H$_2$SiF$_6$ on Pb and Zn extraction at initial free H$_2$SiF$_6$=66.7 g/l.

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Table 15. The effect of H$_2$SiF$_6$ on Pb and Zn extraction at initial free H$_2$SiF$_6$=112 g/l.

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Table 16. The effect of Pb$^{2+}$ concentration on Pb and Zn extraction at Pb$^{2+}$=4.08 g/l.

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Table 17. The effect of Pb$^{2+}$ concentration on Pb and Zn extraction at Pb$^{2+}$=7.90 g/l.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
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<th>3</th>
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<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(min)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Pb%</td>
<td>16.33</td>
<td>46.16</td>
<td>82.56</td>
<td>88.14</td>
<td>96.98</td>
<td>92.29</td>
</tr>
<tr>
<td>Zn%</td>
<td>4.46</td>
<td>4.80</td>
<td>5.15</td>
<td>7.04</td>
<td>7.85</td>
<td>7.22</td>
</tr>
</tbody>
</table>

Table 18. The effect of Pb$^{2+}$ concentration on Pb and Zn extraction at Pb$^{2+}$=14.26 g/l.

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Time(min)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Pb%</td>
<td>17.51</td>
<td>45.00</td>
<td>75.55</td>
<td>88.46</td>
<td>98.32</td>
<td>97.71</td>
</tr>
<tr>
<td>Zn%</td>
<td>4.52</td>
<td>5.12</td>
<td>5.28</td>
<td>5.80</td>
<td>6.61</td>
<td>7.41</td>
</tr>
</tbody>
</table>
Table 19. The effect of various Fe$^{3+}$ concentrations on Pb extraction.

<table>
<thead>
<tr>
<th>Samples</th>
<th>1</th>
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<th>3</th>
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<th>5</th>
<th>6</th>
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</thead>
<tbody>
<tr>
<td>Time(min)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Pb% (Fe$^{3+}$=25g/l)</td>
<td>13.36</td>
<td>31.60</td>
<td>65.37</td>
<td>86.95</td>
<td>96.51</td>
<td>96.04</td>
</tr>
<tr>
<td>Pb% (Fe$^{3+}$=35g/l)</td>
<td>16.67</td>
<td>40.87</td>
<td>71.55</td>
<td>87.61</td>
<td>93.91</td>
<td>94.66</td>
</tr>
<tr>
<td>Pb% (Fe$^{3+}$=45g/l)</td>
<td>19.59</td>
<td>43.09</td>
<td>72.60</td>
<td>89.44</td>
<td>93.92</td>
<td>96.12</td>
</tr>
</tbody>
</table>

Table 20. The effect of pulp density on Pb and Zn extraction at 15 g galena.

<table>
<thead>
<tr>
<th>Samples</th>
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<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(min)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
</tr>
<tr>
<td>Pb$^{2+}$(g/l)</td>
<td>29.48</td>
<td>36.98</td>
<td>37.82</td>
<td>37.68</td>
<td>38.83</td>
</tr>
<tr>
<td>Zn$^{2+}$(g/l)</td>
<td>0.04855</td>
<td>0.05755</td>
<td>0.07315</td>
<td>0.08955</td>
<td>0.1190</td>
</tr>
<tr>
<td>Pb%</td>
<td>74.14</td>
<td>94.07</td>
<td>96.29</td>
<td>95.93</td>
<td>98.97</td>
</tr>
<tr>
<td>Zn%</td>
<td>4.69</td>
<td>5.56</td>
<td>7.07</td>
<td>8.65</td>
<td>11.49</td>
</tr>
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</table>
Table 21. The effect of pulp density on Pb and Zn extraction at 30 g galena.

<table>
<thead>
<tr>
<th>Samples</th>
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<th>5</th>
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</thead>
<tbody>
<tr>
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<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
</tr>
<tr>
<td>Pb$^{2+}$(g/l)</td>
<td>48.76</td>
<td>66.32</td>
<td>75.99</td>
<td>77.19</td>
<td>77.78</td>
</tr>
<tr>
<td>Zn$^{2+}$(g/l)</td>
<td>0.0948</td>
<td>0.1178</td>
<td>0.1363</td>
<td>0.1589</td>
<td>0.1961</td>
</tr>
<tr>
<td>Pb%</td>
<td>62.69</td>
<td>86.02</td>
<td>98.87</td>
<td>100.0</td>
<td>100.0</td>
</tr>
<tr>
<td>Zn%</td>
<td>4.56</td>
<td>5.69</td>
<td>6.58</td>
<td>7.68</td>
<td>9.47</td>
</tr>
</tbody>
</table>

Table 21
2. The effect of pulp density on Pb and Zn extraction at 40 g galena.

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>Time(min)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
</tr>
<tr>
<td>Pb$^{2+}$(g/l)</td>
<td>57.10</td>
<td>75.63</td>
<td>85.98</td>
<td>90.50</td>
<td>95.35</td>
</tr>
<tr>
<td>Zn$^{2+}$(g/l)</td>
<td>0.1155</td>
<td>0.1383</td>
<td>0.1606</td>
<td>0.1803</td>
<td>0.2296</td>
</tr>
<tr>
<td>Pb%</td>
<td>55.33</td>
<td>73.79</td>
<td>84.11</td>
<td>88.61</td>
<td>93.44</td>
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<tr>
<td>Zn%</td>
<td>4.18</td>
<td>5.01</td>
<td>5.82</td>
<td>6.53</td>
<td>8.32</td>
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</table>
Table 23. Pb extraction of type 2 galena at various particle sizes and 38°C.

<table>
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<tbody>
<tr>
<td>Time(min)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Pb%(80x100)</td>
<td>13.14</td>
<td>22.91</td>
<td>45.98</td>
<td>58.71</td>
<td>70.95</td>
<td>79.63</td>
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<tr>
<td>Pb%(270x200)</td>
<td>14.80</td>
<td>37.47</td>
<td>65.60</td>
<td>79.31</td>
<td>79.32</td>
<td>80.20</td>
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<tr>
<td>Pb%(270x325)</td>
<td>16.21</td>
<td>40.42</td>
<td>70.89</td>
<td>81.72</td>
<td>80.77</td>
<td>81.69</td>
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</table>

Table 24. Pb and Zn extraction on leaching of Red Dog concentrate at 45°C.

<table>
<thead>
<tr>
<th>Samples</th>
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<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(min)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Pb%</td>
<td>61.69</td>
<td>68.80</td>
<td>69.10</td>
<td>70.00</td>
<td>70.13</td>
<td>71.72</td>
</tr>
<tr>
<td>Zn%</td>
<td>1.54</td>
<td>2.22</td>
<td>3.43</td>
<td>5.17</td>
<td>8.15</td>
<td>10.93</td>
</tr>
</tbody>
</table>
Table 25. Pb and Zn extraction on leaching of Red Dog concentrate at 65°C.

<table>
<thead>
<tr>
<th>Samples</th>
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<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time(min)</td>
<td>5</td>
<td>10</td>
<td>20</td>
<td>35</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>Pb%</td>
<td>68.85</td>
<td>69.07</td>
<td>72.24</td>
<td>75.03</td>
<td>75.20</td>
<td>76.52</td>
</tr>
<tr>
<td>Zn%</td>
<td>3.97</td>
<td>6.84</td>
<td>11.52</td>
<td>16.60</td>
<td>25.20</td>
<td>32.92</td>
</tr>
</tbody>
</table>