

# Dissolution Characteristics of Galena in Aqueous Ferric Nitrate Lixiviant

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## Abstract

The dissolution characteristics of galena in ferric nitrate system  $[(\text{FeNO}_3)_3\text{-1M NaNO}_3]$  has been studied function of ferric ion concentration, temperature and particle size. All reactions were conducted in a constant temperature bath thermostatically controlled between temperatures of 0 and 100°C. Apart from the determination of the dependence of leaching rate on particle size, uniform particle size of 20 x 40 mesh was used throughout the experiment. Generally leaching rate was seen to increase with increase in temperature and ferric ion concentration but decreased with increase in particle size. The reaction kinetics show that chemical reaction, attributed to electrochemical oxidation of sulphide and reduction of ferric ion occurring at the reaction interface, is the controlling mechanism. The reaction order was 0.47 and the activation energy obtained was 47.87kJ/mole. At all concentrations of nitrate ions, there was no evidence of formation of insoluble salts as is prevalent in ferric chloride systems.

Keywords: Leaching, Ferric Nitrate, Lixiviant, Hydrometallurgy, Pyrometallurgy, film diffusion, Product layer, Chemical reaction.

## 1. INTRODUCTION

The environmental acceptability of hydrometallurgical over pyrometallurgical processes has remained the major driving force spurring the increasing research interests in the area despite the attendant slow recovery rate. Hydrometallurgy also permits recovery of metals from lower grade feedstock and produces a means of processing complex concentrates that otherwise cannot be handled simply or economically by pyrometallurgical processing [1].

Leaching, a step in hydrometallurgical operations involves contacting a material containing a valuable metal with aqueous solution containing a lixiviant. The lixiviant

may be acidic or basic in nature. The type and concentration of the lixiviant is usually controlled to allow some degree of selectivity for the metal or metals that are to be recovered [2]. Leaching is conducted with an aqueous solution in which there is a solubility of the dissolving mineral or compound in the material being leached sufficient to obtain an acceptable concentration of valuable metal in solution. On the other hand, it is important that in the same solution, the waste materials and compounds being rejected by the leaching reaction should have solubility low enough to yield an acceptable separation of valuable and gangue minerals during the leaching and to obtain a leach solution of acceptable purity for subsequent metal extraction [3]

Leaching reagents used conventionally had been water, acids and alkaline liquors capable of converting metals to soluble salts. Oxidised ores; including oxides, silicates, carbonates, hydroxides and chlorides are dissolved effectively with iron oxidising acids or a base like ammonia that form soluble complexes [4]. This explains why oxidising, chloridising or sulphating roasting are used to convert recalcitrant sulphides to oxides, chlorides or sulphates prior to leaching [5]

The quest for hydrometallurgical processing of metals is evident in the lead producing industries where the conventional pyrometallurgical route has the attendant problem of producing  $\text{SO}_2$  gases. This requires sophisticated gas treatment facilities to protect the environment. Present research interests aim at reducing or completely eliminating the production of this environmental pollutant. One of the promising technologies is concerned with preventing  $\text{SO}_2$  formation by removing elemental sulphur [1; 6]

Sulphur is easier to handle and store and can be shipped more economically than sulphuric acid. This study aims at establishing the leaching characteristics of galena in ferric

nitrate solution in view of recovering lead from galena through hydrometallurgical route.

## 2. EXPERIMENTAL MATERIALS AND PROCEDURE

### 2.1 Materials

The galena sample used in this study was collected from the deposit at Enyimgba, Abakaliki, Ebonyi State, Nigeria. The samples were obtained in lumps of about 500mm, crushed and galena cubes isolated from the gangue by careful hand picking. The samples were further crushed and sized into fines 80 x 100 mesh, 60 x 80 mesh, 40 x 60 mesh, 20 x 40 mesh, 10 x 20 mesh and oversize. This range of particle size was used throughout the experiment. Based on the atomic absorption spectrometric analysis carried out, the samples used contained 86.55% Pb.

The chemicals used in the study were of reagent grade. They include  $\text{Fe}(\text{NO}_3)_3$ , HCl, and  $\text{NaNO}_3$  all obtained from commercial laboratories. All aqueous solutions were made in distilled water, distilled out from standard distillation plants.

### 2.2 Procedure

For the  $\text{Fe}(\text{NO}_3)_3$  system studied, the effect of size was eliminated as a variable except for the determination of the dependence of leaching rate on particle size. Uniform particle size of 20 x 40 mesh was therefore used for most of the experiments. The following procedure was adopted in each test:

Desired leaching solution (lixiviant) was prepared and poured into the reaction vessel. The vessel with the leaching solution was placed in the water bath to attain the desired temperature. Once the temperature was reached, stirring commenced and galena sample was introduced. In all the experiments, 0.5g each of galena was leached in 500mls solution which was equivalent to 1g of galena in 1 litre of solution. A 5mls sample of the solution was withdrawn at predetermined time intervals and filtered. 2mls of the stock solution was further diluted to 100mls and sampled for analysis.

## 3. EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 Results

The rate at which leaching was proceeding was first studied as a function of

ferric ion concentration. This is shown in figure 1

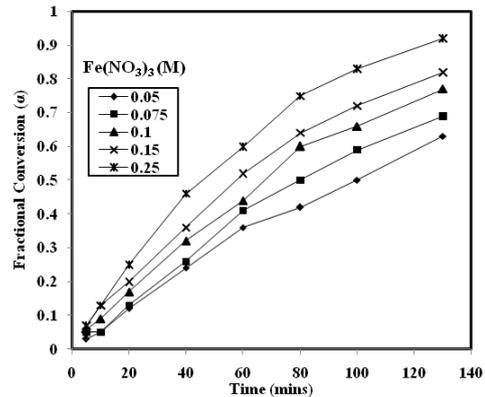


Fig. 1: Effect of ferric nitrate concentration on variation of fractional conversion of 20 x 40 mesh galena with time at 50°C. pH = 1.0 - 1.8

It can be observed that there was an increase in the rate of conversion of lead with  $\text{Fe}^{3+}$  concentration.

The effect of temperature on the rate of dissolution was also studied as can be seen in Figure 2. After 100 minutes of leaching in the presence of 0.1M  $\text{Fe}(\text{NO}_3)_3$ , about 24% of the galena dissolved at 30°C while complete dissolution was achieved at 70°C for the same length of time.

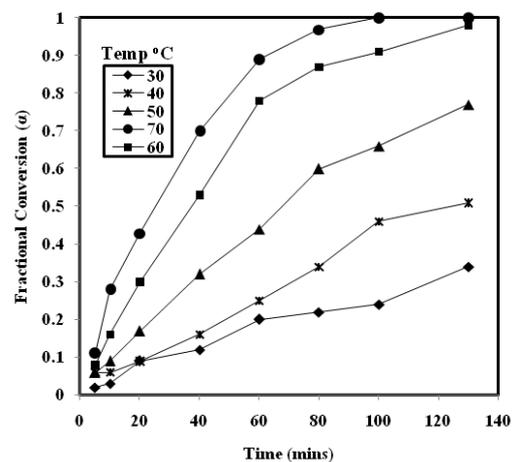


Fig. 2: Effect of temperature on fractional conversion of 20 x 40 mesh galena with 0.1M  $\text{Fe}(\text{NO}_3)_3$ . pH = 1.0 - 1.8

Next, the rate of dissolution of galena was established as a function of particle size (Figure 3). The rate of dissolution increased substantially with decrease in particle size or increase in surface area. After two hours of leaching with 0.1M  $\text{Fe}(\text{NO}_3)_3$  at 50°C, 70% of 20 x 40 mesh particles were dissolved while complete dissolution was achieved for particle

size of 60 x 80 mesh under the same conditions

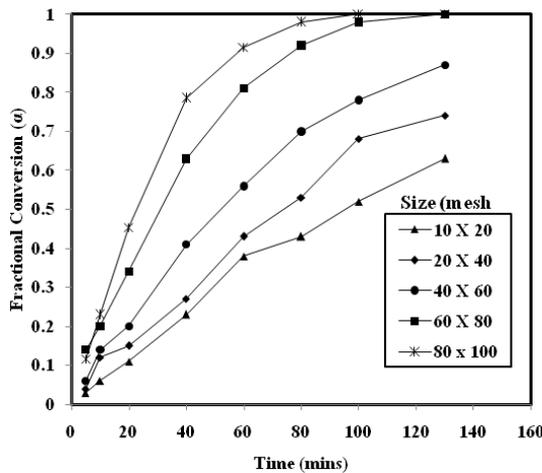


Fig. 3: Effect of particle size on fractional conversion of galena with 0.1M Fe(NO<sub>3</sub>)<sub>3</sub> at 50°C

### 3.2 Discussion

The mechanism likely to control the leaching of cubic samples like the galena under study is either of the following: film diffusion, product layer diffusion, or chemical reaction at the solid liquid interface. Shrinking core models for a cubic system for each of these three mechanisms of leaching are as follows [7; 8; 9]

For film diffusion mechanism

$$\frac{t}{t_{comp}} = \alpha \quad (1)$$

$$t_{comp} = \frac{\rho_B R}{3bk_m C_{Ab}} \quad (2)$$

For product layer diffusion mechanism,

$$\frac{t}{t_{comp}} = [1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)] \quad (3)$$

$$t_{comp} = \frac{\rho_B R}{6bD_e C_{Ab}} \quad (4)$$

For Chemical reaction mechanism

$$\frac{t}{t_{comp}} = 1 - (1 - \alpha)^{1/3} \quad (5)$$

$$t_{comp} = \frac{\rho_B R}{3bk_r C_{Ab}} \quad (6)$$

where:

- t = time of reaction.
- t<sub>comp</sub> = time to complete reaction which is equivalent to t when α = 1
- ρ<sub>B</sub> = molar density of solid reactant (B).

- b = stoichiometric coefficient of B.
- k<sub>b</sub> = mass transfer coefficient.
- C<sub>Ab</sub> = concentration of A in the bulk solution.
- α = fractional conversion;
- l = edge of cube.
- D<sub>e</sub> = effective diffusion coefficient.
- K<sub>r</sub> = heterogeneous reaction rate constant.

To establish the reaction mechanisms for the systems under study, let us consider the equation for:

### 1. Film diffusion controlled mechanism

$$\frac{t}{t_{comp}} = \alpha$$

If film diffusion is the controlling mechanism, it should be expected that plots of fractional conversion (α) vs time of reaction (t) would give straight lines, with slopes equal to 1/t<sub>comp</sub> and passing through the origin. These plots were made in figures 1 to 3. Since none of these plots satisfy the above conditions, they rule out the possibility of film diffusion being the controlling mechanism.

### 2. Product layer controlled mechanism

$$\frac{t}{t_{comp}} = [1 - 3(1 - \alpha)^{2/3} + 2(1 - \alpha)]$$

To ascertain whether product layer is the controlling mechanism, plots of 1 - 3(1 - α)<sup>2/3</sup> + 2(1 - α) vs. time were made. If product layer diffusion is the controlling mechanism, the plots would give straight lines with slope = 1/t<sub>comp</sub>. The plots of figures 4 – 6 rule out the possibility of product layer diffusion as the controlling mechanism

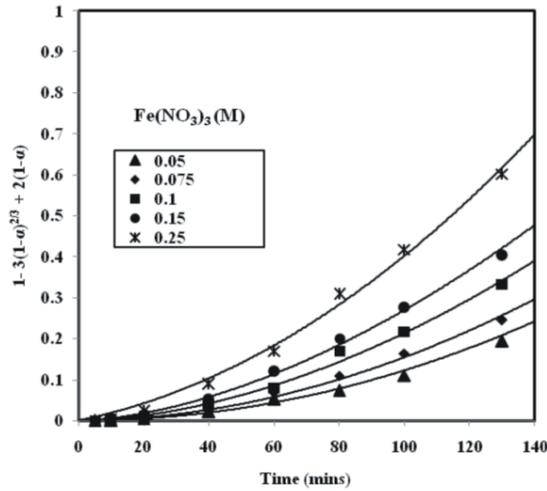


Fig. 4:  $1 - 3(1-\alpha)^{2/3} + 2(1-\alpha)$ ; Product layer diffusion control vs leaching time for various ferric nitrate concentrations.

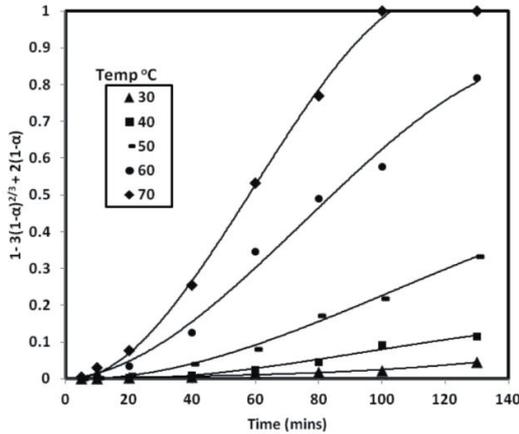


Fig. 5:  $1 - 3(1-\alpha)^{2/3} + 2(1-\alpha)$  Product layer diffusion control vs leaching time at various temperatures

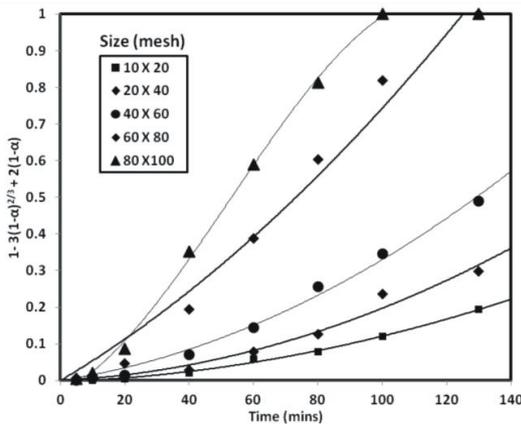


Fig. 6:  $1 - 3(1-\alpha)^{2/3} + 2(1-\alpha)$ ; Product layer diffusion control vs leaching time for various particle sizes.

## 2. Chemical reaction controlled mechanism

$$\frac{t}{t_{\text{comp}}} = 1 - (1 - \alpha)^{1/3}$$

If chemical reaction is the controlling mechanism, a plot of  $1 - (1 - \alpha)^{1/3}$  vs. time would yield a straight line of slope equal to  $1/t_{\text{comp}}$ . This is observed at all temperatures concentrations and particle sizes studied as shown in figures 7 – 9.

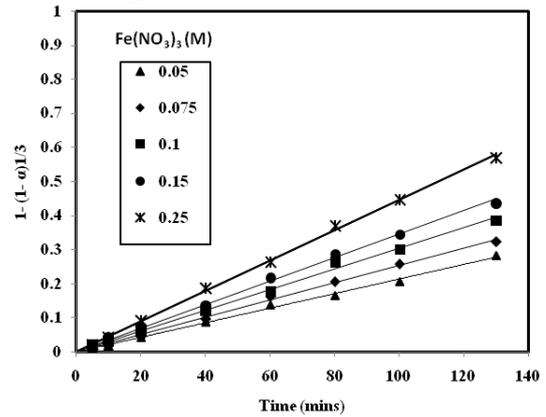


Fig. 7:  $1 - (1 - \alpha)^{1/3}$ ; Chemical reaction control vs leaching time for various ferric nitrate concentrations.

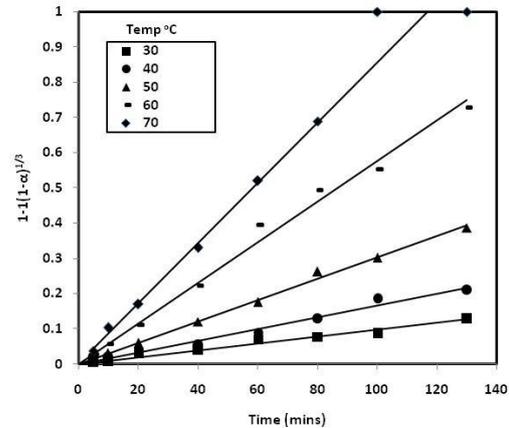


Fig. 8:  $1 - (1 - \alpha)^{1/3}$ ; Chemical reaction control vs leaching time for various temperatures

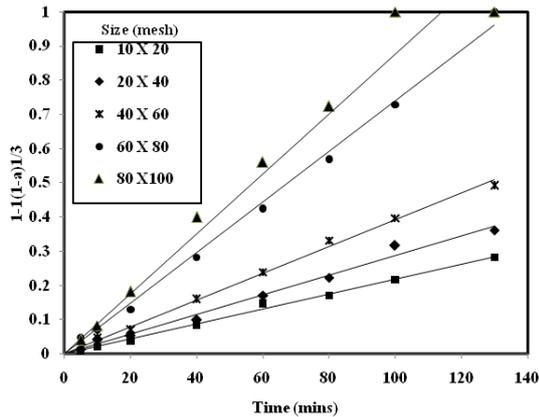
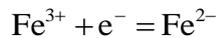
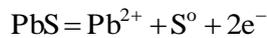


Fig. 9:  $1 - (1 - \alpha)^{1/3}$ ; Chemical reaction control vs leaching time for various particle sizes.

This reaction mechanism observed could be attributed to electrochemical oxidation of sulphide and reduction of ferric ions occurring at the reaction interface. There is electron exchange at this interface and since nitrate does not complex ferric ion, the cathodic reaction is the reduction of ferric ions to ferrous ions as follows:



The anodic reaction would be



### Effect of Temperature

When temperature was considered as a process variable the increase in the recovery of lead with temperature was clearly evident. Such findings have been reported by many authors [1; 5; 6]. The recovery of lead in ferric nitrate system however was higher than that observed in systems like FeCl [8; 9]. This could be attributed to the fact that lead nitrate does not have the solubility problem which reduces the efficiency of ferric chloride as an oxidant for galena leaching.

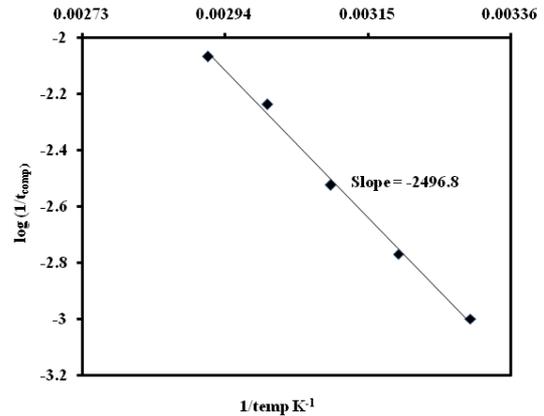


Fig. 10: An Arrhenius plot for the leaching of 20 x 40 mesh galena with 0.1M Ferric Nitrate

An Arrhenius plot (Figure.10) was made for the system under study which gave an activation energy of 47.63 kJ/mole as follows:

$$R = Ae^{-E/RT} \quad (7)$$

where

K = rate constant =  $1/t_{\text{comp}}$

A = constant

E = Activation energy

R = Gas constant =  $1.987 \times 10^{-3}$  kcal/mole °C

$$\ln K = \ln A - \frac{E}{RT}$$

$$\log K = \log A - \frac{E}{2.303RT}$$

$$\log \frac{1}{t_{\text{comp}}} = \log A - \frac{E}{2.303RT} \quad (8)$$

A plot of  $\log(1/t_{\text{comp}})$  vs  $1/T$  yields a straight line whose slope =  $-E/2.303R$ .

$1/t_{\text{comp}}$  values were obtained from the slopes of  $1 - (1 - \alpha)^{1/2}$  vs. time (Figure. 8).

The slopes of  $\log(1/t_{\text{comp}})$  vs  $1/T$  plotted in figure 10 is 2496.8. This implies that for ferric nitrate system,

$$-2497 = -\frac{E}{2.303R}$$

$$E = 2497 \times 2.303 \times 1.9787 \times 10^{-3}$$

$$= 11.38 \text{ kcal/mole} = 47.63 \text{ kJ/mole}$$

This value is consistent with chemical reaction control mechanism. It is known that activation energy below 20.9 kJ/mole is characteristic of diffusional process. Nunez et al [11] obtained activation energy of 48.5 kJ/mole for the leaching of galena in hydrochloric acid chloride solution. The result

in this study is less than that of the earlier work by a factor of 0.87. Ngoc et al [12] also leached an off-grade complex copper concentrate and the activation energy they obtained is less than that of this work by a factor approximately of 12.06. Due to the low activation energy recorded by Ngoc et al, it was not possible for them to establish a definite conclusion on the mechanism of the reaction. They observed a linear rate law indicative of chemical control, but as low as 15.8 kJ/mole activation energy values (similar to diffusion control).

### Effect of Particle size

As the particle sizes of galena decreased there was an increase in the amount of lead dissolved with time. This is in agreement with the reports of several other researchers [6; 7; 10]. When compared with ferric chloride system earlier studied, there is higher increase in recovery with  $\text{Fe}(\text{NO}_3)_3$  system than with ferric chloride system.

The higher recovery in ferric nitrate system may be explained in relation to the formation of insoluble lead chloride in the ferric chloride system. To further confirm whether chemical reaction is the controlling mechanism let us consider the equation for chemical reaction controlled mechanism as follows:

$$t_{\text{comp}} = \frac{6\rho l}{bK_r C_{AB}}$$

Symbols have their usual meanings.

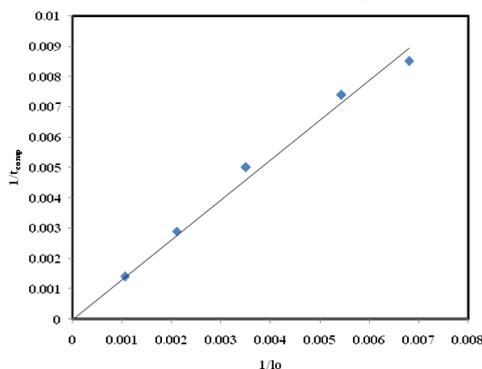


Fig. 11: Plot of  $1/t_{\text{comp}}$  vs inverse initial particle size for the leaching of galena in ferric nitrate lixiviant

If chemical reaction is the controlling mechanism, a plot of  $1/t_{\text{comp}}$  vs. inverse initial particle size ( $1/l_0$ ) will give a straight line passing through the origin. As shown in Figure

11 this phenomenon is observed for ferric nitrate systems studied.

### Order of Reaction

Rate of chemical reaction in systems similar to the one under study is given by

$$R = K[A_0]^n \quad (9)$$

where

R = Rate of reaction

K = Specific reaction rate constant

A = Concentration of the reacting species

n = Order of reaction

$$\log R = \log K + n \log [A_0] \quad (10)$$

But

$$\text{rate} \propto 1/t_{\text{comp}}$$

$$\therefore \log(1/t_{\text{comp}}) \propto \log K + n \log [A_0]$$

$$\log t_{\text{comp}} = \text{constant} - n \log [A_0] \quad (11)$$

Marching the above expression with the system under study we have

$$\log [t_{\text{comp}}] = K' - n \log [\text{Fe}^{3+}] \quad (12)$$

A plot of  $\log t_{\text{comp}}$  vs  $-\log [\text{Fe}^{3+}]$  would give a straight line with intercept  $K'$  and slope  $n$ . Such plot for the system under study is shown in Figure 12. The calculated order of reaction is 0.47

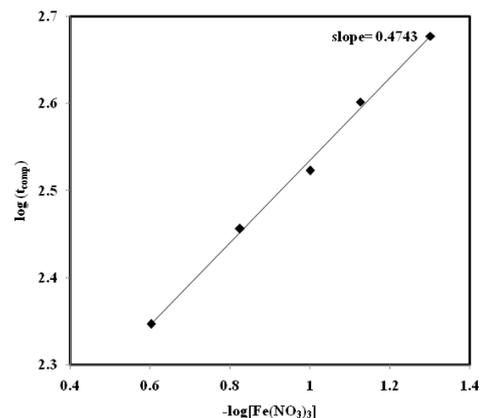


Fig. 12: Relationship between the logarithm of  $t_{\text{comp}}$  and  $-\log[\text{Fe}(\text{NO}_3)_3]$

### 4.0 SUMMARY

The results obtained from the leaching of galena in ferric nitrate system can be summarized as follows:

1. Chemical reaction is observed to be the controlling mechanism under all conditions

studied.

2. Electrochemical oxidation of sulphide and reduction of ferric ion were suspected to occur at the reaction interface during the leaching process.
3. From Arrhenius plot, the apparent activation energy in ferric nitrate leaching of galena is 47.63kJ/mole
4. The dependence of leaching rate on the total ferric ion concentration is of the order of 0.47

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