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Technical Note

Dissolution of galena with acidified hypochlorous acid in excess chloride solution

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ABSTRACT

A study of the dissolution of lead from powdered galena ore using acidified hypochlorous acid in excess chloride has been investigated. The effect of acid concentrations ranging from 10-33.8%, in temperatures between 30-50°C, speed of agitation in the range of 300-600rpm and particle size of between 100-300μm on galena dissolution are reported. The dissolution is significantly influenced by the concentration of hypochlorous acid but temperature of the reactions and size of particles has an inverse relation. The increase in speed of agitation is independent on the dissolution of the galena sample. The apparent activation energy is found to be 45.0kJ/mol suggesting the reaction is chemical control at the surface of the particles.

Keywords: Hydrometallurgy; Galena; Hypochlorous acid

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1. INTRODUCTION

As high-grade easily concentrated ores are becoming scarcer, lower grade ores have been recently used by the metal industry to meet world demands. Lead is produced from concentrates of sulphide ores of galena. The convectional hydrometallurgical process for the extraction of lead from a mixed sulphide concentrate consists of catalytic sulphation roasting, acidic leaching of the metallic values, solvent extraction and selective stripping (Ekinci *et al.*, 1998). Although the method has been established for many years, direct leaching of the concentrate eliminate roasting step, and thus has some advantages, mainly that elemental sulphur is produced rather than sulphur dioxide, a gaseous pollutant. Also high extraction of the base metals may be achieved as insoluble highly ordered; thermodynamically sTable mattes are not formed. However a high oxidation potential is required for the dissolution of sulphide (Habashi, 1978; Biswas, 1991; Gosh and Ray, 1991).

The Falconbridge chloride leach process for extraction of nickel and cobalt from matte opened a new chapter in the application of chlorine metallurgy for the extraction of metals (Houqen, 1975; Stensholt, 1996). Direct chlorination of nickel sulphide concentrates, as well as of the complex sulphides of copper, nickel, iron, has been investigated by several authors (Hohn, 1958; Pilgrim and Ingrahm, 1967; Smith and Wasaki, 1985). Jackson and Strickland (1967) studied the kinetics of dissolution of some common sulphide minerals including chalcopyrite, pyrite, sphalerite and galena in chlorine- saturated water. With all except galena, the consumption of dissolved chlorine by the sulphides was found to follow a first-order reaction and in the case of galena, to be transport controlled. For all the minerals studied, the activation energy was reported to be 20.50kJ/mole in the temperature range of 40-60°C. Ekinci *et al.* (1998) have investigated the use of chlorine-saturated water in the leaching kinetics of sphalerite with pyrite. They found that the dissolution of sphalerite increase with stirring speed, gas flow- rate and decrease with particle size. They also found that leaching rates for both zinc and iron are controlled by diffusion through product layer. The activation energy for sphalerite is 22.68kJ/mole. The activation energies for pyrite are 43.28kJ/mole in the temperature range of 12-20°C and 8.37kJ/mole in the temperature range of 30-60°C, respectively.

Hypochlorous acid is an effective oxidizing agent, with oxidation potential of 1.63V at low pH (Cotton and Wilkinson, 1976). Commercial hypochlorous acid composes as much 35% free chlorine as aqueous solution. There has been no report of the use of hypochlorous acid in dissolution of minerals and on

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consideration of the redox potential; we decided to carry out preliminary studies on its leaching potential. The present investigation was to establish optimum conditions for the dissolution of lead from a Nigerian galena.

2. EXPERIMENTAL

2.1. Materials

The galena used in these experiments was obtained from an ore deposit at Nasarawa state, Nigeria. The ore was concentrated by flotation and sieved by using ASTM standard sieves. The chemical analysis was carried out by using gravimetric method to determine the major elements (Furman, 1963) and AAS for the minor and some trace elements. The percentage chemical composition is given in Table1.

Table1
Percentage elemental composition of the sample

Element	Composition, %
Pb	32.40
Cu	0.12
Fe	0.78
S	29.20
SiO_2	24.20
N.D.*	20.09
Total	100.00

* N.D - Not determined

2.2. Equipment and experimental technique

The leaching experiments were carried out in a glass reactor (250ml) equipped with a mechanical stirrer. It was heated with constant temperature heating mantle within a temperature in the range of ±0.5°C. 50cm^3 of hypochlorous acid, 50cm^3 of the hydrochloric acid and sodium chloride was charged into the reactor. After the desired temperature had been reached, a 1.0g of the galena concentrate was introduced while the content of the reactor was stirred at certain speed. At certain intervals 2cm^3 of the aliquot was then withdrawn and diluted to 25cm^3 in a standard flask and analysed for lead using AAS.

Table 2
Experimental conditions for the leaching of lead from galena

Quantity	Values
Temperature, °C	30, 35, 40*, 45, 50
Concentration of HOCl, %	10, 15, 20 33.8*
Sodium chloride	3.0mol/l*
Hydrochloric acid	2.0mol/l*
Stirring speed,rpm	300*, 400, 500, 600
Particle size, μm	100, 150*, 200, 300

* The values kept constant

The experimental conditions are summarised in Table 2. This involves varying one condition while keeping others constant. Some of these conditions studied include temperature, concentration of hypochlorous acid, stirring speed and particle size.

3. RESULTS AND DISCUSSION

3.1. Dissolution process

Dissolution of complex sulphide minerals has been investigated and reported, it has been found that sulphide/sulphur reacts with chlorine in two stages. In the first stage, the sulphide is converted to S° and in the second stage S° is converted to sulphate (Burkin, 1966; Habashi, 1969; Peters, 1973; Ekinci,1998; Copur, 2001).The dissolution of sulphide by chlorine has been described by Jena and Brocchi (1992) to be adsorption in nature. The work described the reaction as shown in the reaction.

$$PbS_{(s)} + 2HOCl_{(aq)} \longleftrightarrow PbS \cdot (ClOH)_2 + 2H^+ \rightarrow PbCl_{2(s)} + S^o + H_2O \tag{1}$$

The lead chloride formed reacts with excess chloride to form lead chloride complex, which is soluble in aqueous medium.

$$PbCl_{2(s)} + 2Cl^-_{(aq)} \rightarrow PbCl^{2-}_{4(aq)} \tag{2}$$

The choice of 3.0M hydrochloric acid and 2.0M sodium chloride follows the report of Ipinmoroti (1993), Yadav and Khopkar (1971) for complexation of the base metal ions which effect their dissolution by giving sufficient background concentration of chloride to maintain a relative constant ionic strength of the solution.

3.2. Effects of parameters

The quantities presented in Table 2 are measured against the conversion fraction of lead, which is defined as follows:

$$X = \frac{the\ amountof\ dissolved\ Pb}{the\ amount\ of\ Pb\ in\ the\ sample}$$

Results are presented in the form X versus time in Figure 1–4.

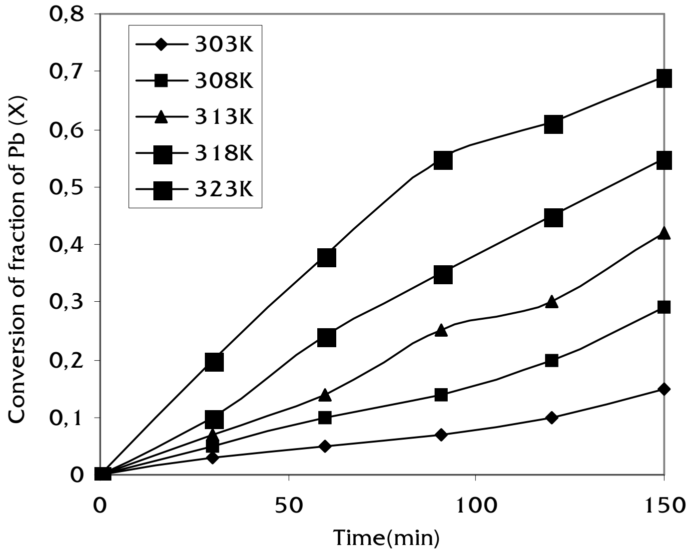

Figure 1. The variation of conversion of fraction of Pb with time at various temperature

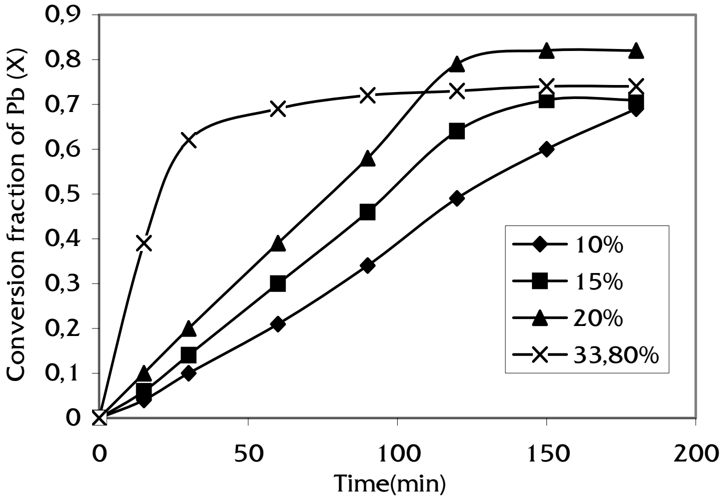

Figure 2. The variation of conversion of fraction of Pb with time at various concentration of HOCl

Figure 1 shows that increases in temperature of the reaction system has a positive effect on the dissolution rate. The effect of hypochlorous acid concentration given in Figure 2 showed that the dissolution rate increased with increase in leachant concentration.

The parabolic nature of the curve at concentration of 33.8% was probably due evolution of free chlorine at higher concentration. The effect of particle size on the dissolution process (Figure 3) shows that particle size has inverse relation to dissolution rate. This is due to more surfaces being exposed as the particle size is reduced. The effect of speed of agitation on the dissolution of galena shown in Figure 4 shows that the dissolution rate is practically independent of the stirring speed.

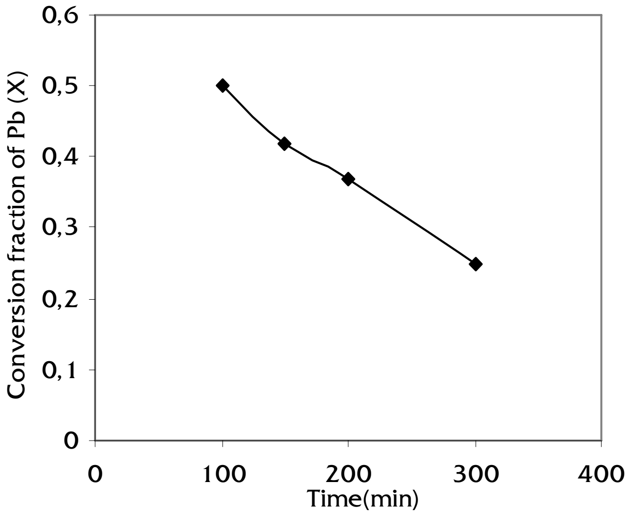

Figure 3. The effect of change of particle size (μm) on dissolution of galena with HOCl

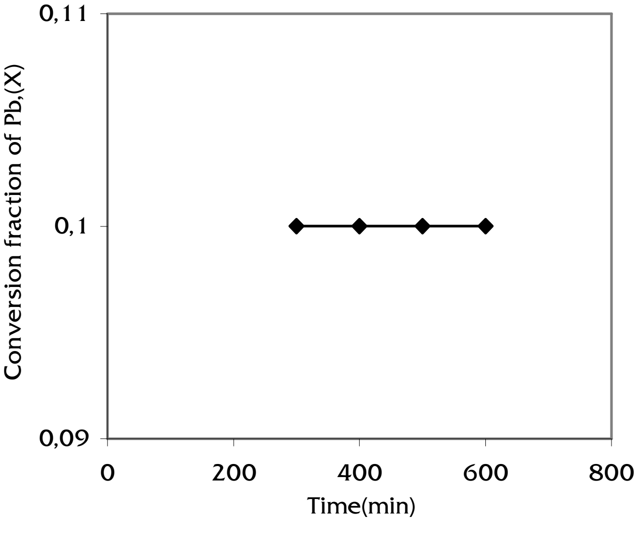

Figure 4. The effect of speed of agitation (rpm) on the dissolution of galena with HOCl

3.3. Kinetics analysis

According to the unreacted-core model, if a reaction such as

$$aA \text{ (fluid)} + bB\text{(solid)} \longrightarrow \text{products} \quad (3)$$

is controlled by diffusion through product layer, the integrated rate equation is given as

$$1-3(1-X)^{2/3}+2(1-X)=\frac{6bDC_A}{C_B R^2}t \quad (4)$$

If the reaction given in equation (3) is chemically controlled then the integral rate expression becomes

$$1-(1-X)^{1/3}=\frac{bkC_A}{C_B R}t \qquad (5)$$

where X is the reacted fraction; t, the time(s); C_B, the average apparent concentration of the ore (mol/m^3); R, the radius of the solid particle(μm); b, the stochiometric coefficient of the solid reacting with 1 mol of gas; k, the rate constant for surface reaction (m/s); D, diffusion coefficient (m^2/s); and C_A, the concentration of the hypochlorous acid (mol/m^3).

Plots of the equation 4 and 5 as a function of time were examined for the leaching of the ore at temperature between 30–60°C. Plot of equation 6 gives the best straight line (Figure 5), which shows that the dissolution process is chemical control. The rate constant of the experimental plots from Figure 1 were determined and plotted against $^1/_T$ shown Figure 6.

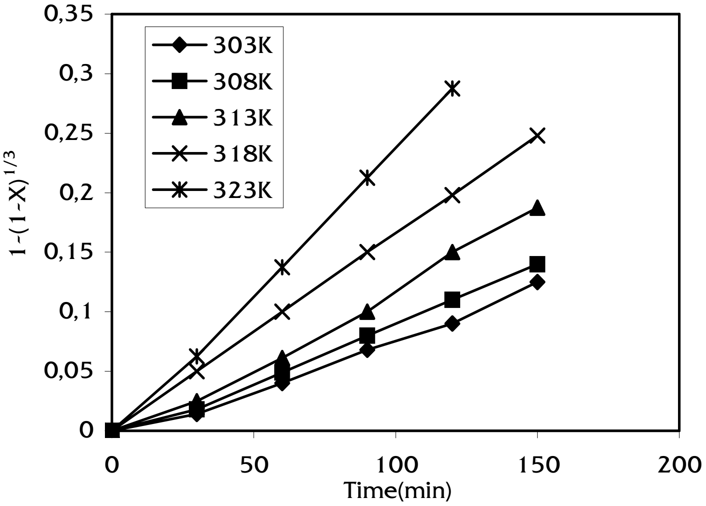

Figure 5. Variation of 1-(1-X)$^{1/3}$ with respect to time at various temperature

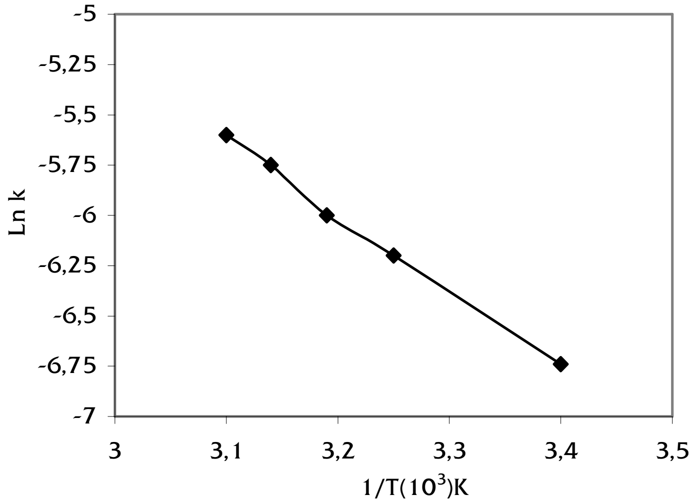

Figure 6. Arrhenius' plot for the dissolution of galena with HOCl

The slope of this plot was used to determine the apparent activation energy with value to be 45.0kJ/mol. Based on the value of the activation energy it could be concluded that chemical reaction is the rate - controlling step for the dissolution of galena by hypochlorous acid and hydrochloric acid solutions. Gosh and Ray (1991) and Biswas (1991) have earlier concluded that chemical reaction controlled kinetics is characterized by high energy of activation.

4. CONCLUSIONS

The dissolution of galena with hypochlorous acid in excess sodium chloride acidified with hydrochloric acid has been studied. It can be concluded that dissolution of galena has an inverse relation with increases in temperature and particle size but has direct relation with increase in concentration of hypochlorous acid, and independent of changes in speed of agitation. The activation energy was found to be 65.0kJ/mole in the temperature range 30-50°C, suggesting a chemical reaction control.

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