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HYDROCHLORIC ACID LEACHING OF SPHALERITE IN THE PRESENCE OF AN OXIDIZING AGENT

E O Olanipekun[*a] and R A Oderinde* [b]

[a]*Department of Chemistry, Ondo State University, Ado - Ekiti, Nigeria*

[b]*Department of Chemistry, University of Ibadan, Ibadan, Nigeria*

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Dissolution experiments of a natural sphalerite ore from Nigeria were carried out in hydrochloric acid - potassium chlorate (v) solutions at various temperatures to study the physico-chemical factors and the mechanism for the leaching of zinc from this mineral. The dissolution rate was strongly influenced by the temperature and concentration of the leaching reagent. It was, however, independent of the stirring speed over the range 0 - 400 rpm and fitted the kinetic equation based on the shrinking core model for chemical reaction control. An activation energy of about 43 kJ mol^{-1} was calculated for the leaching process.

Key words: Leaching, Hydrochloric acid, Potassium chlorate (v), Sphalerite, Kinetics.

Introduction

Sphalerite (ZnS) constitutes the largest resource of zinc, and zinc-bearing minerals, with widely distributed deposits throughout the world. Sphalerite is the principal zinc mineral currently being processed, accounting for nearly all primary zinc production from sulphide ores (Dutrizac and MacDonald 1978). In Nigeria, sphalerite occurs in association with other sulphide minerals but mainly with galena, and the deposits are rather extensive in the cretaceous sediments scattered along the Benue Trough. However, exploitable quantities occur around Abakaliki (Anon 1987).

Floatation of sphalerite ores generally leads to a high-grade zinc concentrate containing over 50 percent zinc. These concentrates are treated commercially by the methods such as: horizontal retorts, vertical retorts, electrothermic furnaces, the Imperial Smelting Furnace (ISF), and roast - leach-electrolysis. Many zinc plants capacities have been accounted for by the ISF or electrolytic processes with the latter method finding much wider application. Both processes are technically and economically well established for conventional concentrates, although there are certainly enough problems with either to justify additional research into new processing techniques. For instance, both processes produce SO$_2$ - rich gases which must be collected and marketed; the electrolytic process suffers from the ferrite problem and the complexities of its treatment. These and other processing difficulties have led to the examination of a number of alternative technologies (Kawulka *et al* 1975; Dutrizac and MacDonald 1978).

In the past few decades, ferric salt-acid solutions have been widely employed in the hydrometallurgical treatment of sphalerite concentrates. In this process, the ferric salt serves as an oxidizing agent, thus enhancing the dissolution of the ore and ferric chloride has been the most common salt used in this regard (Venkataswamy and Khangaonkar 1981; Crundwell 1987and 1988; Rath *et al* 1988) In spite of the favourable leaching rates observed, ferric chloride solutions are corrosive to most metals. However, this problem may be overcome with the use of plastic materials (Neou-Singouna and Fourlaris 1990). Moreover, the accumulation of ferrous chloride in the leach solution, results in a slow rate of reaction. Consequently, it is desirable to seek other alternatives of dissolving the mineral.

In this study, therefore, potassium chlorate (v) was employed as an alternative oxidizing agent to ferric chloride in the hydrochloric acid leaching of sphalerite. It is envisaged that this compound will not cause the usual problems associated with the use of ferric chloride as an oxidizing agent.

The dissolution of sphalerite by hydrochloric acid in the presence of potassium chlorate (v) as an oxidizing agent can be represented as:

$$5ZnS + 2KC10_3 + 12HCl > 5ZnCl_2 + 2KCl + 6H_2O + 5S + Cl_2 \quad .....(1)$$

In view of the promising potential of the above process, kinetics and mechanism of sphalerite dissolution in hydrochloric acid - potassium chlorate (v) solutions were studied to obtain the essential data on zinc leaching.

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*Author for correspondence

Experimental

*Materials.*A natural sphalerite ore, obtained from Abakaliki in Ebonyi State of Nigeria was used in this study. The mineral was crushed, ground, and screened to produce the fractions: 25 to 37µm, 45 to 53µm, and 88 to 105µm. The chemical analysis of the latter fraction is given in Table 1 which does not differ significantly from those of the other fractions.

*Reagents.*Aqueous hydrochloric acid-potassium chlorate (v) solutions prepared from the reagent-grade chemicals (Aldrich).

*Apparatus.*The reaction vessel was a 500ml three necked round bottomed Pyrex flask equipped with a condenser, a stirring rod (mechanically-driven), and a thermometer (0-110°C). The flask was heated by a thermostatically controlled heating mantle capable of maintaining the temperature within 1°C.

*Procedure.*Apart from the particle size experiments, all other experiments were performed using the 88 to 105µm fraction. For each run, 300 ml of the leaching solution of predetermined concentration of $KClO_3$ and HCl was charged into the reaction flask and heated to the desired temperature. About 2 g of the sample was added to the reactor. The contents were well agitated. Solution samples of 2 ml were withdrawn at regular time intervals during a run, diluted and analyzed for zinc using an atomic absorption spectrophotometer (Buck 200 Model).

Results and Discussion

Figure 1 illustrates the effect of stirring speed on the rate of dissolution of zinc from the sphalerite in 4 h at 60°C (HCl 4M, $KClO_3$ 0.02mol). The results of this test obviously indicate the non-dependence of leaching rate on stirring speed over the range 0 to 400 rpm, thereby eliminating mass-transfer as the rate controlling step of the leaching process. Acid leaching of sulphide minerals in the presence of oxidizing agents usually proceed with the formation of sulphur or hydrogen sulphide as one of the reaction products. Depending on the concentration of the oxidizing agent, the sulphur formed may sometimes coat the mineral surface and as such the dissolution rate will be influenced by agitation. As can be observed from equation 1, there was sulphur formation but that did not seem to have coated the mineral surface as to hinder further reaction and this probably explains why the rate of dissolution of zinc was apparently not affected by the stirring speed.

Table 1

Chemical analysis of sphalerite

Constituent	Content %
Zn	57.03
S	32.68
Fe	7.25
Pb	0.92
Cu	0.60
Cd	0.26
Mn	0.12
Ca	0.07
Mg	0.05
Ni	0.03
Co	0.02

A series of experiments was performed using the three different particle sizes of the ore, but keeping other parameters constant. The results (Fig 2) clearly show an inverse relationship between the fraction of zinc leached at a particular time, and the average initial diameter of the particle. This is so because smaller particles provide a greater and uniform surface area for a reaction to occur faster.

The rate of dissolution of zinc vs time at various leaching temperatures is shown in Fig 3. The data show a strong and linear dependence of leaching rate on the temperature. The fraction of zinc leached with time at 50°C is in the first instance relatively slow but this increases systematically with increasing temperature and at 85°C reasonably attractive leaching rates are observed, 90% extraction, being optimum under the conditions of test.

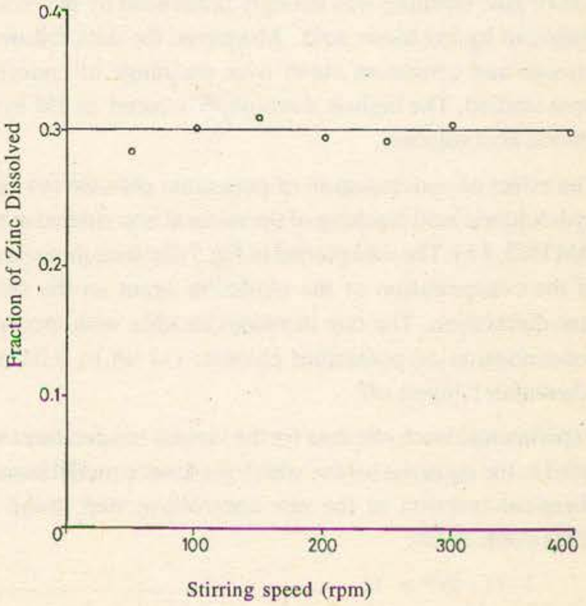

Fig 1 Effect of stirring speed on the dissolution of Zn (4M HCl, 0.02 mol $KClO_3$, 88 to 105µm, 60°C, 4 h).

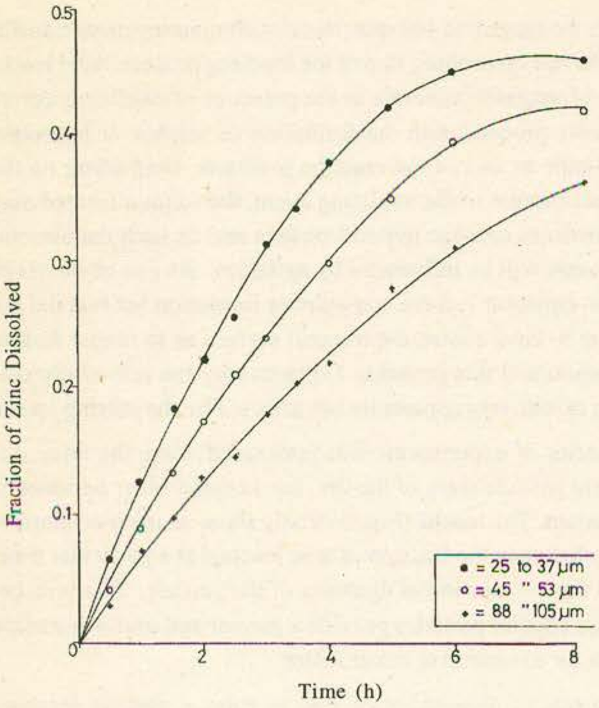

Fig. 2 Effect of particle size on the dissolution of Zn (200rpm, 4M HCl, 0.02 mol $KClO_3$, 60°C)

The effect of hydrochloric acid concentration on the rate of dissolution of zinc was studied at 60°C, with other parameters being constant. The acid concentration was varied from 3 to 5M and plots of fraction of zinc reacted vs. time for the various concentrations are given in Fig 4. It is obvious that the rate of zinc leaching was strongly influenced by the concentration of hydrochloric acid. Moreover, the data followed a smooth and consistent curve over the range of concentrations studied. The highest dissolution occured in 5M hydrochloric acid solution.

The effect of concentration of potassium chlorate (v) on the hydrochloric acid leaching of the mineral was studied at 60°C (4M HCl, 4 h). The data plotted in Fig 5 illustrate the influence of the concentration of the oxidizing agent on the rate of zinc dissolution. The rate increases steadily with increasing concentration of potassium chlorate (v) up to 0.04 mole whereafter it tapers off.

Experimental leach rate data for the various temperatures were fitted to the equation below, which is a kinetic model based on chemical reaction as the rate-controlling step (Sohn and Wadsworth 1979):

$$1 - (1 - a)^{1/3} = kt \qquad \text{.................................. .... (2)}$$

where a is the fraction of zinc reacted at time t, and k is the overall rate constant. The quantity at the left of equation (2) is

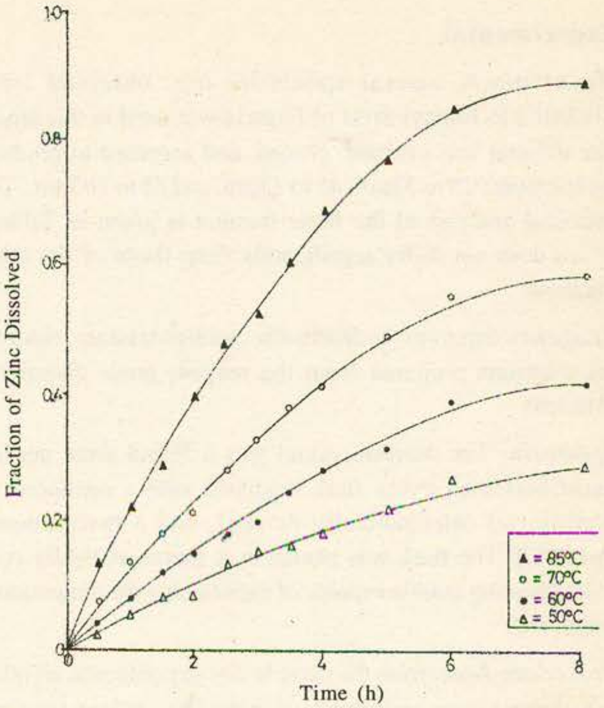

Fig 3 Effect of temperature on the dissolution of Zn (200rpm, 4M HCl, 0.02 mol $KClO_3$, 88 to 105µm)

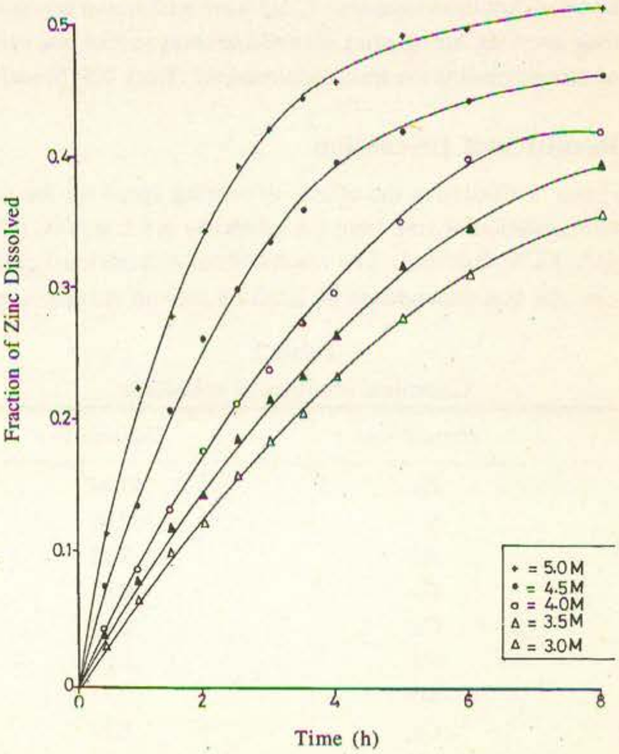

Fig 4 Effect of HCl concentration on the dissolution of Zn (200rpm, 0.02 mol $KClO_3$, 88 to 105µm, 60°C)

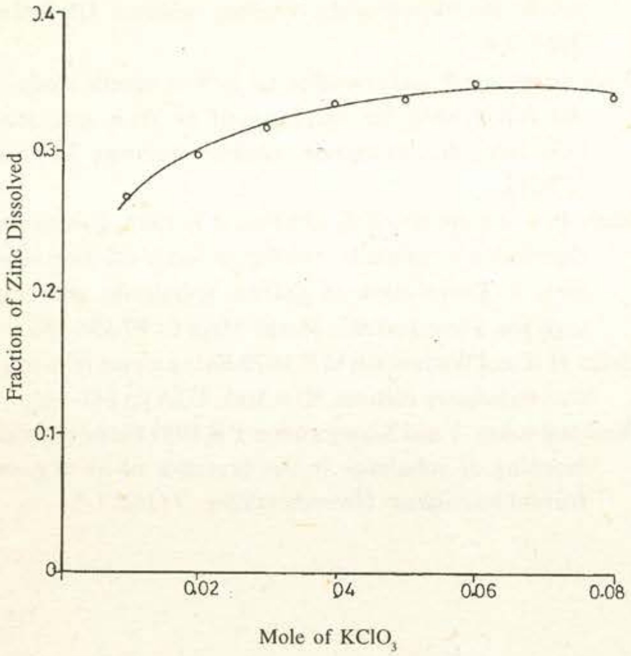

Fig 5 Effect of $KC10_3$ concentration on the dissolution of Zn (200 rpm, 4M HCl, 88 105μm, 60°C)

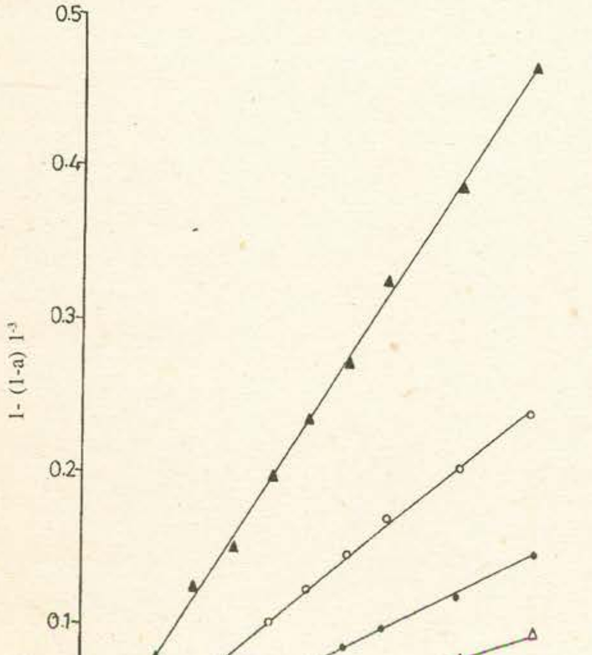

Fig 6 Plots of $1\text{-}(1\text{-}a)^{1/3}$ versus time for the dissolution of Zn (200 rpm, 4M HCl, 0.02 mol $KC10_3$, 88 to 105μm)

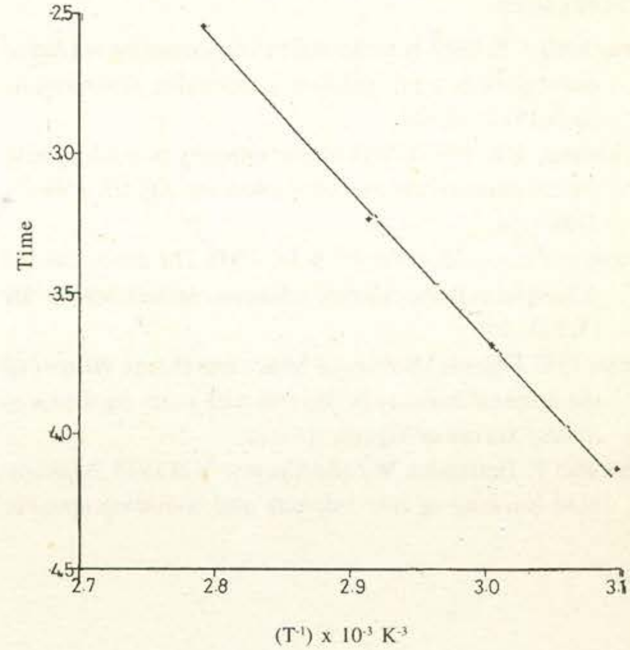

Fig 7 Arrhenius plot, Ink versus T^{-1} for the dissolution of Zn (200rpm, 4M HCl, 0.02 mol $KC10_3$, 88 to 105μm).

plotted against t (Fig 6) and the straight lines so obtained are indicative of a surface chemical reaction mechanism. The slope of each of the lines in Fig 6 is k and these k values are plotted against the temperature in accordance with the Arrhenius relationship as shown in Fig 7. The result shows that Ink is inversely proportional to T (temperature). The apparent activation energy for the leaching rate of zinc, calculated from the slope of the Arrhenius plot to be 43.22 kJ mol^{-1}. This value is considerably higher than that of a diffusion-controlled process however, is typical of reactions being controlled by chemical reaction at the surface of the mineral. This is in agreement with previous work (Dutrizac and MacDonald 1978) on the dissolution of sphalerite in ferric chloride solutions.

Conclusion

The following conclusions can be drawn from this study:

1. Both temperature and concentration of the hydrochloric acid-potassium (V) chlorate leaching solution have a significant effect on the rate of dissolution of zinc from the sphalerite ore. In all the tests more than 10% of zinc remained in the residue.

2. The dissolution rate is independent of the stirring speed and inversely proportional to the average initial size of the sphalerite particles.

3. The rate of dissolution of zinc is controlled by a surface chemical reaction mechanism with an apparent activation energy of about 43 kJ mol^{-1}.

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