Effect of Sodium Chloride on Dissolution of Galena in Aqueous Acid Solution

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Abstract. This paper presents the results obtained on the kinetic study of non-oxidative dissolution of natural galena in aqueous hydrochloric acid with the addition of sodium chloride. A chemical reaction on the surface of galena controlled the dissolution rates under the experimental conditions of investigation. The galena dissolution rate was of the first order with respect to hydrochloric ion activity in hydrochloric acid solution. The addition of sodium chloride to the acid solution greatly enhanced the dissolution rate. The effect of sodium chloride has two possible interpretations: firstly, it may be the result of an increase in the hydrogen ion activity; secondly, the enhancement of the dissolution rate, observable at the high sodium chloride concentration, may be due to the specific absorption of chloride ions or the surface complexing of chloride ions on galena surface.

Keywords: dissolution mechanism, kinetics of galena, effect of sodium chloride, non-oxidative dissolution, galena dissolution rate

Introduction

Non-oxidative dissolution of the base metal sulfide in acidic solution has been studied in order to understand the leaching kinetics and to develop suitable conditions for a non-oxidative leaching method for the treatment of base metal sulfide ores. The kinetics of sphalerite in sulfuric acid solutions, with and without the addition of sodium chloride, have been reported (Eguchi *et al.,* 1982). These authors noted that addition of sodium chloride to the sulfuric acid solution containing zinc ions greatly enhanced the dissolution rate which depended on the concentration of zinc ions. Tarabaev and Milyutina (1956) studied the kinetics of the dissolution of synthetic and natural sulfides of lead, copper, zinc and iron in sulfuric acid solutions containing chloride ions. They reported that sulfides of base metals dissolved most readily in these solutions. Scott and Nicol (1976) also studied base metal dissolution in concentrated chloric acid solutions and proposed a general model for the diffusion-controlled dissolution. On the contrary, Awakura *et al.* (1980) proposed that base metal dissolution in concentrated acid solution is controlled by the first order chemical reaction. Nunez *et al.* (1990; 1988) reported that the order of reaction for ionic activity of $HClO_4$ is of the first order, whereas for HCl the order of reaction over a wide range of concentration is 3/2 with respect to mean ionic activity of hydrochloric acid. They also reported that activation energy is independent of the chloride ion used to increase the activity of HCl. Mackovich and Ptitsyn (1999) studied the leaching kinetics of galena with a mixture of nitrous acid and sulfuric acid. They

observed a dependence on the content of H_2SO_4 in the presence of the leaching agent HNO_2, which had a catalytical effect, thus increasing the oxidation rate of galena to two times even at a very low concentration (0.01 mole per litre). These kinetic studies are, however, insufficient to explain the mechanism of dissolution of galena in acidic solution. It was, therefore, considered appropriate to reinvestigate the kinetics in order to better understand the dissolution of galena in acidic solution. This paper thus presents the results of a kinetic study on non-oxidative dissolution of galena in hydrochloric acid with the addition of sodium chloride.

Materials and Methods

Materials. A natural galena sample, having a composition of 85.54% Pb and 14.46% S, was used in this study. The main impurities identified by spectrographic analysis were silica and silver. The sample was mounted in such a way that only a cleavage face of galena was introduced to a dissolution medium. The galena surface was ground with corundum number 1500 and then polished with fine alumina. Distilled and deiodized water with the average specific conductivity of 10^7 Ω/cm was used in all the experiments. Hydrochloric acid solution of the desired concentration was prepared by diluting the standard IM HCl solution. Nitrogen gas was used for deoxygenation of the solution and purging of the reactor. All chemical reagents used were of Analytical grade.
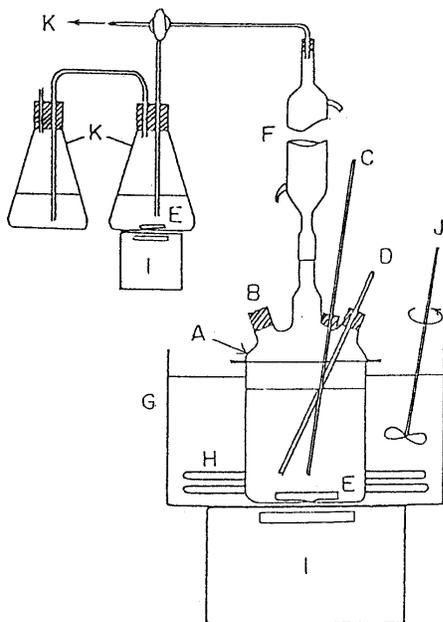
Experimental procedure. A 500 ml separable glass flask, with lid having four necks was used as the reaction vessel for

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all dissolution experiments (Fig. 1). The central hole of the lid was used for the accommodation of condenser. The other three necks were used for the introduction of nitrogen gas into the dissolution medium, thermometer and the fixation of galena specimen at the predetermined place, respectively. The evolved hydrogen sulfide gas was collected, through the other end of condenser, in the absorbing flask. A waterbath provided with a temperature controller was used as the thermostat. Each dissolution medium was deoxygenated with nitrogen gas for 30 min prior to each experiment. A galena sample was placed, facing downwards, in a dissolution medium (500 ml) stirred with a magnetic stirrer. Nitrogen gas was bubbled into the dissolution medium throughout each run. Dissolution rate was followed by the analysis of hydrogen sulfide gas absorbed in the absorbing solution ($KOH + H_2O_2 + MoO_3$). The Pb ion concentration in the pipetted solution, drawn at appropriate time intervals, was quantitatively analysed for dissolved Pb by atomic absorption spectrophotometry (Sidney, 1984).

Results and Discussion

Linear rate determination. The dissolution of Pb in 1 M HCl solution was determined by maintaing constant the stirring speed at 1100 rpm and temperature of 328 K for 20 h (Table 1). The results show that galena dissolved at a constant rate except at the initial stage of dissolution. The reaction rate was, therefore, determined from the data given in Table 1. It

appears that the rate was 0.4×10^{-5} moles/cm^2 per h for the 0-6 h, but then it attained its constant value of 0.6×10^{-5} moles/cm^2 per h for the next 15 h. Therefore, this reaction rate was used for the subsequent examination of reaction kinetics.
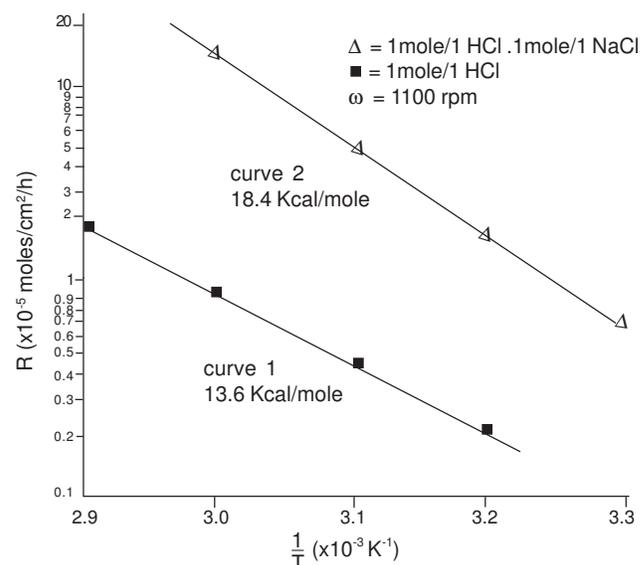
Effect of temperature. The effect of different temperatures on the dissolution rates was examined over a range of 313-343 K at the constant stirring speed of 1100 rpm in solutions containing 1M HCl, and 1M HCl-1M NaCl (Fig. 2). The dissolution rates so obtained, as shown in Table 2, were plotted against 1/T, which showed a linear relationship over the entire temperature range studied (Fig. 2). The activation energies were found to be 13.6 Kcal/mole for 1M HCl, 18.4

Table 1. The dissolution of Pb in 1 M HCl as a function of time at 1100 rpm stirring speed at 328 K

Time (h)	0	2	4	6	8	10	12	14	16	18	20
Pb dissolved (x 10^{-5} moles/cm^2)	0.0	0.6	1.3	2.4	3.6	4.8	6.0	7.2	8.4	9.6	10.8

Table 2. Effect of different temperatures on the dissolution rate of Pb in I M HCl and 1 M HCl-I M NaCl at 100 rpm stirring speed

Temperature	$\frac{1}{T}$	Dissolution rate, R (x10^{-5} moles/cm^2/h)	
(K)	(K^{-1})	1M HCl	1 M HCl - 1 M Nacl
313	3.2×10^{-3}	0.32	1.6
323	3.1×10^{-3}	0.45	2.5
333	3.0×10^{-3}	0.93	5
343	2.9×10^{-3}	1.81	12

Fig. 1. Experimental apparatus: A, reaction flask (500 ml, inner dia 85 mm); B, sample feed and sampling hole; C, thermometer; D, bubbling tube; E, stirrer; F, condenser; G, waterbath; H, heater; I, magnetic stirrer; J, bath agitator; K, absorption bottle.

Fig. 2. The effect of temperature on the dissolution rate of galena; R = dissolution rate, $\frac{1}{T}$ = reciprocal of absolute temperature.

Table 3. Effect of stirring speed on linear dissolution rates (R = x10^{-5} moles/cm^2/h)

	Stirring speed (rpm)									
	400	500	600	700	800	900	1000	1100	1200	1300
Linear dissolution rate (R moles/cm^2/h)	2.00	3.00	4.75	6.10	7.00	7.10	7.15	7.18	7.20	7.21

Kcal/mole for 1M HCl-1M NaCl. These high activation energies found for non-oxidative dissolution of galena showed that dissolution in this system was controlled by the diffusion of either the reactants at the surface, or the reaction products from the surface of galena instead of diffusion in the solution. The rate would not be, therefore, dependent on the stirring speed of the solution in this case. Similar tendency was also reported by Awakura et al. (1980) who also observed the independence of dissolution rate from stirring speed.

Effect of stirring speed. Different stirring speeds were used to determine their effects on the dissolution of galena (Table 3). Linear dissolution rates at the stirring speeds of 900-1100 rpm were independent of stirring speed, which were slightly higher than that at 800 rpm. This independent behaviour of the dissolution rate from stirring speed seems to suggest that diffusion was not a rate controlling step. It is reasonable to consider that the rates of non-oxidative dissolution of galena in HCl, with or without the addition of sodium chloride, were controlled by a chemical reaction on the surface of galena. Hereafter, all experiments were run at 1100 rpm throughout the later studies.

Effect of hydrochloric acid concentration. Dissolution rates of galena were measured at different acid concentrations, ranging from 0.1 M to 4.0 M HCl, with or without the addition of NaCl, keeping constant the stirring speed of 1100 rpm at the temperature of 328 K. Dissolution rates were plotted against hydrogen ion concentration of hydrochloric acid (Fig. 3), which show that dissolution rates increased with increase in acid concentration in all the solutions examined. It seems that the reaction rate was of the first order with respect to the hydrogen ion concentration over the concentration range from 0.1 M to 2.0 M hydrochloric acid solutions (Fig. 3; curve 1) and its value at 2 M HCl was 10^{-5} moles/cm^2/h. The dissolution rate of galena exhibited a higher dependence, than first order, upon hydrogen ion concentration in HCl solutions having concentration beyond 2 M. Nunez *et al.* (1988) also observed similar tendency during base metal dissolution in HCl and HClO$_4$. Therefore, with the analogy to their studies, it may be considered that a special role of chloride ions of HCl, such as
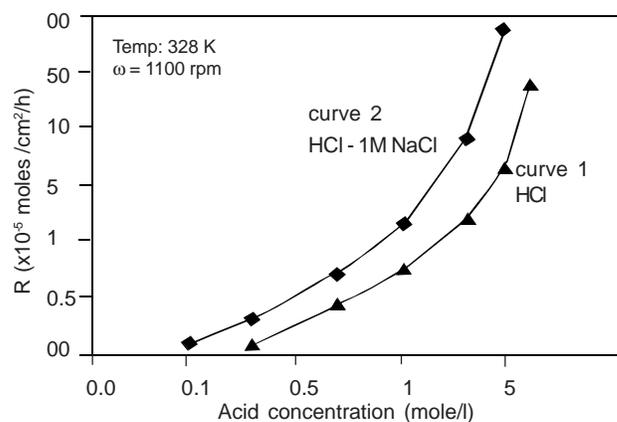
Fig. 3. Effect of acid concentration with and without NaCl on the dissolution rates of galena; R = dissolution rate.

specific absorption and/or complexing ability, would affect the dissolution rate.

Since acid concentration appears to be the most appropriate parameter to determine dissolution kinetics, it can be speculated that a rate determining process is the release of HS$^-$ from the surface of galena as follows:

$$PbS + H^+ \longrightarrow PbS\,H^+_{ad}$$
$$PbSH^+_{ad} \rightleftharpoons Pb^{2+} + HS^-$$
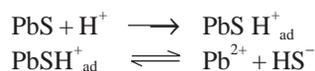
The hydrogen sulfide ion, HS$^-$, thus formed may react rapidly with a hydrogen ion to form hydrogen sulfide.

The dissolution rate for HCl solution containing 1 M NaCl was also of the first order with respect to HCl concentration when total chloride ion concentration was less than 2 M and its value was 5 x 10^{-5} moles/cm^2/h at the acid concentration of 2 M (Fig. 3; curve 2). These findings suggest that HCl concentration determined the dissolution kinetics, which was of first order for HCl solution in the presence of NaCl when total chloride ion concentration did not exceed 2 M. It is also concluded that the addition of sodium chloride upto the total chloride ion concentration of 2 M to acid solutions resulted in the enhancement of dissolution rate, which may be due to the increase in hydrogen ion concentration of the leachant. Similar behaviour was also observed by Awakura *et al.* (1980) during their kinetic studies on galena dissolution.
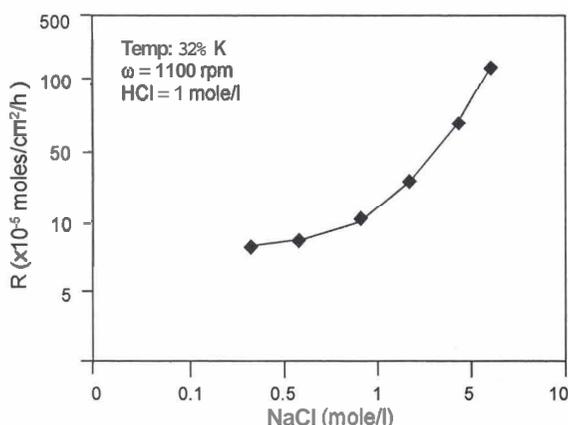
Fig. 4. Effect of the addition of sodium chloride to hydrochloric acid on dissolution rates of galena.

Effect of sodium chloride. The effects of the addition of sodium chloride to 1 M HCl solution were examined at 328 K and 1100 rpm (Fig. 4). From the data shown in Fig. 4, it appears that dissolution rate was slow between the concentration of NaCl from 0-1 M. It was, however, greatly enhanced at the concentration of more than 1 M NaCl. From this observation it may be speculated that increase in the chloride ion concentration itself played a role in the increase of the dissolution rate. This effect of chloride ions was revealed at higher concentrations of NaCl. Such an effect was also studied by a number of researchers (Awakura *et al.,* 1980; Majima *et al.,* 1980; Tarabev and Milyutina, 1956). It is concluded, therefore, that it may be due to specific absorption of chloride ions on the protonated galena surface, or due to the surface complexing of chloride ions on the galena surface playing an important role in the enhancement of dissolution rate.

Conclusion

The non-oxidative dissolution of galena was studied kinetically in hydrochloric acid solution, with and without the addition of sodium chloride. Under the experimental conditions employed during this study, the dissolution rates were controlled by a chemical reaction on the surface of the galena sample. The galena dissolution rate was of the first order with respect to hydrogen ion activity in hydrochloric acid solution. The addition of sodium chloride to the acid solutions

greatly enhanced the dissolution rate. This effect of sodium chloride has two possible interpretations: firstly, it may be the result of an increase in the hydrogen ion activity; secondly, the enhancement of the dissolution rates observable at high sodium chloride concentration may be due to the specific absorption of chloride ions or the surface complexing of chloride ions on galena surface. A combination of these effects is supported by the observations made.

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