# Non-oxidative Dissolution of Lead Sulphide in Hydrochloric Acid Solution

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(Received 29th September 2003, revised 21st March, 2005)

**Summary:**This paper reveals the results obtained through a kinetic study of non-oxidative dissolution of lead sulphide in aqueous hydrochloric acid with and without addition of sodium chloride. A chemical reaction on the surface of lead sulphide sample controlled the dissolution rates under the experimental condition employed. The lead sulphide dissolution rate is 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. First, it may be the result of an increase in 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 lead sulphide surface.

## Introduction

Non-oxidative dissolution of the base metal sulfide in acidic solution has been studied in laboratories in order to understand leaching kinetics and to develop suitable conditions for non-oxidative leaching method for the treatment of base metal sulfide ores. M. Eguchi & A. Khalique [1] studied the kinetics of sphalerite in sulfuric acid solutions with and without the addition of sodium chloride. They reported that addition of sodium chloride to the sulfuric acid solution containing zinc ions greatly enhanced the dissolution rate depending upon the concentration of zinc ions. Tarabaev and Milyntina [2–3] 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 others [4-7] also studied base metal dissolution in concentrated chloric acid solutions and proposed a general model for diffusion-controlled dissolution. On contrary, Yasuhiro Awakura [6-8] et.al. proposed that base metal dissolution in concentrated acid solution is controlled by a first order chemical reaction. Nunez et al [9-13] reported that order of reaction for ionic activity of $HClO_4$ is of first order and 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 chloride ion used to increase activity of HCl. Markovich and others [14, 15], studied leaching kinetics of galena with a mixture of Nitrous acid and sulfuric acid, showed dependence on the content of $H_2SO_4$ in the presence of leaching agent $HNO_2$ which has a catalytical effect, increasing the oxidation rate of lead sulphide 2 times even at very low concentration (i.e. 0.01 mole).

However, these kinetic studies are insufficient to explain the mechanism of dissolution of lead sulfide in acidic solution. It was, therefore, necessary to study the kinetics again in order to gain a better understanding of dissolution of lead sulfide in acidic solution.

This paper presents the results obtained through a kinetic study of non-oxidative dissolution of lead sulfide in hydrochloric acid with and without the addition of sodium chloride.

## Results and Discussion

### *Linear Rate Determination*

Some experiments were conducted by using 1M HCl solution, keeping constant stirring speed of 1100 rpm and at temperature of $55^0$C for 20 hrs. The results are shown in Fig. 1.

The results in the figure show that Lead Sulphide dissolves at a constant rate except at the initial stage of dissolution. The reaction rate was therefore determined from the slope of linear rate line. As can be seen from the Fig. 1, the value of rate is $0.5 \times 10^{-5}$ moles/cm$^2$ – hr for 0 – 5 hrs, but then it attains its constant value $0.6 \times 10^{-5}$ moles/cm$^2$ – hr for next 15 hrs. Therefore, this reaction rate was used for the examination of reaction kinetics.

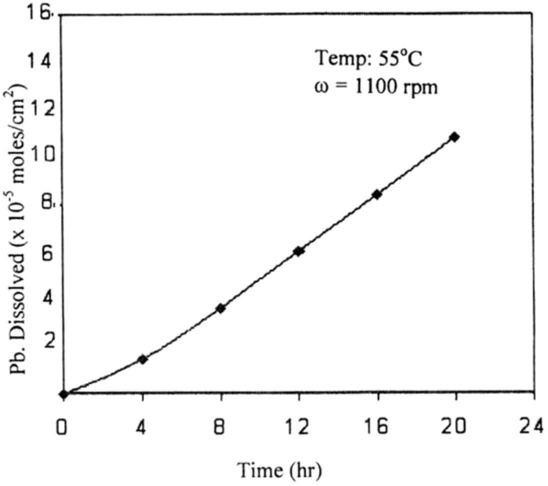

Fig. 1: Dissolution of Pb v time

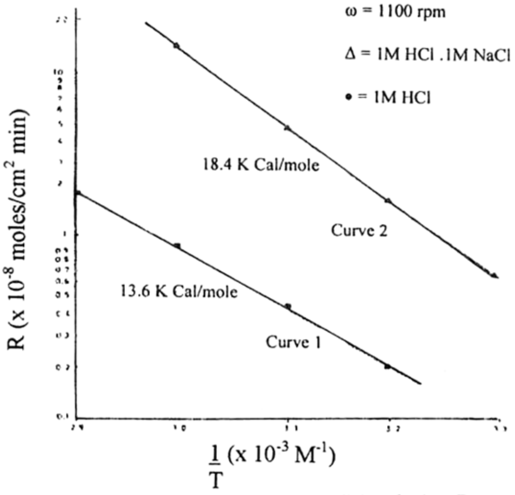

Fig. 2: Effect of Temperature on Dissolution Rate

*Effect of Temperature:*

The effects of temperature on dissolution rates were examined over a range from 40 – 70°C keeping a constant stirring speed of 1100 rpm in solutions containing 1M HCl and 1M HCl – 1M NaCl respectively (Fig. 2)..

Linear dissolution rates obtained from the results shown in Fig.-2 were plotted against 1/T, showing the linear relation over the whole temperature range studied. The activation energies were found to be 13.6 Kcal/mol for 1M HCl, 18.4 Kcal/mol for 1M HCl – 1M NaCl. These high activation energies found for non-oxidative dissolution of lead sulphide showed that dissolution in this system was controlled by either diffusion of either reactants to the surface or reaction products from surface of the lead sulphide instead of diffusion in solution. The rate would not be, therefore dependent on the stirring speed of the solution in this case. Similar tendency was also reported by Yashiro et al [8] who also observed the independence of dissolution rate from stirring speed.

*Effect of Stirring Speed*

In order to examine the effects of stirring speed, various experiments at different stirring speeds were performed. The results are shown in Fig.-3. Linear dissolution rates corresponding to the slope in Fig. 3 at stirring speed 900-1600 rpm were independent from stirring speed and it is slightly higher than that of 800 rpm. This independent behaviour of the dissolution rate from stirring speed seems to suggest that diffusion is not a rate controlling step. It is reasonable to consider that the rates of non-oxidative dissolution of lead sulphide in HCl, with or without the addition of sodium chloride, were controlled by a chemical reaction on the surface of lead sulphide. Hereafter, all experiments were run at 1100 rpm through out the studies.

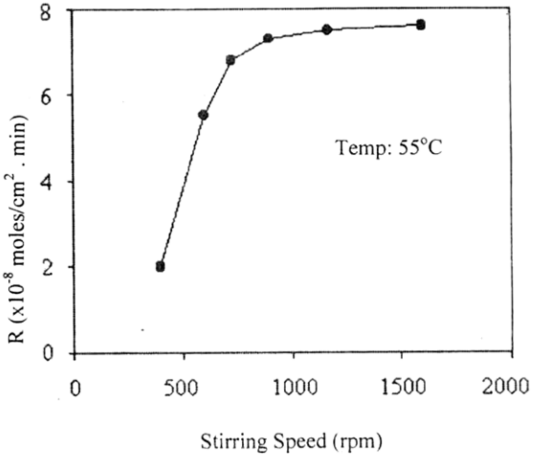

Fig. 3: Effect of stirring speed on linear Dissolution Rate

*Effect of Hydrochloric Acid Concentration*

Dissolution rates of lead sulphide were measured at different concentrations ranging from 0.1M to 4.0M HCl with or without the addition of

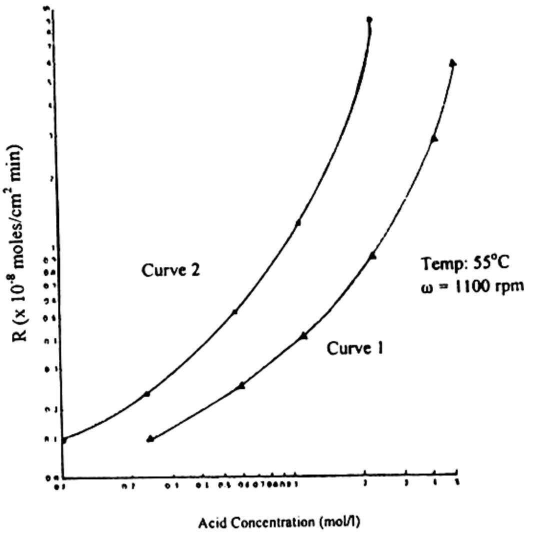

Fig. 4: Effect of Acid Concentration with and without NaCl on Dissolution Rate

NaCl, keeping constant stirring speed of 1100 rpm and at temperature of 55°C. Dissolution rates were plotted against hydrogen ion concentration of hydrochloric acid in Fig.-4. The results in Fig. 4 show that dissolution rates increased with increase in acid concentration in all solution examined and it seems that the reaction rate is of the first order with respect to the hydrogen ion concentration over the concentration range from 0.1 M to 2.0 M HCl hydrochloric acid solutions (see curve 1) & its value is 0.9 x 10-8 moles/cm2 –min at acid concentration of 2M. The dissolution rate of lead sulphide exhibit a higher dependence than first order upon hydrogen ion concentration in HCl solutions having concentration beyond 2M. Nunez et al [9] also observed similar tendency during base metal in HCl and $HClO_4$. Therefore, with the analogy to their studies, we may consider a special role of chloride ions of HCl such as specific adsorption and/or complexing ability, would affect the dissolution rate.

Since acid concentration appears to be the most appropriate parameter to determine dissolution kinetics, we can speculate that a rate determining process is a release of HS– from the surface of galena as follows:

$$PbS + H^{+} \longrightarrow PbSH^{+}_{ad}$$

$$PbSH^{+}_{ad} \rightleftharpoons Pb^{2+} + HS$$

The hydrogen sulfide ion, $HS^{-}$, thus formed may react rapidly with a hydrogen ion to form hydrogen sulfide.

The results in Fig. 4 corresponding to curve 2 show that the dissolution rate for HCl solution containing 1M NaCl was also of the 1st order with respect HCl concentration when total chloride ion concentration was less than 2M and its value is 5 x $10^{-8}$ moles/cm$^2$ min at acid concentration of 2M. These findings suggests that HCl concentration determines the dissolution kinetics is of first order for HCl solution in presence of NaCl when total chloride ion concentration does not exceed 2M. It is also concluded that the addition of sodium chloride upto the total chloride ion concentration of 2M to acid solutions results in the enhancement of dissolution rate which may be due to increase in hydrogen ion concentration of leachant. Similar behaviour was also observed by Yashiro *et al* [8] during kinetic studies of galena dissolution.

*Effect of Sodium Chloride*

The effects of the addition of sodium chloride to 1M HCl solution were examined at 55°C and 1100 rpm. These results are shown in Fig. 5.

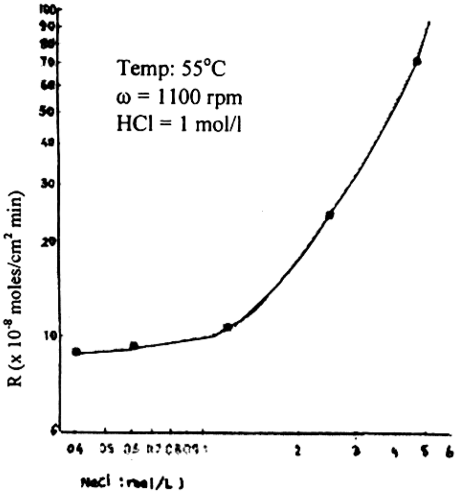

Fig. 5: Effct of Sodium Chloride on Dissolution Rate

From Fig.-5 it appears that dissolution rate was slow between concentration of NaCl from 0 – 1M, after that it was greatly enhanced at concentration more than 1M NaCl. From this observation, we may speculate that increase in chloride ion concentration itself play a role to increase dissolution rate. This effect of chloride ions is revealed at higher concentrations of NaCl. This effect was also studied by a number of researchers [1-3, 6-8]. Therefore, it is concluded that it may be due to specific adsorption of chloride ions on the protonated lead sulphide surface or a surface complexing of chloride ions on the lead sulphide plays an important role in the enhancement of dissolution rate.

## Experimental

### *Materials*

A lead sulfide sample having 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 as such a way that only a cleavage face of lead sulfide was introduced to a dissolution medium. The Lead Sulphide surface was ground with corundum No. 1500 and then polished with fine Alumina used. Distilled and deiodized water with average specific conductivity of $10^7$ $\Omega$/cm was used in all experiments. Hydrochloric acid solution of desired concentration was prepared by dilution of standard solution. Nitrogen gas was used for deoxygenation of solution and purging of the reactor. All chemical reagents used were of analytical grade.

### *Experimental Procedure*

A 500 ml glass separable flask with a fitted lid having five necks was used as a reaction vessel for all dissolution experiments. The central hole of the lid was used for the accommodation of a stirring rod. The other four necks were used for the introduction of nitrogen gas into the dissolution medium, the accommodation of condenser, the fixation of lead sulfide specimen at predetermined place against a stirrer, and the accommodation of a sampling tube, respectively. The evolved hydrogen sulfide gas was collected through the other end of condenser to the absorbing flask. A water bath provided with a temperature controller was used as a thermostat (± 0.5°C). Each dissolution medium was deoxygenated with nitrogen gas for 30 minutes prior to each experiment.

A lead sulphide sample was placed facing downward in a dissolution medium then the stirrer was activated to begin a dissolution experiment. Nitrogen gas was bubbled into the dissolution medium throughout each run. Dissolution rate was followed by the analysis of hydrogen sulfide gas absorbed in (KOH + $H_2O_2$ + $MoO_3$) adsorbing solution and lead ion concentration in the pipetted solution drawn at appropriate time interval was subjected to quantitative analysis for dissolved lead by using atomic absorption spectrometer [15].

## Conclusions

The non-oxidative dissolution of lead sulfide was studied kinetically in hydrochloric acid with and without the addition of sodium chloride. Under the experimental conditions employed in this study, the dissolution rates were controlled by a chemical reaction on the surface of the lead sulfide sample. The lead sulfide dissolution rate is 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 rates. This effect of sodium chloride has two possible interpretations: First, it may be the result of an increase in hydrogen ion activity. Second, the enhancement of the dissolution rates observable at high sodium chloride concentration may be due to the specific adsorption of chloride ion or the surface complexing of chloride ions on lead sulfide surface. A combination of these effects is supported by the evidence.

## References

1. M. Equchi, A. Khalique and H. Nakamurah, *J. Japan insti. metals*, **47** (11), 1061 (1982).
2. H. Majima and Y. Awakura: 13th Intern. Min. Process Congr., Warszawa, **1**, 665 (1979).
3. S.I. Iasabaev and N. A. Mulyyutina, *Isvest. Akad. Nauk. Kazakh. S.S.R. Ser. Gom. Dela, Stroimaterialov Met.*, **6**, 76 (1956).
4. P.D. Scott and M.J. Nicol, *Trans. IMM.*, **1**, 40 (1976).
5. K.J. Vetter: Electro Chemical Kinetics, Academic Press, New York, 49 (1967).
6. H. Majima, Y. Anakusa, T. Yazaki, and Y. Chikamosi, *Met. Trans. B.*, **11**, 209 (1980).
7. L.D. Locker and P.L. de Bruyn, *J. Electro Chem. Soc.*, **112**, 1659 (1969).
8. Y. Awakura, S. Kamel and H. Majuna,. *Met. Trans. B.*, **11**, 377 (1980).
9. C. Nunez and F. Espiell, *J. Metall. Trans. B*, **19**(4), 541 (1988).

10. C. Nunez and Espieic, *F. Metall. Trans. B*, **21**(1), 11 (1990).
11. Havlik and Tomas, Hutn. Fak., *Vys. SK. Tech.*, **38**(1), 17 (1990).
12. Hasanovic and Jasminka, *Hem. Ind.* **45**, 6, (1992).
13. Hasanovic and Jasmiuka, Hem. Ind. **45,** 4 (1992).
14. M., Madhuchand, N.B. Rao and K. Soinivasa, *Trans. Inst. Met.*, **53,** 71 (2000).
15. T.I. Mackovich and A.B. Ptitsyn, *Fiz. Tekh. Probi. Razrab. Polezn.*, **4**, 56 (1999).