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# Determination of Leaching Conditions of Sphalerite Concentrate in Acidic Ferric Chloride Solution

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ÖZET: Bu çalışmada sfalerit (ZnS) konsantresinin FeClj/HCl çözeltisinde liçing şartlarının belirlenmesi araştırmaları yapılmıştır. Araştırmalarda karıştırma hızının, ferrik iyonları derişiminin (O-I.O M), katı/sıvı oranının (5/500-100/500 g/ınl). liç sıcaklığının (40-90 °C) ve tane boyutunun Zn çözünmesine etkisi incelenmiştir. Elde edilen sonuçlara göre Zn çözünme veriminin; katı/sıvı oranı ve tane boyutu ile ters orantılı, sıcaklık ve ferrik iyonları derişimi ile doğru orantılı olarak arttığı ve karıştırma hızından bağımsız olduğu belirlenmiştir. 8. saatin sonunda 80 °C sıcaklık. 10/500 g/ınl katı/sıvı oranında ve 1.0 M Fe*'' derişiminde %82'lere varan verimle Zn kazanımı sağlanmıştır.

ABSTRACT: In this study, the determination of leaching conditions of sphalerite concentrate (ZnS) in FcCli/HCI solution was investigated. Effects of stirring speed, Fe" ion concentration (0-1.0 M), solid/liquid ratio (5-500-100/500 g/ml), leaching temperature (40-90 °C) and particle size on dissolution of Zn were determined in the experimental study. According to the results obtained, the Zn extraction varied inversely with solid/liquid ratio and particle size, and directly proportional with temperature and Fe'^{1+} ion concentration, and independent from stirring speed. At the end of leaching time of 8 hours, the Zn extraction increased to approximately 82^c/r at the temperature of 80 °C, the solid/liquid ratio of 10/500 g/ml and the concentration of 1.0 M Fe * ion.

## 1 INTRODUCTION

Sphalerite (ZnS) generally associated with other sulphidic minerals ($CuFeS_2$, PbS, FeS etc.) form complex sulphide ores. About 6 million tones/year of world's zinc production is produced via treatment of concentrates recovered using notation method from sulphide ores containing sphalerite. Zinc is frequently produced by roasting + leaching + electrowinning methods from concentrates. $SO_2$ gas formed during the roasting process causes some environmental problems (Wills 1984; Çopur, 2001).

Environmental problems and requirement of use of small and complex mineral sources lead to development of new alternative methods. Leaching of sulphidic ores bearing zinc has been important at the last 40 years. Advantages such as elimination of roasting step and high zinc extraction increased the importance of hydrometallurgical processes. In this scope, leaching studies were performed by sulphuric-acid ($H_2SO_4$) (Demopoulos and Baldwin, 1999: Parker, 1961), nitric acid (HNO,) (Çopur, 2001) hydrochloric acid (HCl) (Mizoguchi and Habashi, 1981: Majima et al.. 1981: Canbazoğlu and Özkol. 1980). ferric ions ($Fe^{3+}$) in the acidic medium (Dutrizac and MacDonald, 1974, 1978; Bobeck and Su, 1985; Warren et al., 1987; Rath et al., 1988; Palencia and Durtizac, 1991) and ammonia (NH,) solutions (Rao et al., 1992; Ghosh et al., 2002)

It is possible to dissolve some sulphidic minerals using only acid. For example, sulphidic minerals decompose according to Equation ( 1 ) under the only (non-oxidative) acidic conditions;

$$MS + 2H^+ \rightarrow M^{2+} + H_2S \quad (1)$$

Equation ( 1 ) is true for CuS, PbS, CdS, ZnS, NiS, CoS and FcS, however, this reaction does not occur placed for $CuFeS_2$ and $FeS_2$ under the same leaching conditions (Majima and Awakaura, 1979). Majima and Awakaura (1979) expressed the solubility of base-metal sulphides under non-oxidative leach conditions as a function of hydrogen ion concentration or pH (Fig. 1). From Equation (1) the solubility product K can be written;

$$K = (aM^+ . P_{H_2S})/(aH^+)^2$$

Thus

$$pH = 1/2 (\log K - \log aM^{2+} - \log P_{H_2S})$$

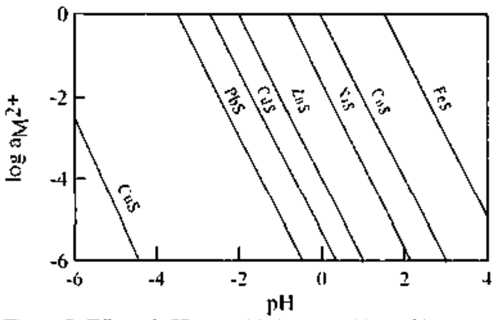


Figure I. Effect of pH on acid decomposition of base-metal sulphides (Majima and Awakura. 1979)

Use of oxidative factors in the acidic medium is commonly investigated for dissolution of sulphides. Ions used as oxidative agents are kupric and ferric ions. Ferric ion is one ot the most importirnl in the the oxidative agents. Potential of Fc~7Fc~$^{+}$ couple can be given by Nernst equation;

$$E= E° - 0.0591 \log \frac{a_{Fe^{3+}}}{a_{Fe^{2+}}} \qquad (2)$$

where E°: Half-cell standard potential, R: Gas constant, F: Faraday constant, z: Number of exchanging electrons, a: activity of ions in solution phase. According to Equation (2), even if Fe$^{+}$ amount is million fraction of Fe~$^{+}$, potential of Fe 7Fe~$^{+}$ couple is 0.416 V. This potential value can oxidize all of the base metals and also Zn (Çakır. 1976). However, it is not possible to keep iron, form of ferric ions in solution at normal conditions. In order to prevent this situation, the solution must be strongly acidified. Ferric sulphate (Fe2(SO$_4$)0 and ferric chloride (FeCIO may be used as source of Fe$^{'1+}$. In this situation, possible dissolution reaction equations of ZnS are given in Equation (3) and (4) (Dutrizac and MacDonald, 1974, 1978).

ZnS + 2FeCl, -> ZnCl-, +2FcCl, + S° (3)
ZnS + FcMSOah -> ZnS0$_4$ + 2FeSÖ$_4$ + S° (4)

It was reported that ferric chloride has more advantage than ferric sulphate (Dutrizac and MacDonald, 1974, 1978).

## 2 MATERIAL AND METHODS

### *2.1 Material*

The sphalerite concentrate (ZnS) recovered by notation from Sivas-Koyulhisar CuFeS$_2$-PbS-ZnS complex ore was used in the experimental study. The concentrate used were sieved to -212+106, -106+75, -75+45, -45+38 and -38 urn panicle size fractions. First, wet sieving was made and the materials were dried, and then dry sieving was performed using the same screens. The chemical analysis of each fractions are given in Table 1.

Table I. Chemical analysis of each fraction of sphalerite concentrate

| Particle Size (um) | Element *(%)* | | |
|---|---|---|---|
| | Zn | Cu | Pb |
| -212+106 | 57.87 | - | 0.03 |
| -106+75 | 59.97 | - | - |
| -75 +45 | 61.73 | 0.85 | 0.04 |
| -45 +38 | 57.70 | 0.53 | 0.75 |
| -38 | 39.53 | 1.43 | 5.00 |
| Total | 48.76 | 0.90 | 2.71 |

### 2.2 *Experimental procedure*

In order to provide the Zn dissolution from ZnS concentrate, $Fe^{3+}$ ion leaching in acidic medium was performed. FeCl, was used as source of Fe$^{+}$. Experiments were carried out in a glass vessel put in the hot water bath whose temperature can be adjusted in the range of 0-100°C with ±0.2°C accuracy. Stirring process was provided via a mechanical stirrer with teflon shaft whose stirring speed can be adjustable between the 0-2000 rpm.

500 ml of Fe$^{'1+}$ solution was used for each parameters. To prevent of hydrolysis of Fe ions, pH value of the solution was kept constant (pH=1.0) by adding HCl.

The experiments were carried continuously. In the experiments to investigate the effect of temperature, a denser system was used to prevent evaporation. In order to determine the dissolution recovery of Zn, 2 ml of sample solution was taken from leach solution at the end of leaching experiment. After, 2 ml of original solution was added to leach solution. Zn analysis was determined by a Vista AX CCD model ICP-AES apparatus.

In the experimental studies, the effects of stirring speed, Fe$^{u}$ ion concentration, solid/liquid ratio, temperature and particle size on the dissolution of Zn were investigated.

## 3 RESULTS AND DISCUSSION

### *3.1 Effect of stirring speed*

The effect of stirring speed on the dissolution of Zn was performed at different stirring speeds and leaching times. The results from these experiments are shown in Fisiurc 2.



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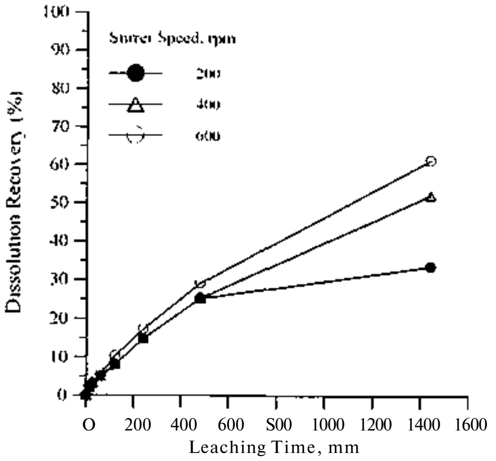
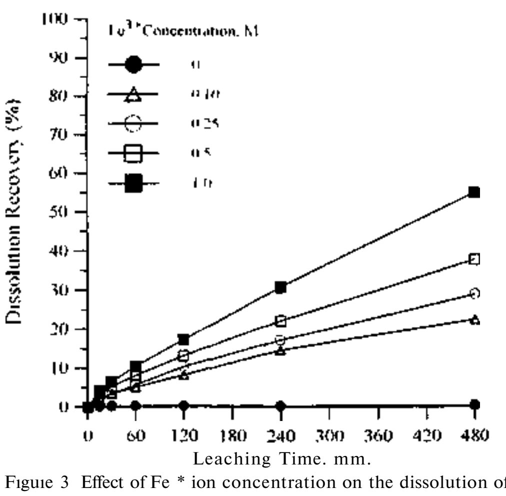



Figuie 2 Effect of stining speed on the dissolution of Zn (Temperature: 50 'C, $Fe^{\cdot +}$ concentration- 0.25 M. solid/liquid latio. 10 g/500 ml. particle size: -75+45 pin)

As seen from Figure 2, the dissolution recovery of Zn was not changed in the range of 0-480 minutes for stirring speed values of 200 and 400 rpm. At the stirring speed of 600 rpm, the dissolution recovery of Zn reached to 60% at the end of leaching lime of 1440 minutes. Therefore, stirring speed value of 600 rpm was selected for investigation of the effect of other parameters.

### *3.2 Effect of Fe * ion concentration*

The effect of $Fe'^{+}$ ion concentration was investigated using solutions of 0, 0.1, 0.25, 0.5 and 1.0 M $Fe^{1+}$ concentration. HCl (pH=1.0) was the only one used in non-ferrous medium. The results of those are given in Figure 3.




Figuie 3 Effect of Fe * ion concentration on the dissolution of Xn (Temperature 50 C. stirring speed' 600 rpm. solid/liquid ratio 10 g/500 nil. panicle size: -75+45 urn)

From Figure 3;

i) The dissolution recovery of Zn increased with increasing $Fe'^{,+}$ ion concentration. At the end of leaching lime of 480 minutes, the dissolution recoveries of Zn for without $Fe^{u}$ ions and 0.1 M $Fe^{3+}$ ion concentration reached to 0.5% and 22,13%), respectively. In addition, this recovery value increased to -55% for 1.0 M concentration of $Fe^{3+}$ ion.

ii) The dissolution recoveries at the beginning of leaching increased as directly proportional with increasing $Fe^{+}$ ion concentration.

iii) For the experiments performed using only HCl, the dissolution recovery of Zn was very slow according to ferric medium. This result is consistent with that of Majima and Awakura ( 1979).

The highest dissolution recovery of Zn was obtained with 1.0 M concentration of $Fe^{1+}$ ion. Therefore, this concentration value was used for further investigations.

### *3.3 Effect of solid/liquid ratio*

The effect of solid/liquid ratio were investigated at solid/liquid ratio values of 5/500, 10/500, "20/500, 50/500 and 100/500 g/ml. The obtained results arc shown in Figure 4.

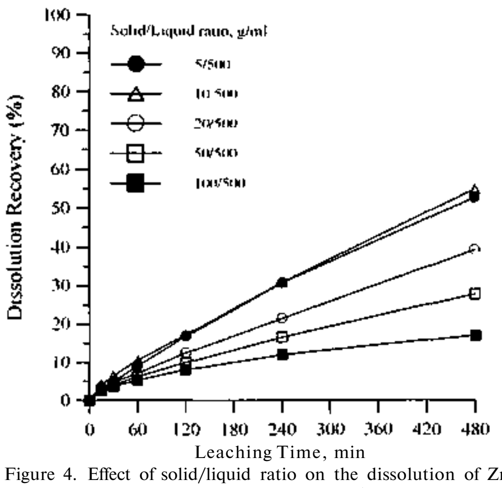



Figure 4. Effect of solid/liquid ratio on the dissolution of Zn (Temperature. 50 "C. staring speed- 600 rpm. $Fe^{1+}$ ion concentration- I 0 M. panicle size -75+45 urn)

As seen from Figure 4, there was not any important variation on the dissolution recovery of Zn for the solid/liquid ratio values of 5/500 and 10/500 g/ml. Solid/liquid ratio value of 10 g/500 ml was used for investigation of effects of other parameters.

### *3.4 Effect of temperature*

Figure 5 shows the effect of leaching temperature on the dissolution recovery of Zn. It is possible to reach following conclusions from the Figure 5:

i) As leaching temperature increases, the dissolution recovery of Zn increases.

ii) Although the dissolution recovery of Zn increased with increasing temperature at the first 15 minutes of leaching time, the dissolution recovery of Zn remained at almost same values for the temperatures of 80 and 90 °C. For these temperature values, the dissolution recovery increased to -90% at the end of leaching time of 480 minutes.

### *3.5 Effect of panicle size*

The experiments for determination of the effect of particle size on the dissolution of Zn were performed at 80 °C. -212+106,-106 +75. -75 +45, -45 +38 and -38 urn particle size fractions and original concentrate (not sieved to fractions) were used in the leaching studies as shown in Figure 6.

As seen from Figure 6;

i) The dissolution recovery of Zn generally increased with decreasing particle size. At the end of leaching time of 120 minutes, while the dissolution recovery of Zn was 85% for -38 urn particle size, this ratio remained at -52% for -45+38 |im particle size fraction.

ii) The dissolution recoveries obtained for -212+106 and -106+75 urn particle size fractions were very close to each other. In addition, these recovery values gave similar results for the size fraction of -75 +45 and -45 +38 um.

iii) At the end of leaching time of 480 minutes, the dissolution recovery of Zn for original concentrate (-212 urn) was reached to -82%..

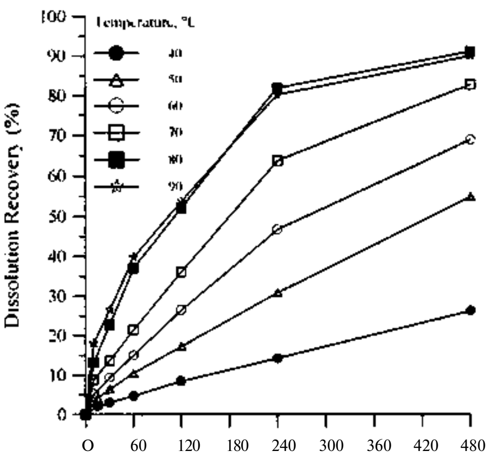



Figure 5. Effect of temperature on the dissolution of Zn (Stirring speed- 600 rpm. $Fe^{3+}$ ion concentration: 1.0 M. solid/liquid ratio- 10 g/500 ml. particle size: -75+45 um)

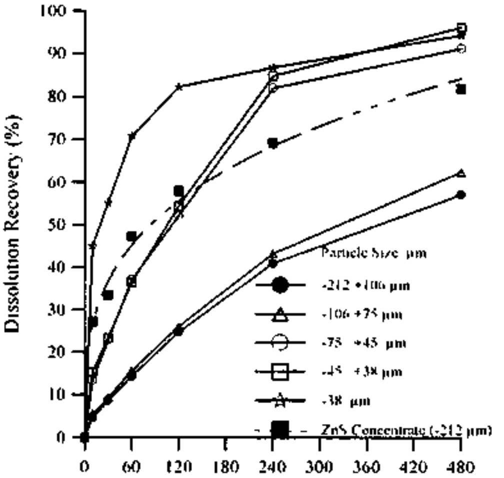



Figure 6. Effect of particle size on the dissolution of Zn (Leaching temperature' SO T. sniring speed 600 rpm. $Fe^{3+}$ ion concentration- I 0 M. solid/liquid mho- 10 g/500 ml)

## 4 CONCLUSIONS

The following conclusions can be drawn from the ferric chloride leaching tests on the concentrates recovered by the flotation method from Sivas-Koyulhisar Cu-Pb-Zn ore.

The dissolution of Zn was not affected by the stirring speed in the range of 200-400 rpm. At the stirring speed of 600 rpm. an increase on the Zn dissolution was observed. On the other hand, the Zn dissolution recovery varied proportionally with ferric ion concentration and temperature, however this recovery varied as inversely proportionally with solid/liquid ratio and particle size.

The optimum leaching conditions were determined as: stirring speed of 600 rpm, $Fe^{+}$ concentration of 1.0 M, solid/liquid ratio of 10/500 g/ml and leaching temperature of 80 °C. At the end of leaching time of 480 minutes under the above conditions, the Zn dissolution recoveries increased to 85%.. 89% and 92% for -75+45 urn, -45+38 urn and -38 (am particle size, respectively. Moreover, the Zn dissolution recovery reached to 82%' value for original concentrate (-212 urn).

## REFERENCES

Bobeck. G.E., and Su. H., 1985. The kinetics of dissolution of sphalerite in ferric chloiide solutions. *Melul. Trimx.* 16B:413-424

Canbazoğlıı. M. and Ûzkol, S.. 1980 Leaching of Çayeli complex sulphide ore by HCl+MgG: solution: recovery of Pb. Zn and CuFeS; concentrates. *Coinple.\ Sulphide Ores Gmfemit e,* The Institution of Mining and Metallurgy. Rome. Italy. 7-11.

Çakır. A F . 1976 Harşıt Köprübaşı Kompleks Cu-Pb-Zn-Sb-Ag-Cd Cevher Konsantresinin Fenik Klorür Çözeltisinde Lıçı. I T U Maden Fakültesi

Çopur. M. 2001. Solubility of ZnS concentrate comainin pyııte and chulcopynte in $HNO_($ solutions. *Chem. Binchem. Ena. Q-* 1-">(4>: 181-184.

Demopoulos, G.P. and Baldwin. S.A.. 1999. Stoichiometric and kinetic aspects on the pressure leaching of zinc concentrates. *In Mishit. B. (Eil.). TMS Animal Meeting.* San Diego. 567-583

Dutrizac. .I.E. and MacDonald. R.J.C. 1974. Ferric ion as a leaching medium. *Minerals Sı İ. Eiinnn-* 6. no 2. 59-100

Dutrizac. J.E. and MacDonald. R J.C. 1978. The dissolution of sphalette in ferric chloride solutions. *Metall. Trans..* 9B:543-55I

Ghosh. M.K.. Das. R.P. and Biswas. A.K. 2002. Oxidative ammonia leaching of sphalerite I : Noncatalytic kinetics. *Int. J. Miner Process.* 66:241-254.

Majima. H. and Awakaura. Y.. 1979. Non-oxidative leaching of base metal sulphide ores. *In XIII International Mineral PriKessmu Congress.* Warsaw, preprints of papers volume I Laskowski J. Ed. (Warsaw: Polish Scientific Publishers. 19791.665-689.

Majima. H.. Awakaura. Y.. Misaki. N.. 1981. A kinetic study on nonoxidative dissolution of sphalerite m aqueous hydrochloric acid .solution. *Metall. Trans.* 12B. 645-649.

Mizoguchi. T. and Habashi. F. 1981. The aqueous oxidation of complex sulfide concentrates in hydrochloric acid. *Int. J. Miner process.* 8:177-193.

Parker. E.G.. 1961. Oxidative pressure leaching of zinc concentrate. *CIM Bull.* 74 (51:145-150

Palencia Perez, 1. and Dutrizac. .I.E.. 1991. The effect of the iron content of sphalerite on its rate of dissolution in ferric sulphate and ferric chloride media. *Hvtlrmnetalhtrxv* 26. 211-232.

Rao. K.S.. Anand. S.. Das. R.P. and Ray. H.S. 1992. Kinetics of ammonia leaching of multimetal sulphides. *Miner. Process. E\tr. Metal.* Rev. 10:11-27.

Rath. P.C.. Paramguru. R.K. and Jena. P.K. 1988. Kinetics of dissolution of sulphide minerals in ferric chloride solution. I: dissolution of galena, sphalerite and chalcopyrite. *Trans. Instil Min. Metal.* Sect. C. 97:150-158

Sarveswara Rao. K. and Ray, H.S. 1998. A new look at characterisation and oxidative ammonia leaching behaviour of multimetal sulphides. *Miner. Ena.* 11(11). 1011-1024

Warren. G.W., Kim. S.H. and Henein H. 1987. The effect of chloride ion on the ferric chloride leaching of galena concentrale. *Metall. Trans..* l8B:59-69

Wills. B.A.. 1984. The separation by flotation of copper-lead-zinc sulphides. *Min. Man..* 36-41