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Recovery of Zinc from Zinc Oxide Ore by Sulfuric Acid Leaching

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Abstract. This study investigates the extraction from zinc oxide ore by leaching using sulfuric acid. Effects of some parameters such as leaching time, acid concentration, leaching temperature, particle size and solid/liquid ratio were studied for maximum zinc extraction and minimum acid consumption. Optimum leaching conditions were determined to be 120 minutes of leaching time, 55 g/L H_2SO_4 of acid concentration, 25 ˚C of leaching temperature, -780 µm of particle size and a solid/liquid ratio of 1/10. In these optimum conditions, 93.42% of zinc extraction and 1.58 (ton H_2SO_4/dissolved ton Zn) of acid consumption were achieved.

Keywords: Zinc oxide ore, acid leaching, sulfuric acid.

Sülfürik Asit Liçi ile Çinko Oksit Cevherinden Çinko Geri Kazanımı

Özet. Bu çalışmada sülfürik asit kullanılarak liç ile çinko oksit cevherinin kazanımı araştırılmıştır. Liç süresi, asit konsantrasyonu, liç sıcaklığı, partikül boyutu ve katı/sıvı oranı gibi bazı parametrelerin etkileri maksimum çinko ekstraksiyonu ve minimum asit tüketimi için araştırılmıştır. Optimum liç koşulları 120 dakika liç süresi, 55 g/L H_2SO_4 asit konsantrasyonu, 25 ˚C liç sıcaklığı, -780 µm partikül boyutu ve 1/10 katı/sıvı oranı olarak belirlenmiştir. Bu optimum koşullarda, %93.42 çinko ekstraksiyonu ve 1.58 (ton H_2SO_4/ çözünen ton Zn) asit tüketimi elde edilmiştir.

Anahtar Kelimeler: Çinko oksit cevheri, asit liç, sülfürik asit.

1. INTRODUCTION

Zinc is one of the three most important metals after aluminum and copper among non-ferrous metals in terms of utilization. In the past year, as other metals, the increasing demand for zinc in the world has required intensive studies for extraction of metals from zinc oxide ores. Zinc production can be achievable by both hydrometallurgical and pyrometallurgical processes. The hydrometallurgical process mainly contains acid leaching, alkaline leaching and ammonia leaching.

The term "oxide zinc ores" covers all of the oxide, carbonate and silicate of zinc minerals. Main zinc minerals are smithsonite ($ZnCO_3$), zincite (ZnO), hemimorphite ($Zn_4Si_2O_7(OH)_2$ $2H_2O$) and willemite (Zn_2SiO_4). Leaching of these zinc oxide minerals by sulfuric acid can be described by Eqs. 1-4 [1-3].

$$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_{4(aq)} + H_2O + CO_2 \quad (1)$$

$$ZnO + H_2SO_4 \rightarrow ZnSO_{4(aq)} + H_2O \quad (2)$$

$$Zn_4Si_2O_7(OH)_2.H_2O + 4H_2SO_4 \rightarrow 4ZnSO_{4(aq)} + Si_2O(OH)_6 + 3H_2O \quad (3)$$

$$Zn_2SiO_4 + 2H_2SO_4 \rightarrow 2ZnSO_{4(aq)} + Si(OH)_{4(aq)} \quad (4)$$

Hematite (Fe_2O_3), limonite ($FeO(OH).nH_2O$), dolomite ($CaMg(CO_3)_2$), calcite ($CaCO_3$) and quartz (SiO_2) are common gangue minerals in zinc oxide ores. Leaching of zinc oxide ores consumes

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a great deal of acid because of the presence of large amounts of these gangue minerals. Therefore, it is of great significance to effectively achieve beneficiation by leaching these zinc oxide ores.

Sulfuric acid leaching of zinc ores has been studied by many researchers: Abdel-Aal [1] studied the kinetics of sulfuric acid leaching of low-grade zinc silicate ore, and the results showed that leaching of about 94% of zinc was achieved using a -200+270 mesh ore particle size at a reaction temperature of 70 °C for 180 minutes of reaction time with 10% sulfuric acid concentration and a solid:liquid ratio of 1:20 g/mL. Bodas [4] performed leaching of zinc silicate ore by sulfuric acid and found that the maximum zinc extraction (95% Zn) was obtained at a 4.5 M concentration of sulfuric acid in 3 h of leaching at 70 ˚C, keeping the solid:liquid weight ratio at 1:5. Canbazoğlu et al. [5] investigated dissolution of zinc in sulfuric acid solution from low-grade lead&zinc ore, and they reported that leaching of zinc could be achieved with 90% of zinc extraction with a consumption of 5607 kg of acid in the optimum leaching conditions as; leaching temperature: 60 °C, leaching time: 60 minutes, acid concentration: 100 g/L; particle size: 83.27% below 45 µm and stirring speed: 350 rpm. Uysal [6] studied evaluation of low-grade zinc oxide ore using sulfuric acid leaching, and the best leaching conditions were obtained to be 350 rpm of stirring speed, 60 minutes of leaching time, 75 g/L of acid concentration, 80 °C of leaching temperature, particle size of 80% below 60 µm and solid/liquid ratio of 1/10.

As known, zinc is produced mostly from zinc sulfide ores because sulfides are easy to separate from gangue. With declining reserves of zinc sulfides, there is an increasing focus on processing zinc oxide ores. Extensive studied have been performed to upgrade zinc ores by flotation, but this method had limited effect on their qualities. Many studies focused on using the hydrometallurgical route for zinc oxide ores in sulfuric acid or alkaline. The aim of this study is to achieve the maximum zinc extraction and minimum acid consumption from zinc oxide ore by leaching using sulfuric acid. Effects of several parameters such as leaching time, acid concentration, leaching temperature, particle size and solid/liquid ratio on zinc leaching were investigated.

2. MATERIALS AND METHODS

The zinc oxide sample for the leaching study was obtained from Hakkari in Turkey. The results of the chemical analysis of the ore sample are shown in Table 1. X-ray diffraction (XRD) spectra of the sample were obtained using a Rigaku DMAX IIIC model X-ray diffractometer using CuKά radiation at 35 kV and 15 mV. X-ray diffraction analysis indicated that the mineralogical constituents were smithsonite ($ZnCO_3$), cerussite ($PbCO_3$) and goethite (FeOOH) (Figure 1).

In order to prepare the sample for experiments, the following steps were pursued: crushing (-2.8 mm), grinding (-250 µm) and sieving. H_2SO_4 from Merck, with an analytical purity of 95-98% was used in all leaching experiments. The leaching experiments were performed in a 1 L glass beaker that was placed in a thermostatically controlled water bath. The beaker was covered with a plastic cap that contained four holes for placing the mechanical stirrer, thermometer, pH meter or condenser and for taking samples. After leaching, the leach residue filtered from the leach solution, then washed with distilled water and dried at 105 ˚C to obtain total dissolved weight values. At the end of each experiment, the leach solution was analyzed by atomic adsorption spectrometry (AAS) to determine the degree of zinc extraction. The amount of sulfuric acid in the pregnant leach solution was determined by NaOH titration in order to determine the amount of consumed acid in the leaching experiments.

Zinc extraction and acid consumption were calculated using following equations (5-6):

$$\mathrm{ZE}\ (\%) = \frac{\left[\mathrm{V1\ (mL)\ x\ S\ x\ \frac{1}{1000}\ x\ \frac{D\ (mg/L)}{1000}}\right]\ \mathrm{x\ N\ (g)}}{100} \quad (5)$$

ZE: Zinc extraction (%)
V1: The volume of H_2SO_4 used in leaching experiments (mL)
S: Dilution factor
D: Value of read in AAS (mg/L)
N: Amount of solid used in leaching experiments (g)

$$AC\ (g) = \left[LA\ (M)\ x\ V1\ (mL) - \frac{\left(\frac{M\ (mol)\ x\ T1\ (mL)}{T2\ (mL)}\right)\ x\ S}{2}\ x\ V1\ (mL)\right]\ x\ H\ (g/mol) \quad (6)$$

AC (g): Acid consumption (g)
LA: The molarity of H_2SO_4 used in leaching experiments (M)
V1: The volume of H_2SO_4 used in leaching experiments (mL)
M: The molarity of NaOH (M)
T1: The volume of NaOH spent in titration (mL)
T2: The volume of leaching solution used in titration (mL)
S: Dilution factor
H: Molecular weight of H_2SO_4 (g/mol)

Table 1. Chemical analysis of ore sample.

Component	Weight (%)
Zn	25.44
Fe	21.20
Pb	4.20
Cu	<0.01
Mn	0.17
Ca	0.47
Cd	0.09
Ni	<0.01
SiO_2	3.68
S	0.18
As	0.28
K	<0.10
Na	<0.10
Moisture	0.51

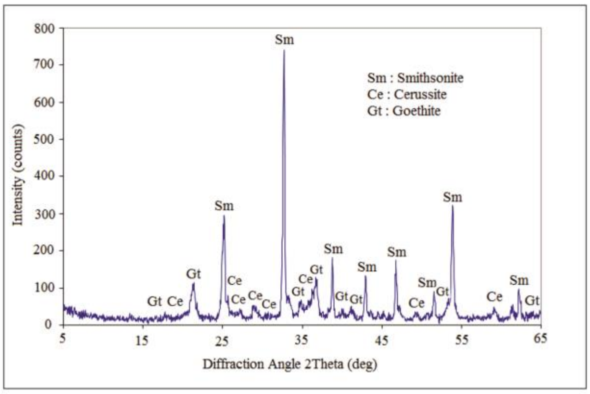

Figure 1. XRD pattern of the zinc oxide ore used in the experiments.

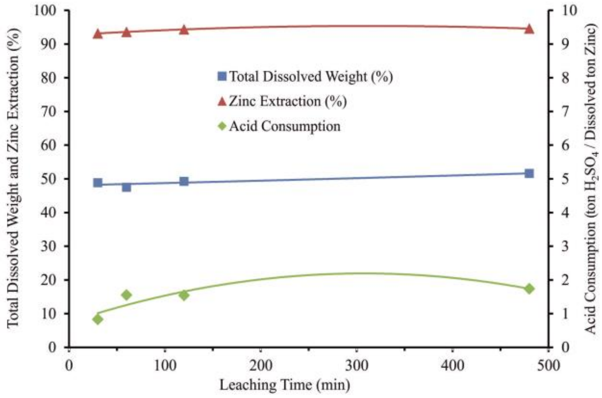

Figure 2. Effect of leaching time on the extraction of zinc.

3. RESULTS AND DISCUSSION

3.1. Effect of Leaching Time

The effect of leaching time was studied under the conditions that H_2SO_4 concentration was 75 g/L, leaching temperature was 40 ˚C, ore particle size was -250 µm and ratio of solid/liquid was 1/10. The results are shown in Figure 2. When the leaching time increased from 30 to 480 minutes, zinc extraction (%) increased from 93.16% to 94.58%, while total dissolved weight (%) only increased from 48.85% to 51.62%. It was seen that zinc extraction (%) and total dissolved weight (%) were not affected much by increasing the leaching time. Similarly, Xu et al. [3] observed that leaching time had no remarkable effects on the percentage of zinc extraction. On the other hand, acid consumption (ton H_2SO_4/dissolved ton Zn) increased by increasing the leaching time. As seen in Figure 2, 93.60% zinc was extracted in 60 minutes by 1.55 (ton H_2SO_4/dissolved ton Zn) acid consumption. Based on experimental results the leaching time of 60 minutes was chosen as the most suitable leaching time.

3.2. Effect of Acid Concentration

The experiment for the effect of acid concentration was carried out in the range of 25-125 g/L H_2SO_4 (Figure 3). The effect of acid concentration was investigated for a leaching time of 60 minutes at the temperature of 40 ˚C, particle size of -250 µm and solid/liquid ratio of 1/10. As observed in Figure 3, by increasing acid concentration, the amount of total dissolved weight (%) increased, and consequently, zinc extraction (%) increased. This behavior was previously observed by Abdel-Aal [1] and Bodas [4] in sulfuric acid media. However, increase in acid concentration causes an increase in acid consumption (ton H_2SO_4/dissolved ton Zn). Figure 3 shows that the total dissolved weight was 47.50%, and zinc extraction of 93.60% could be achieved at 75 g/L of H_2SO_4 concentration. For this reason, the acid concentration value was selected as 75 g/L in the experiments. Additionally, for economic reasons, the acid consumption was kept constant at 75 g/L.

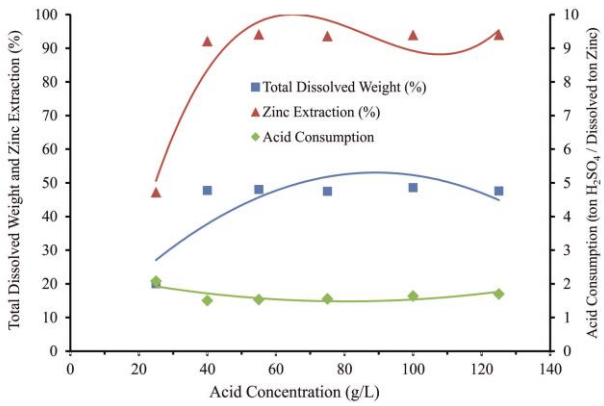

Figure 3. Effect of acid concentration on the extraction of zinc.

3.3. Effect of Leaching Temperature

The results that were obtained in the leaching experiments under different temperatures at the leaching time of 60 minutes using the 75 g/L H_2SO_4 concentration, the particle size of -250 µm and the 1/10 solid/liquid ratio are presented in Figure 4. The effect of temperature was investigated in the range of 25-90 ˚C. The leaching temperature did not have a significant effect on total dissolved weight (%) and zinc extraction (%). Moreover, acid consumption (ton H_2SO_4/dissolved ton Zn) increased as temperature increased. It seems that higher values of total dissolved weight (%) and zinc extraction (%) and a lower value of acid consumption (ton H_2SO_4/dissolved ton Zn) are achieved by lower temperatures. Consequently, the best results were obtained with the leaching temperature of 25 °C.

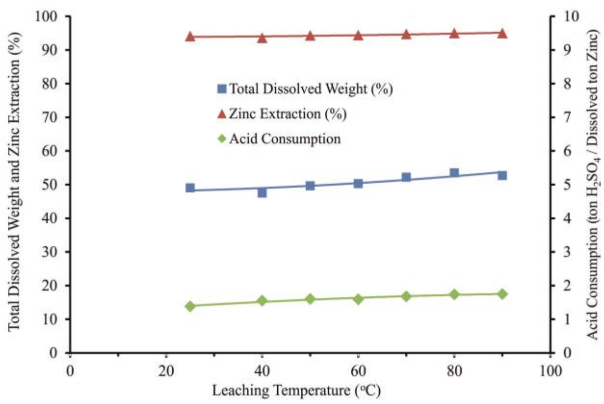

Figure 4. Effect of leaching temperature on the extraction of zinc.

3.4. Effect of Particle Size

Effect of particle size on leaching was studied in the range of 90 µm to 1050 µm using ASTM standard sieves. The experiments were performed with different particle sizes for 120 minutes using 55 g/L H_2SO_4 at 25 ˚C temperature and 1/10 solid/liquid ratio. The results are given in Figure 5. As seen in Figure 5, total dissolved weight (%) and zinc extraction (%) increased with a decrease in particle size. Usually, the literature shows that the smaller the particle size, the faster the leaching of zinc, as observed by Souza et al. [7] and Wang et al. [8]. When the initial particle size (-1050 µm) of the ore decreased to -90 µm, zinc extraction (%) increased from 71.90% to 94.02%. However, the decrease in particle size did not affect total dissolved weight (%) and acid consumption (ton H_2SO_4/dissolved ton Zn) positively. The best results were obtained with the particle size of -780 µm because of the high total dissolved weight (46.34%) and high zinc extraction (93.42%) and low acid consumption (1.58 (ton H_2SO_4/dissolved ton Zn)) values.

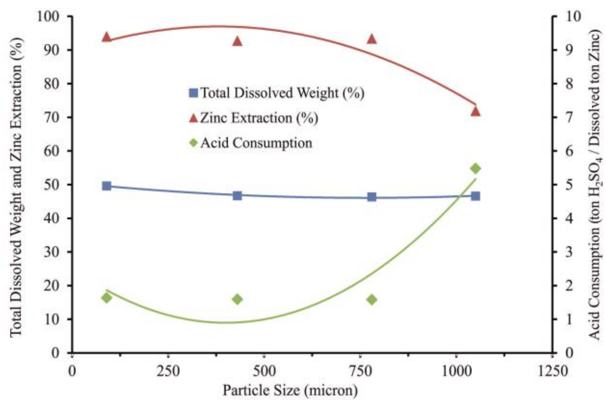

Figure 5. Effect of particle size on the extraction of zinc.

3.5. Effect of Solid/Liquid Ratio

Figure 6 presents the results of leaching with different solid/liquid ratios that was studied in the range of 1/4 to 1/10. The effect of solid/liquid ratio was investigated for a leaching time of 120 minutes at the temperature of 25 ˚C using 55 g/L H_2SO_4 and -780 µm of particle size. Figure 6 shows that the decrease in solid/liquid ratio increased total dissolved weight (%) and zinc extraction (%). Zinc extraction (%) increased from 50.09% at solid/liquid = 1/4 to 93.42% at solid/liquid = 1/10. Lower acid consumption by the 1.58 (ton H_2SO_4/dissolved ton Zn) value was obtained at the solid/liquid ratio of 1/10, too. Thus, it was determined to keep the solid/liquid ratio at 1/10. When the solid/liquid ratio was increased, the amount of dissolved per unit liquid increases, and hence, the rate of leaching decreases [9]. This is consistent with the result of Espiari et al. [10] in the treatment of zinc oxide ore by acidic leaching.

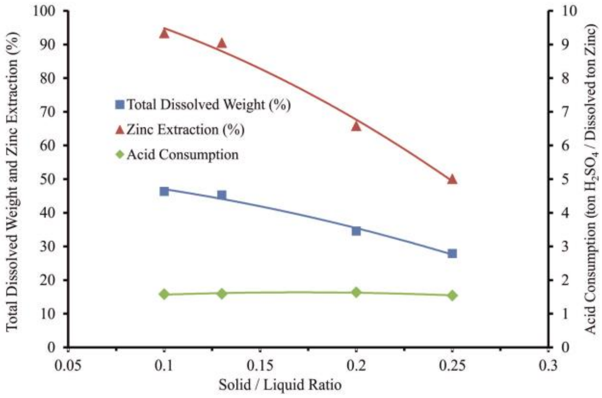

Figure 6. Effect of solid/liquid ratio on the extraction of zinc.

4. CONCLUSIONS

By optimizing the leaching parameters as summarized in Table 2, the experiments showed that it was possible to extract 93.42% of zinc with 46.34% total dissolved weight by 1.58 (ton H_2SO_4/dissolved ton Zn) acid consumption.

Table 2. The results of sulfuric acid leaching under optimum process conditions.

Leaching Time (minute)	120
Acid Concentration (g/L)	55
Leaching Temperature (ºC)	25
Particle Size (µm)	-780
Solid/Liquid Ratio	1/10

It was observed that the following conclusions could be drawn:

- Leaching time and leaching temperature did not have significant effects on leaching recovery of zinc oxide ore,
- Zinc extraction (%) increased gradually with sulfuric acid concentration,
- With decrease in particle size of zinc oxide sample, zinc extraction (%) increased,
- Zinc extraction (%) decreased as the solid/liquid ratio increased.

This study demonstrated that zinc oxide ore from Hakkari in Turkey could be successfully processed to recover zinc by sulfuric acid leaching.

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REFERENCES

[1]. Abdel-Aal E.A., Kinetics of Sulfuric Acid Leaching of Low-Grade Zinc Silicate Ore, Hydrometallurgy, 55 (2000) 247-254.

[2]. Havlik T., Turzakova M., Stopic S., Friedrich B., Atmospheric Leaching of EAF Dust with Diluted Sulphuric Acid, Hydrometallurgy, 77 (2005) 41-50.

[3]. Xu H., Wei C., Li C., Fan G., Deng Z., Li M., Li X., Sulfuric Acid Leaching of Zinc Silicate Ore Under Pressure, Hydrometallurgy, 105 (2010) 186-190.

[4]. Bodas M.G., Hydrometallurgical Treatment of Zinc Silicate Ore from Thailand, Hydrometallurgy, 40 (1996) 37-49.

[5]. Canbazoğlu M., Kaya Ö., Kulaksız M.I., Nizamoğlu Y.S., Sulphuric Acid Leaching of Zinc from Low Grade Lead&Zinc Ores, Proceedings of the XIII Balkan Mineral Processing Congress, 2 (2009) 587-593.

[6]. Uysal G., The Evaluation of Low Grade Zinc Oxide Ore of Niğde Öküzgönü Tepe Using Sulfuric Acid Leaching and Solvent Extraction, MSc thesis, Cumhuriyet University, Department of Mining Engineering, (2011) Sivas, Turkey.

[7]. Souza A.D., Pina P.S., Lima E.V.O., Silva C.A., Leão V.A., Kinetics of Sulfuric Acid Leaching of a Zinc Silicate Calcine, Hydrometallurgy, 89 (2007) 337-345.

[8]. Wang R.X., Tang M.T, Yang S.H, Zhagn W.H, Tang C.B., He J. Yang J.G., Leaching Kinetics of Low-Grade Zinc Oxide Ore in NH_3-NH_4Cl-H_2O System, J. Cent. South Univ. Technol., 15 (2008) 679-683.

[9]. Bayrak B., Laçin O., Saraç H., Kinetic Study on the Leaching of Calcined Magnesite in Gluconic Acid Solutions, J. Ind. and Eng. Chem., 16 (2010) 479-484.

[10]. Espiari S., Rashchi F., Sadrnezhaad S.K., Hydrometallurgical Treatment of Tailings with High Zinc Content, Hydrometallurgy 82 (2006) 54-62.