Extraction of Zinc from Smithsonite by Ammonia Leaching

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Abstract – In this study, an ore taken from Kayseri region of Turkey was used. Characterization studies showed that the run-of mine ore is rich in oxide minerals, cerussite (PbCO₃) and smithsonite (ZnCO₃). The aim of the study was extraction of zinc from smithsonite by ammonia leaching on cerussite flotation tailings. Initial lead and zinc grades of the ore were 13.31% and 27.86%, respectively. As a result of a series of cerussite flotation tests, a lead concentrate containing 63.25% Pb was produced with 82.76% recovery. After that, tailing of flotation was treated with ammonia (NH₃) to extract zinc. For that purpose, 5M and 7M of NH₃ solutions were used for 30 minutes, 1 hour, 3 hours, 6 hours and 12 hours. In consequence of the leaching experiments, the highest extraction rate was obtained as 76.66% using 7M NH₃ solution with 12 hours of treatment.

Keywords: Smithsonite, ammonia, leaching

1. Introduction

Lead and zinc are two of the most widely used commodities and have a big importance for industry. Even though their major sources are sulfides, finding new sources for production of lead and zinc concentrates as an alternative for depleting sulfide sources is a matter of issue (Ejtemaei et al, 2014). Cerussite and smithsonite are the most abundant non-sulfide minerals of lead and zinc and they have a considerable potential to produce lead and zinc concentrates (Moradi & Monhemius, 2011; Ma et al, 2011; Abkhoshk et al, 2014). Most commonly, hydrometallurgical processes or froth flotation are performed for concentration of cerussite and smthisonite (Gupta & Yan, 2006; Abkhoshk et al, 2014). Even though flotation of oxide minerals is quite hard due to consumption of excessive amounts of flotation reagents, lower selectivity and surface coating problems, flotation is still applicable and widely used method (Şentürk, 1987; Lan et al, 2013). Although it requires more time, hydrometallurgy is more adventageous especially for low grade ores and finely disseminated particles (Habashi, 1970; Meng & Han, 1996).

Despite in many studies possibility of smithsonite flotation has been proven (Şentürk et al, 1993; Fa et al, 2005; Ejtemaei et al, 2011; Mehdilo et al, 2014), in some cases flotation become less viable by virtue of complex structure of the mineral. At that case, leaching may be preferred. Sulfuric acid is used commonly as leaching reagent for extraction of oxide zinc minerals, but due to silica gel forming, usage of new chemicals such as ammonia and its salts is gaining importance (Ju et al, 2005; Liu et al, 2012). Several studies were carried out to investigate the leachability of zinc oxide using ammonia and ammonium salts (Ju et al, 2005; Moghaddam et al, 2005; Wang et al, 2008; Ma et al, 2011). Main conclusions of these studies are ammonia can be used as a leaching reagent for extraction of Zn but concentration of the reagent, leaching duration, particle size of the test sample and temperature are some main parameters that need to be controlled for a successive process.

Turkey has a lot of oxide zinc sources mainly distributed in Central Anatolia (SOP, 2011) and the aim of this study is to beneficiation of an ore taken from Central Anatolia, containing smithsonite with 28.31% Zn by agitated ammonia leaching by investigating the effect of reagent concentration and leaching duration on Zn extraction rate.

2. Experimental

2.1. Material

The ore used throughout the study was collected from Kayseri-Develi region of Turkey where oxide lead and zinc minerals are predominant. Characterization studies were completed using polorized microscope, X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD) analysis. Cerussite (PbCO₃) and smithsonite (ZnCO₃) were identified as predominant species with 13.59% Pb and 28.31% Zn grade. Hemimorphite ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$), limonite (Fe(OH)₃), calcite (CaCO₃) and dolomite (CaMg(CO₃)₂) were also present as accessory minerals. Formations of galena (PbS), sphalerite (ZnS) were also seen from microsocopic image of the sample but most of galena and sphalerite particles were transforming to cerussite and smithsonite. Concentrations of major constituents obtained from XRF analysis is presented in Table 1.

Table 1: Chemical analysis result of run-of mine ore.

Pb (%)	Zn (%)	Ag (ppm)	Al (%)	Ca (%)	Fe (%)	Mg (%)	Cu (ppm)	Si (%)
13.31	27.86	89	0.49	2.57	5.41	0.78	9.4	5.28

Particle size of the representative sample determined by sieve analysis and metal distribution of the representative sample is determined using Atomic Absroption Spectroscopy (AAS). The results of particle size analysis together with metal distribution analysis are provided in Table 2. Zinc grade is decreasing related to particle size. On the other hand lead grade is increasing with decreasing particle size up to 210 μ m.

P. Size(µm)	% Wt.	Cum. U/S (%)	Pb (%)	Zn (%)	Pb Distr. (%)	Zn Distr. (%)
1300	27,76	100,00	12,40	30,00	25,87	29,89
1168	23,98	72,24	13,45	29,60	24,24	25,47
600	5,42	48,26	14,60	28,10	5,95	5,47
417	4,24	42,84	15,50	27,90	4,94	4,25
295	7,03	38,60	16,60	27,70	8,77	6,99
210	2,37	31,56	17,15	26,60	3,05	2,26
150	5,02	29,20	15,05	24,70	5,68	4,45
106	4,10	24,17	15,95	25,70	4,91	3,78
74	20,08	20,08	11,00	24,20	16,59	17,44
	100,00		13,31	27,86	100,00	100,00

Table 2: Particle size and metal distribution of test sample.

Graphical representation of metal distributions is given in Fig. 1. From the figure, it can be stated that both lead and zinc were distributed significantly in coarse size fractions.



Fig. 1: Cumulative metal distribution of the representative sample.

2.2. Method

The experimental procedure followed during this study is presented in Fig. 2.



Fig. 2: Flowsheet of the study.

First grinding tests were carried out. The test material was ground for 5, 10 and 15 minutes in a rod mill and then sieve analysis was applied to ground material. 10 minutes of grinding was decided to be used for the rest of the study and with this grinding condition, approximately 97% of the material was -75 µm. Lead flotation tests were performed using Denver flotation cell with 30% solid by weight pulp density. Optimum flotation parameters for this lead concentration were determined by a series of flotation tests with examining several flotation parameter such as effect of amount and conditioning time of sulfidizing agent, collector type and amount, desliming and pH. As a result of these tests, as sulfidizer 2000 g/t Na2S with 10 minutes of conditioning, as collector 400 g/t potassium amyl xanthate (KAX) and as frother 53 g/t F-533 (mixture of alcohols, esters and glycols) at pH 9-9.5 with one stage cleaning were determined as optimum conditions for the study.

In the second part, tailings of lead flotation were tried to be floated to obtain Zn concentrate but due to finely and disseminated Zn particles, smithsonite flotation tests were not successful in terms of grade and recovery despite many tests conducted by changing various operational parameters. For that reason ammonia leaching was decided to be performed for tailings of lead flotation. Within the context of leach experiments, 5M and 7M of NH3 solutions were prepared and samples were treated for various leaching durations (30, 60, 180, 360 and 720 minutes) at ambient temperature (~ 25°C). Solid/liquid ratio was taken as 1:10 during all leaching tests. At the end of each leach test, solutions were filtered and both filtrate and residues were analysed using Atomic Absroption Spectroscopy (AAS). Examined parameters during leaching tests are presented in Table 3 and the reaction takes place during the process is given in Equation 1.

Leaching Reagent	Concentration (M)	Leaching Duration (min.)
NH ₃	5	30, 60, 180, 360, 720
NH ₃	7	30, 60, 180, 360, 720

Table 3: Examined test parameter

$\Sigma \Pi C O_3 (s) + 4 \Pi \Pi_3 (aq) \leftrightarrow \Sigma \Pi (\Pi \Pi_3)_4 (aq) + C O_3$	$ZnCO_3$	$(s) + 4 \text{ NH}_{3}(aq)$	$\leftrightarrow Zn(NH_3)_4^2$	$^{+}(aq) + CO_3^{2-}$
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(1)

3. Results and Discussion

From the results it can be concluded that both NH₃ concentration and leaching duration have considerable importance on Zn extraction rate. Increase in reagent concentration causes sharp increase in extraction rate up to 180 minutes durations. Additionally longer leaching durations resulted with increase in extraction rate of Zn.

Even the maximum recovery result was obtained using 7M NH_3 with 720 minutes of treatment, 7M concentration and 360 minutes duration is also viable. On the other hand extraction rate results of 5M for 360 and 720 minutes must also be considered since using 5M of solution would reduce reagent consumption. The results of the experiments are given in Table 4 and graphical representation is provided in Fig. 3.

Table 4: Effect of reagent concentration and leaching duration on Zn extraction rate.	
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Leaching Reagent	Concentration (M)	Leaching Time (min.) Zn Extraction (%)					
		30	60	180	360	720	
NH_3	5	25.79	32.40	59.42	72.77	75.04	
NH_3	7	35.63	49.75	66.37	74.30	76.66	



Fig. 3: Effect of NH₃ concentration on Zn extraction with respect to leaching duration.

This study is progressing with different ammonia salts such as ammonium chloride (NH₄Cl) or ammonium carbonate ((NH₄)₂CO₃) to more comprehensively understand the leachability of smithsonite and to investigate the effect of different reagents on Zn extraction.

4. Conclusions

This study proves the suitability of ammonia (NH₃) for extraction of Zn from smithsonite obtained from Central Anatolia, Turkey. Within the scope of the study, NH₃ was used for 5 and 7 M concentrations and leaching duration was changed to see its effect on zinc extraction. Experiments revealed the positive effect of high ammonia concentration and longer leaching duration on extraction rate of Zn. As leaching duration gets longer, extraction rate of zinc gets higher both for 5 and 7 M concentrations. The maximum extraction rate was 76.66% using 7M of NH₃ for 12 hours.

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