

Received April 4, 2018; reviewed; accepted July 10, 2018

## Leaching behaviour of zinc from a smithsonite ore in sodium hydroxide solutions

Ilhan Ehsani, Ayse Ucyildiz, Abdullah Obut

Hacettepe University, Mining Engineering Department, 06800 Beytepe, Ankara, Turkey

Corresponding author: [ilhan.ehsani@hacettepe.edu.tr](mailto:ilhan.ehsani@hacettepe.edu.tr) (Ilhan Ehsani)

**Abstract:** In this study, the leaching behaviour of zinc from a smithsonite ore sample (23.43% Zn) having goethite and calcite as main gangue minerals was investigated in sodium hydroxide solutions using X-ray diffraction and chemical analyses. Within the studied NaOH concentration range (1-4 mole/dm<sup>3</sup>), higher leaching ratio values for Zn were obtained by leaching at 298 K because of the decreased stability of soluble zincate species in solution at higher temperatures. When the concentration of NaOH solution was increased from 1 to 3 mole/dm<sup>3</sup> at 298 K, leaching ratio value of Zn increased from 3.8 to 70.1%. At 4 mole/dm<sup>3</sup> NaOH concentration, Zn leaching ratio value (70.9%) levelled off due to the formation of solid hydrated calcium zincate phase in leaching solution. On the other hand, very low leaching ratio values of Zn were obtained by leaching in 1 mole/dm<sup>3</sup> NaOH solution at 298 K (3.8%) and 363 K (1.4%) due to the formation of solid zinc hydroxide and solid zinc oxide phases, respectively. It was observed that increasing leaching time from 1800 to 14400 s at 3 mole/dm<sup>3</sup> NaOH concentration, favoured the formation of hydrated calcium zincate phase and so decreased the leaching ratio of Zn to a lower value (60.6%). The effect of solid/liquid ratio was also investigated and it was found that when solid/liquid ratio was decreased, Zn leaching ratio values decreased at constant OH/Zn mole ratio and increased at constant NaOH concentration conditions. Besides, for some of the experiments, leaching ratio values of lead were also given.

**Keywords:** alkaline leaching, calcium zincate, nonsulfide zinc ore, smithsonite, zinc carbonate

### 1. Introduction

Zinc is an industrially important bluish-white, lustrous, low boiling point metal, and often used for galvanization and alloying. It has a valence of +2 and may form complexes with ammonia, halide ions, etc. (Graf, 2005; ILZSG, 2017). Zinc is found mainly in two different types of ores, namely the sulfide and the nonsulfide ores. In sulfide ores, sphalerite (ZnS) is the main ore mineral and is easily concentrated by conventional flotation method. Most of the world zinc production comes from the sulfide deposits. However, because of the steadily decreasing sulfide ore reserves and the increasing demand for zinc, in recent years, the scientific and economic interest for the processing of nonsulfide ores are increasing (Qin et al., 2007; Liu et al., 2011; Irannajad et al., 2013; Abkhoshk et al., 2014; Feng et al., 2015; Rao et al., 2015; Zhang et al., 2016; Ghasemi and Azizi, 2017). In nonsulfide ores, the economically important zinc minerals may be smithsonite (ZnCO<sub>3</sub>), hemimorphite (Zn<sub>4</sub>Si<sub>2</sub>O<sub>7</sub>(OH)<sub>2</sub>·H<sub>2</sub>O), hydrozincite (Zn<sub>5</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>6</sub>), willemite (Zn<sub>2</sub>SiO<sub>4</sub>) and sauconite (Na<sub>0.3</sub>Zn<sub>3</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O) (Hitzman et al., 2003), and due to their lower grades and comparatively complex nature, these ores cannot be effectively beneficiated (Hosseini and Forssberg, 2009; Ejtemaei et al., 2014). As a result, leaching becomes a good option for the extraction of zinc from these zinc ores.

Other than acidic leaching systems using sulfuric (Frenay, 1985; Espiari et al., 2006; Abdel-Aal et al., 2016; Ghasemi and Azizi, 2017), hydrochloric (Dhawan et al., 2011; Ghasemi and Azizi, 2017), nitric (Ghasemi and Azizi, 2017), citric (Irannajad et al., 2013; Ghasemi and Azizi, 2017), boric (Abali et al.,

2017), sulfamic (Wu et al., 2013), methane sulfonic (Feng et al., 2015), trichloroacetic (Deng et al., 2015), 5-sulphosalicylic (Wu et al., 2015) and gluconic (Hursit et al., 2009) acids, different alkaline leaching systems, e.g. sodium hydroxide solutions (Mujahed, 1966; Frenay, 1985; Zhao and Stanforth, 2000; Ghasemi and Azizi, 2018), ammoniacal solutions (Frenay, 1985; Ju et al., 2005; Moghaddam et al., 2005; Feng et al., 2007; Xia et al., 2015), diethylenetriamine (Frenay, 1985), weakly alkaline aqueous iminodiacetate solutions (Dou et al., 2011) etc., were also tested for the dissolution of zinc from different smithsonite samples. The alkaline leaching systems are more selective for smithsonite ores when compared to acidic leaching systems, i.e. main gangue minerals, the carbonates (calcite and/or dolomite) and the iron-(hydr)oxides (goethite and/or hematite), in the ore do not dissolve and cleaner pregnant solutions could be obtained (Zhao and Stanforth, 2000; Qin et al., 2007; Liu et al., 2011; Rao et al., 2015). Besides, the energy consumption during electrowinning in sodium hydroxide solutions was found to be lower when compared to electrowinning in acidic solutions (Baroch et al., 1953; Brown et al., 1983; St-Pierre and Piron, 1986; Zhao and Stanforth, 2000).

In Turkey, there are several nonsulfide zinc ore deposits differing in mineralogy and grade (DPT, 2001; Hanilci and Ozturk, 2011; Santoro et al., 2013), and the effective utilization of these sources is very important. However, according to the knowledge of authors, there is no detailed study on sodium hydroxide leaching of a Turkish smithsonite ore focusing on the dissolution behaviour of zinc. So, in this study, the leaching behaviour of zinc from a local smithsonite ore sample (Yahyali-Kayseri, central Turkey) containing goethite and calcite as the main gangue minerals was investigated in sodium hydroxide solutions using X-ray diffraction and chemical analyses. In some of the experiments, the leaching ratio values of lead were also determined.

## 2. Materials and methods

In the experimental studies, Merck grade reagents, classical laboratory equipments, deionized water, and a ground smithsonite ore sample were used. The representative ore sample taken from the nonsulfide zinc ore deposit in Kayseri was first crushed with a jaw crusher then it was ground using closed circuited ball mill with a sieve. The particle size distribution of the sample determined by wet sieving showed that cumulative 80% passing size of the sample was 124.5  $\mu\text{m}$  and 52.5% of the sample was finer than 38  $\mu\text{m}$ . The sample also contained other than the main chemical components (Table 1), i.e. 1.92% Pb, 0.26% K, 0.30% Mg, 0.111% Cd and 0.11%  $\text{TiO}_2$ , and the contents of S, Mn,  $\text{P}_2\text{O}_5$ , Na,  $\text{Cr}_2\text{O}_3$ , Ba, Cu, Ag, Ni, Co and As were less than 0.1%. On the other hand, the moisture content and loss on ignition value of the sample were determined as 1.42% and 24.37%, respectively. The X-ray diffraction (XRD) pattern (Rigaku Dmax-2200, operated at 40 mA/40 kV using  $\text{CuK}\alpha$  radiation at scanning speed of  $2^\circ/60$  s), the thermal (TG/DTA) curves (Setaram Labsys, obtained under static air atmosphere at a heating rate of 0.167 K/s) and the infrared (FTIR) spectrum (Perkin Elmer, KBr pellet method) of the ore sample collectively indicated that the sample was mainly composed of smithsonite, goethite and calcite, and it also contained quartz, clay minerals (kaolinite, trace illite), hemimorphite, hematite and cerussite in lower amounts.

Table 1. Main chemical components of the ore sample

Component	Value (%)
Zn	23.43
Fe	18.54
CaO	7.37
$\text{SiO}_2$	6.75
$\text{Al}_2\text{O}_3$	3.16

The leaching experiments were conducted in a magnetically stirred Pyrex reactor (0.6  $\text{dm}^3$ ) equipped with a reflux condenser inside a temperature controlled water bath. In a representative experiment, an aqueous solution of sodium hydroxide (NaOH) at predetermined concentration (1, 2, 3 and 4 mole/ $\text{dm}^3$ ) was transferred into the reactor, brought to the selected temperature (298, 323, 343 and 363 K) and then the sample, whose amount was calculated according to the selected solid/liquid (S/L) ratio (0.075, 0.10 and 0.15 kg dry ore/ $\text{dm}^3$  solution), was added to the solution. The leaching experiment was continued

for the selected leaching times (1800, 3600, 7200 and 14400 s) under constant magnetic stirring. The studied concentrations and temperatures of NaOH solutions, S/L ratio values and leaching times were selected according to the preliminary tests and previous literature studies. Following leaching, the undissolved leach residues were separated by filtration, water-washed, dried, weighed and stored in sealed bottles for further analyses. Finally, leaching ratio values (%) of zinc and lead were calculated according to Eq. 1. Because it is very important to conduct the experiments under the same conditions in zinc-sodium hydroxide-water system, i.e. small changes in experimental conditions cause different results (McBride et al., 2003; Moezzi et al., 2011; Mukhopadhyay et al., 2015; Top and Cetinkaya, 2015), some of the randomly selected leaching experiments were repeated three times and the experimental errors were found to be always less than  $\pm 3.5\%$ .

$$\text{Leaching ratio (\%)} = \frac{(\text{amount of Zn in the ore sample}) - (\text{amount of Zn in the leach residue})}{(\text{amount of Zn in the ore sample})} \times 100 \quad (1)$$

### 3. Results and discussion

The dissolution of smithsonite, which is insoluble in water, in NaOH solution can be described by Eq. 2. As the most important parameter on leaching of Zn, in accordance with Eq. 2, the effect of NaOH concentration was investigated in the first place at values of 1, 2, 3 and 4 mole/dm<sup>3</sup> (Table 2) for constant leaching time of 3600 s and a S/L ratio of 0.15 kg/dm<sup>3</sup>. In these experiments, the leaching temperature was also kept constant at 298 K, because lower leaching ratio values of Zn were obtained at higher temperatures in the studied NaOH concentration range. As an example, the leaching ratio values of Zn in 3 mole/dm<sup>3</sup> NaOH solution at 323, 343 and 363 K were 62.7, 52.5 and 40.5%, respectively, probably due to the decreased stability of soluble zincate ( $\text{Zn(OH)}_4^{2-}$ ) species at higher temperatures, which caused solid zinc oxide formation according to Eq. 3 (Debiemme-Chouvy and Vedel, 1991; Uekawa et al., 2004; Li et al., 2007; Moezzi et al., 2011).

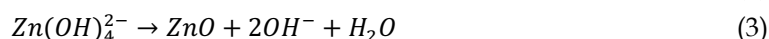
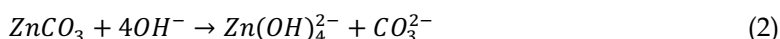


Table 2. Effects of NaOH concentration on leaching of Zn and Pb

NaOH concentration (mole/dm <sup>3</sup> )	Leaching Ratio (%)	
	Zn	Pb
1	3.8	18.1
2	46.0	37.5
3	70.1	43.8
4	70.9	47.2

As shown in Table 2, the leaching ratio of Zn increased about eighteen times when the concentration of NaOH increased from 1 to 3 mole/dm<sup>3</sup>, and over 3 mole/dm<sup>3</sup> NaOH, it was levelled off and maximum leaching ratio of 70.9% was obtained by leaching in 4 mole/dm<sup>3</sup> NaOH solution at 298 K. The leaching ratio values of Zn obtained from various smithsonite bearing nonsulfide ores in the related literature were very different due to the differences in both mineralogy and chemical compositions of the ores used, and the experimental conditions applied during leaching. For example, Mujahed (1966) reported Zn leaching ratio value of 90.5% from a -700  $\mu\text{m}$  Develi (Turkey) oxidized ore containing 14.8% Zn by leaching in 5.25 mole/dm<sup>3</sup> NaOH solution (temperature: 363 K, S/L ratio: 0.15 kg/dm<sup>3</sup>, time: 14400 s). Frenay (1985) obtained Zn leaching ratio values between ~22-36% and ~86-100% from -400  $\mu\text{m}$  Belgian oxidized ores having Zn grades ranging between 15.6-44.4% by leaching in 1 and 6 mole/dm<sup>3</sup> NaOH solutions, respectively (temperature: 293 K, S/L ratio: 0.05 kg/dm<sup>3</sup>, time: 3600 s). Zhao and Stanforth (2000) reported Zn leaching ratio values of about 12, 23, 40, 61 and 85% from a -150  $\mu\text{m}$  oxide ore having 20.66% Zn by leaching in 1, 2, 3, 4 and 8 mole/dm<sup>3</sup> NaOH solutions, respectively (temperature: 373 K, S/L ratio: 0.14 kg/dm<sup>3</sup>, time: 7200 s). Liu et al. (2011) reported Zn leaching ratio value of 85.14% from a -200  $\mu\text{m}$  Mengzi (China) oxidized ore containing 17.3% Zn by leaching in 6 mole/dm<sup>3</sup> NaOH solution (temperature: 363 K, S/L ratio: 1:5 wt.:vol., time: 7200 s). Zhang et al. (2013) reported Zn leaching ratio of 81% from a -150  $\mu\text{m}$  Lanping (China) oxide ore with 10.15% Zn by leaching

in a 20% NaOH solution solution (temperature: 373 K, S/L ratio: 1:80, time: 14400 s). Ghasemi and Azizi (2018) obtained Zn leaching ratio values of 18, 45, 54 and 67% from a -150  $\mu\text{m}$  smithsonite containing Goshfil (Iran) mine tailings having  $\sim 4.75\%$  Zn by leaching in 0.5, 1, 2 and 4 mole/dm<sup>3</sup> NaOH solutions, respectively (temperature: 343 K, S/L ratio: 0.05 kg/dm<sup>3</sup>, time: 3600 s). On the other hand, the leaching ratio values of Pb (Table 2), which were generally lower than Zn leaching ratio values, continually increased, but the increase in leaching ratio value slowed down over 3 mole/dm<sup>3</sup> NaOH concentration.

According to Table 2, the most efficient NaOH concentration was selected as 3 mole/dm<sup>3</sup> considering the obtainment of higher leaching ratio value for Zn and lower concentration of used NaOH solution. Then, XRD pattern of the leach residue obtained after leaching of the sample in 3 mole/dm<sup>3</sup> NaOH solution was determined (Fig. 1). The peaks belonging to smithsonite (JCPDS File No: 8-0449) in the XRD pattern of sample (Fig. 1) observed at  $2\theta=25.01^\circ$ ,  $32.49^\circ$ ,  $38.61^\circ$ ,  $42.75^\circ$ ,  $46.57^\circ$ ,  $51.29^\circ$  and  $53.63^\circ$  disappeared in the patterns of leach residues obtained after leaching in both 3 and 4 mole/dm<sup>3</sup> NaOH solutions, showing the dissolution of smithsonite in the ore sample. The XRD peaks of other main components, i.e. goethite and calcite, in the ore sample did not affect much as smithsonite peaks by NaOH leaching and stayed practically unchanged.

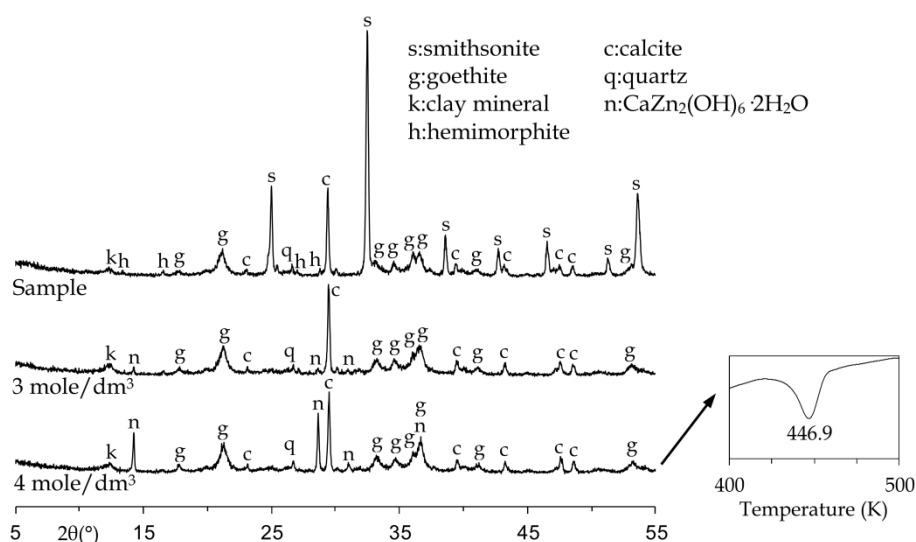


Fig. 1. XRD patterns of the sample and leach residues obtained after leaching at indicated NaOH concentrations (for inset, please see the text)

The dissolution of smithsonite in the ore sample was also followed with the help of FTIR and TG/DTA analyses. The FTIR spectra and TG/DTA curves of the sample and leach residue obtained after leaching in 3 mole/dm<sup>3</sup> NaOH solution were given in Fig. 2. The characteristic absorption band for planar bending of carbonate group of smithsonite in the sample at 744 cm<sup>-1</sup> (Fig. 2a) disappeared and was not observed in the spectra of residue, indicating again the dissolution of smithsonite in the sample by NaOH leaching. For the leach residue, the band for out-of-plane bending of carbonate group at 871 cm<sup>-1</sup> in the spectra of sample observed at higher, i.e. 876 cm<sup>-1</sup>, and the broad band for asymmetric stretching of carbonate group at 1428 cm<sup>-1</sup> in the spectra of sample observed at lower, i.e. 1424 cm<sup>-1</sup>, wavenumbers. Both observations may indicate that smithsonite in the sample was dissolved and calcite in the sample remained as an undissolved phase (Weir and Lippincott, 1961). The main difference in DTA curves of the sample and the residue (Fig. 2b) was the disappearance of endothermic peak at 630.8 K, which was attributed to decomposition of smithsonite phase according to Eq. 4 (Zhang et al., 2013). As their presence were substantiated by XRD analyses, the endotherms at 566.7 and 1080.4 K were attributed the decomposition of goethite (Prasad et al., 2006) and calcite (Smykatz-Kloss et al., 2003) phases in the sample according to Eqs. 5 and 6, respectively. The presence of these peaks in DTA curves of both the sample and the residue showed that goethite and calcite phases were resistant to leaching in NaOH solution under the applied experimental conditions. On the other hand, the formation of double peak at the calcite decomposition region in DTA curve of the residue should be studied in future by detailed thermal studies. With the dissolution of smithsonite, the weight loss value at about, for

example, 750 K decreased greatly for the leach residue. As will be mentioned in the next paragraph, the very small intensity endothermic peak near 440 K indicated the presence of hydrated calcium zincate phase in the leach residue.

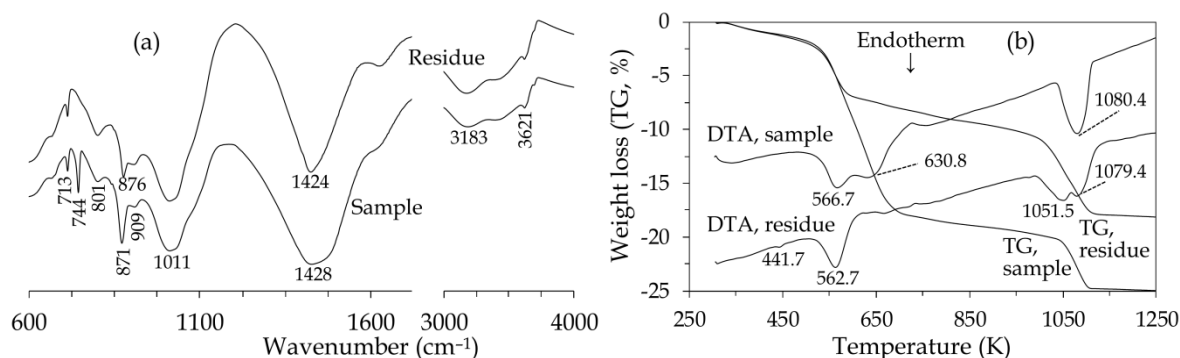
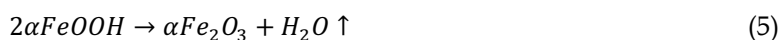


Fig. 2. FTIR spectra (a) and TG/DTA curves (b) of the sample and leach residue obtained after leaching in 3 mole/dm<sup>3</sup> NaOH solution

The XRD pattern of leach residue obtained after leaching in 4 mole/dm<sup>3</sup> NaOH solution was also determined and given in Fig. 1 to reveal why leaching ratio value of Zn at this concentration did not increase more when compared to leaching in 3 mole/dm<sup>3</sup> NaOH solution. It was found that this situation was caused by the formation of hydrated calcium zincate phase (CaZn<sub>2</sub>(OH)<sub>6</sub>·2H<sub>2</sub>O, JCPDS File No: 24-0222) during leaching, which was also observed to form in different zinc containing alkaline systems, e.g. the hydration of cement in the presence of zinc oxide (Liebau and Amel-Zadeh, 1972; Gawlicki and Czamarska, 1992) or in alkaline Zn/NiOOH batteries (Gagnon, 1986; Wang, 1990). According to the knowledge of the authors, the formation of hydrated calcium zincate phase was observed to form for the first time during leaching of a nonsulfide Zn ore using NaOH as the leaching agent. The inset in Fig. 1 showed a section of DTA curve of the residue obtained after leaching in 4 mole/dm<sup>3</sup> NaOH solution. The characteristic endothermic peak at 446.9 K in the DTA curve was also substantiated the presence of CaZn<sub>2</sub>(OH)<sub>6</sub>·2H<sub>2</sub>O phase in this residue (Wang et al., 2008; Hao et al., 2014). One separate leaching experiment was also conducted in highly concentrated 8 mole/dm<sup>3</sup> NaOH solution (OH/Zn mole ratio: 14.89, according to Eq. 2 stoichiometric OH/Zn mole ratio: 4) at 298 K to observe the change in Zn leaching ratio value and the presence of XRD peaks of hydrated calcium zincate in the pattern of leach residue. Both the increase in leaching ratio of Zn, which was 78.5% (58.2% for Pb), and the presence of very low intensity XRD peaks of hydrated calcium zincate phase in the leach residue obtained after leaching in 8 mole/dm<sup>3</sup> NaOH solution (pattern was not given) indicate the decomposition (or nonformation) of hydrated calcium zincate phase in highly concentrated alkaline solutions, as also observed by Wang (1990).

As mentioned previously, the dissolution of smithsonite, which is insoluble in water, in NaOH solution can be described by Eq. 2. The 2 mole/dm<sup>3</sup> NaOH solution (OH/Zn mole ratio: 3.72) approximately contained the stoichiometric amount of NaOH (OH/Zn mole ratio: 4) required to dissolve ZnCO<sub>3</sub> in the used ore sample according to Eq. 2. Then, NaOH solutions of 1 mole/dm<sup>3</sup> (OH/Zn mole ratio: 1.86), 3 mole/dm<sup>3</sup> (OH/Zn mole ratio: 5.58) and 4 mole/dm<sup>3</sup> (OH/Zn mole ratio: 7.44) contained approximately 0.5, 1.5 and 2 times stoichiometric NaOH for dissolving ZnCO<sub>3</sub> according to Eq. 2. Besides, for 1 mole/dm<sup>3</sup> NaOH solution, the general reaction given in Eq. 7 could also occur, where the reaction product zinc hydroxide is a water insoluble compound. Although the amount of NaOH in 1 mole/dm<sup>3</sup> leaching solution was approximately equal to the half of NaOH required to dissolve Zn stoichiometrically in the ore sample, the very low leaching ratio value for Zn (3.8%) obtained after leaching in 1 mole/dm<sup>3</sup> NaOH solution at 298 K may be the result of Eq. 7. In order to check this statement, the leach residue obtained after leaching in 1 mole/dm<sup>3</sup> NaOH solution for leaching time of

3600 s and S/L ratio of 0.15 kg/dm<sup>3</sup> at 298 K was dried under room conditions to prevent the possible thermal transformation of zinc hydroxide to zinc oxide under the applied drying conditions (Nicholas et al., 2012; Top and Cetinkaya, 2015), and then XRD pattern of this residue was obtained (Fig. 3, pattern 298 K). Fig. 3 (pattern 298 K) showed that part of smithsonite phase in the sample was converted into solid zinc hydroxide (JCPDS File No: 38-0385) in 1 mole/dm<sup>3</sup> NaOH solution, probably following a dissolution and reprecipitation path (Usui, 2009; Giannakoudakis et al., 2015), resulting very low Zn leaching ratio value. The XRD peaks belonging to zinc hydroxide phase were not observed (Fig. 3, pattern 363 K) in the pattern of room temperature-dried leach residue obtained after leaching in 1 mole/dm<sup>3</sup> NaOH solution at 363 K, for which again very low leaching value for Zn (1.4%) was obtained. The zinc oxide (JCPDS File No: 36-1451), observed by the appearance of XRD peaks at 2θ=31.84°, 34.52°, 36.36° and 47.60° in the pattern of this residue, may be formed either according to Eq. 3 or according to Eq. 8, for which formed zinc hydroxide transformed into zinc oxide by different routes, probably faster at 363 K than at 298 K (Usui, 2009; Li et al., 2010; Moezzi et al., 2011; Wang et al., 2011; Nicholas et al., 2012; Mukhopadhyay et al., 2015).

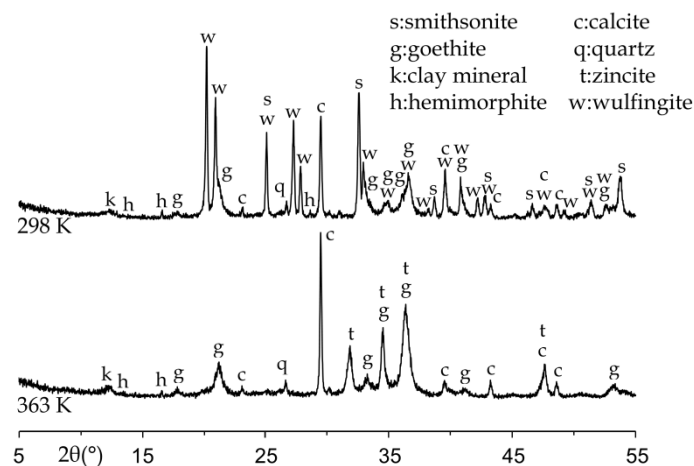
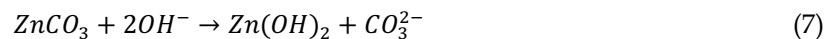


Fig. 3. XRD patterns of room temperature-dried leach residues obtained after leaching in 1 mole/dm<sup>3</sup> NaOH solution at 298 K (up) and 363 K (down)

The effects of leaching time were studied at 3 mole/dm<sup>3</sup> NaOH concentration for temperature and S/L ratio values of 298 K and 0.15 kg/dm<sup>3</sup>, respectively. The Table 3 showed that Zn dissolution was very fast and 70.8% of Zn in the sample was leached just in 1800 s. When the leaching time increased over 7200 s, the leaching ratio value of Zn started to decrease and reached 60.6% after 14400 s, mainly due to the increased formation of hydrated calcium zincate phase (Wang, 1990) in the solution (Fig. 4). On the other hand, the leaching ratio values of Pb, again being lower than the leaching ratio values of Zn, practically stayed unchanged in the studied range of leaching times.

The effects of solid/liquid ratio were studied at 2 mole/dm<sup>3</sup> NaOH concentration for leaching temperature and leaching time of 298 K and 3600 s (Table 4), respectively, where an average Zn leaching ratio value (46.0%) was obtained and by this way higher and lower leaching ratio values could easily be seen. The possible formation of different zinc containing phases as observed before also led the authors to choose approximately stoichiometric 2 mole/dm<sup>3</sup> NaOH solution concentration. When the S/L ratio was decreased keeping OH/Zn mole ratio value constant at about 3.72, the leaching ratio values of Zn were also reduced due to the decrease in concentration of NaOH solution (for S/L ratio values of 0.075, 0.10 and 0.15 kg/dm<sup>3</sup>, the approximate solution concentrations were 1, 1.35 and 2 mole/dm<sup>3</sup> NaOH, respectively). When the S/L ratio was decreased keeping NaOH solution concentration constant at 2 mole/dm<sup>3</sup> NaOH, the leaching ratio values of Zn increased due to the increase in OH/Zn mole ratio values in the solution (for S/L ratio values of 0.075, 0.10 and 0.15 kg/dm<sup>3</sup>, the corresponding OH/Zn mole ratio values were 7.44, 5.58 and 3.72, respectively), as expected. The

leaching ratio values of Pb were affected less by the changes in the S/L ratio values when compared to the corresponding leaching ratio values of zinc.

Table 3. Effects of leaching time on leaching of Zn and Pb

Leaching time (s)	Leaching Ratio (%)	
	Zn	Pb
1800	70.8	44.7
3600	70.1	43.8
7200	70.7	43.6
14400	60.6	42.9

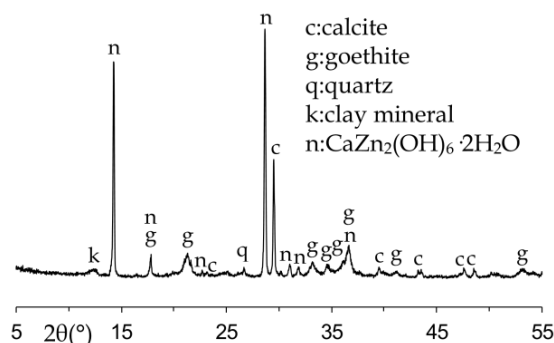


Fig. 4. XRD pattern of leach residue obtained after leaching in 3 mole/dm<sup>3</sup> NaOH solution for 14400 s

Table 4. Effects of solid/liquid ratio on leaching of Zn and Pb

Solid/Liquid ratio (kg/dm <sup>3</sup> )	Leaching Ratio (%)			
	At constant NaOH concentration		At constant OH/Zn mole ratio	
	Zn	Pb	Zn	Pb
0.075	71.7	48.7	31.0	41.1
0.100	68.4	44.8	40.1	40.2
0.150	46.0	37.5	46.0	37.5

#### 4. Conclusions

The leaching behaviour of Zn from a Turkish smithsonite ore sample containing 23.43% Zn was investigated in sodium hydroxide solutions at different temperatures, leaching times and solid/liquid ratio values using XRD and chemical analyses. Between the studied 1-4 mole/dm<sup>3</sup> NaOH concentration range, most of the leaching experiments were conducted at 298 K, because higher Zn leaching ratio values were obtained at 298 K due to the lowered stability of soluble zincate species at higher temperatures, i.e. 363 K. The increase in NaOH concentration from 1 to 3 mole/dm<sup>3</sup> greatly increased the leaching ratio of Zn (from 3.8 to 70.1%) at 298 K, and for 4 mole/dm<sup>3</sup> NaOH concentration, the leaching ratio of Zn (70.9%) levelled off because of the formation of hydrated calcium zincate in the leaching solution. When the leaching process was conducted at 1 mole/dm<sup>3</sup> NaOH concentration, very low leaching ratio values of Zn were obtained by the formation of solid zinc hydroxide at 298 K and solid zinc oxide at 363 K. With the increase of leaching time at 3 mole/dm<sup>3</sup> NaOH concentration, leaching ratio value of Zn decreased because of the increase in the amount of formed solid hydrated calcium zincate phase in the solution. The solid/liquid ratio parameter affected significantly leaching of zinc. It was observed that when solid/liquid ratio was decreased, at constant OH/Zn mole ratio the leaching ratio values of Zn decreased and at constant NaOH concentration the leaching ratio values of Zn increased. For some of the leaching experiments, the leaching ratio values of Pb were also determined and it was observed that the leaching ratio values of Pb were generally lower than the corresponding values for Zn. As conclusion, due to the hydrolysis of zinc and the possibility of formation of different zinc compounds during alkaline leaching of nonsulfide zinc ores having different gangue components, each parameter affecting leaching must be carefully tested in detail.

## Acknowledgments

This study was supported by OYP research project funding units of The Turkish Higher Education Institute. The authors wish to acknowledge Dedeman Mining company for the supply of ore sample and Assoc.Prof.Dr. Elif Varol Muratcay for XRD analyses.

## References

- ABALI, Y., BAYCA, S.U., GUMUS, R., 2017. *Dissolution kinetics of smithsonite in boric acid solutions*. Physicochem. Probl. Miner. Process. 53, 161-172.
- ABKHOSHK, E., JORJANI, E., AL-HARAHSEH, M.S., RASHCHI, F., NAAZERI, M., 2014. *Review of the hydrometallurgical processing of non-sulfide zinc ores*. Hydrometallurgy 149, 153-167.
- ADBEL-AAL, E.A., RASHAD, M.M., EL-SHAZLY, A.N., IBRAHIM, I.A., EL-SHAHAT, M.F., 2016. *Hydrometallurgical treatment of non-sulfide zinc ore for precipitation of zinc oxide nanoparticles*. Physicochem. Probl. Miner. Process. 52, 729-737.
- BAROCH, C.T., HILLIARD, R.V., LANG, R.S., 1953. *The caustic electrolytic-zinc process*. J. Electrochem. Soc. 100, 165-172.
- BROWN, A.P., MEISENHOLDER, J.H., YAO, N.-P., 1983. *The alkaline electrolytic process for zinc production: A critical evaluation*. Ind. Eng. Chem. Prod. R.D. 22, 263-272.
- DEBIEMME-CHOUVY, C., VEDEL, J., 1991. *Supersaturated zincate solutions: A study of the decomposition kinetics*. J. Electrochem. Soc. 138, 2538-2542.
- DENG, J., SUN, Q., LIN, P., SONG, G., WEN, S., DENG, J., WU, D., 2015. *Dissolution kinetics of zinc oxide ore with an organic acid*. Int. J. Metall. Mater. Eng. 1, 109, 7 pages.
- DHAWAN, N., SAFARZADEH, M.S., BIRINCI, M., 2011. *Kinetics of hydrochloric acid leaching of smithsonite*. Russ. J. Non-Ferr. Met+ 52, 209-216.
- DOU, A., YANG, T., YANG, J., WU, J., WANG, A., 2011. *Leaching of low grade zinc oxide ores in  $Ida^2$ - $H_2O$  system*. T. Nonferr. Metal. Soc. 21, 2548-2553.
- DPT, 2001. *State Planning Organization, Eighth Five-year Development Plan, Mining Specialization Commission Report, Subcommittee of Metal Mines, Lead-Zinc-Cadmium Study Group Report*. DPT:2628, OIK:639, Ankara, pp. 85-167 (in Turkish).
- EJTEMAEI, M., GHARABAGHI, M., IRANNAJAD, M., 2014. *A review of zinc oxide mineral beneficiation using flotation method*. Adv. Colloid Interfac. 206, 68-78.
- ESPIARI, S., RASHCHI, F., SADRNEZHAAD, S.K., 2006. *Hydrometallurgical treatment of tailings with high zinc content*. Hydrometallurgy 82, 54-62.
- FENG, L., YANG, X., SHEN, Q., XU, M., JIN, B., 2007. *Pelletizing and alkaline leaching of powdery low grade zinc oxide ores*. Hydrometallurgy 89, 305-310.
- FENG, Q., WEN, S., ZHAO, W., BAI, X., CHEN, Y., 2015. *Dissolution regularities of smithsonite in methane sulfonic acid*. Russ. J. Non-Ferr. Met+ 56, 365-371.
- FRENAY, J., 1985. *Leaching of oxidized zinc ores in various media*. Hydrometallurgy 15, 243-253.
- GAGNON, E.G., 1986. *Effects of KOH concentration on the shape change and cycle life of Zn/NiOOH cells*. J. Electrochem. Soc. 133, 1989-1995.
- GAWLICKI, M., CZAMARSKA, D., 1992. *Effect of ZnO on the hydration of portland cement*. J. Therm. Anal. 38, 2157-2161.
- GHASEMI, S.M.S., AZIZI, A., 2017. *Investigation of leaching kinetics of zinc from a low-grade ore in organic and inorganic acids*. J. Min. Environ. 8, 579-591.
- GHASEMI, S.M.S., AZIZI, A., 2018. *Alkaline leaching of lead and zinc by sodium hydroxide: kinetics modeling*. J. Mater. Res. Technol. 7, 118-125.
- GIANNAKOUDAKIS, D.A., ARCIBAR-OROZCO, J.A., BANDOSZ, T.J., 2015. *Key role of terminal hydroxyl groups and visible light in the reactive adsorption/catalytic conversion of mustard gas surrogate on zinc (hydr)oxides*. Appl. Catal. B-Environ. 174&175, 96-104.
- GRAF, G.G., 2005. *Zinc*. Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH, pp. 1-23.
- HANILCI, N., OZTURK, H., 2011. *Geochemical/isotopic evolution of Pb-Zn deposits in the Central and Eastern Taurides, Turkey*. Int. Geol. Rev. 53, 1478-1507.
- HAO, J., YANG, C., ZHAO, F., 2014. *A facile route for the preparation of calcium zincate and its application in Ni-Zn batteries*. J. Electrochem. Soc. 161, A704-A707.



- HITZMAN, M.W., REYNOLDS, N.A., SANGSTER, D.F., ALLEN, C.R., CARMAN, C.E., 2003. *Classification, genesis, and exploration guides for nonsulfide zinc deposits*. Econ. Geol. 98, 685-714.
- HOSSEINI, S.H., FORSSBERG, E., 2009. *Smithsonite flotation using mixed anionic/cationic collector*. T. I. Min. Metall. C 118, 186-190.
- HURSIT, M., LACIN, O., SARAC, H., 2009. *Dissolution kinetics of smithsonite ore as an alternative zinc source with an organic leach reagent*. J. Taiwan Inst. Chem. E. 40, 6-12.
- ILZSG, 2017. *International Lead & Zinc Study Group*. <http://www.ilzsg.org/static/enduses.aspx?from=1>, accessed 27/09/2017.
- IRANNAJAD, M., MESHKINI, M., AZADMEHR, A.R., 2013. *Leaching of zinc from low grade oxide ore using organic acid*. Physicochem. Probl. Miner. Process. 49, 547-555.
- JU, S., MOTANG, T., SHENGHAI, Y., YINGNIAN, L., 2005. *Dissolution kinetics of smithsonite ore in ammonium chloride solution*. Hydrometallurgy 80, 67-74.
- LI, P., LIU, H., ZHANG, Y., WEI, Y., WANG, X., 2007. *Synthesis of flower-like ZnO microstructures via a simple solution route*. Mater. Chem. Phys. 106, 63-69.
- LI, P., LIU, H., LU, B., WEI, Y., 2010. *Formation mechanism of 1D ZnO nanowhiskers in aqueous solution*. J. Phys. Chem. C 114, 21132-21137.
- LIEBAU, F., AMEL-ZADEH, A., 1972. *The crystal structure of  $\text{Ca}[\text{Zn}_2(\text{OH})_6] \cdot 2\text{H}_2\text{O}$  - a retarder in the setting of portland cement*. Krist. Tech. 7, 221-227.
- LIU, Q., ZHAO, Y., ZHAO, G., 2011. *Production of zinc and lead concentrates from lean oxidized zinc ores by alkaline leaching followed by two-step precipitation using sulfides*. Hydrometallurgy 110, 79-84.
- MCBRIDE, R.A., KELLY, J.M., MCCORMACK, D.E., 2003. *Growth of well-defined ZnO microparticles by hydroxide ion hydrolysis of zinc salts*. J. Mater. Chem. 13, 1196-1201.
- MOEZZI, A., CORTIE, M., MCDONAGH, A., 2011. *Aqueous pathways for the formation of zinc oxide nanoparticles*. Dalton T. 40, 4871-4878.
- MOGHADDAM, J., SARRAF-MAMOORY, R., YAMINI, Y., ABDOLLAHY, M., 2005. *Determination of the optimum conditions for the leaching of nonsulfide zinc ores (high-SiO<sub>2</sub>) in ammonium carbonate media*. Ind. Eng. Chem. Res. 44, 8952-8958.
- MUJAHED, S.B., 1966. *Electrowinning in Alkaline Medium - Electrolytic Production of Lead and Zinc from an Oxidized Ore from Develi (Kayseri) via Caustic Leaching*. MSc Thesis, Middle East Technical University.
- MUKHOPADHYAY, S., DAS, P.P., MAITY, S., GHOSH, P., DEVI, P.S., 2015. *Solution grown ZnO rods: Synthesis, characterization and defect mediated photocatalytic activity*. Appl. Catal. B-Environ. 165, 128-138.
- NICHOLAS, N.J., FRANKS, G.V., DUCKER, W.A., 2012. *The mechanism for hydrothermal growth of zinc oxide*. CrystEngComm 14, 1232-1240.
- PRASAD, P.S.R., PRASAD, K.S., CHAITANYA, V.K., BABU, E.V.S.S.K., SREEDHAR, B., MURTHY, S.R., 2006. *In situ FTIR study on the dehydration of natural goethite*. J. Asian Earth Sci. 27, 503-511.
- QIN, W., LI, W., LAN, Z., QIU, G., 2007. *Simulated small-scale pilot plant heap leaching of low-grade oxide zinc ore with integrated selective extraction of zinc*. Miner. Eng. 20, 694-700.
- RAO, S., YANG, T., ZHANG, D., LIU, W., CHEN, L., HAO, Z., XIAO, Q., WEN, J., 2015. *Leaching of low grade zinc oxide ores in  $\text{NH}_4\text{Cl}$ - $\text{NH}_3$  solutions with nitrilotriacetic acid as complexing agents*. Hydrometallurgy 158, 101-106.
- SANTORO, L., BONI, M., HERRINGTON, R., CLEGG, A., 2013. *The Hakkari nonsulfide Zn-Pb deposit in the context of other nonsulfide Zn-Pb deposits in the Tethyan Metallogenic Belt of Turkey*. Ore Geol. Rev. 53, 244-260.
- SMYKATZ-KLOSS, W., HEIDE, K., KLINKE, W., 2003. *Applications of thermal methods in the geosciences*. Handbook of Thermal Analysis and Calorimetry, Vol. 2, pp. 451-593.
- ST-PIERRE, J., PIRON, D.L., 1986. *Electrowinning of zinc from alkaline solutions*. J. Appl. Electrochem. 16, 447-456.
- TOP, A., CETINKAYA, H., 2015. *Zinc oxide and zinc hydroxide formation via aqueous precipitation: Effect of the preparation route and lysozyme addition*. Mater. Chem. Phys. 167, 77-87.
- UEKAWA, N., YAMASHITA, R., WU, Y.J., KAKEGAWA, K., 2004. *Effect of alkali metal hydroxide on formation processes of zinc oxide crystallites from aqueous solutions containing  $\text{Zn}(\text{OH})_4^{2-}$  ions*. Phys. Chem. Chem. Phys. 6, 442-446.
- USUI, H., 2009. *Surfactant concentration dependence of structure and photocatalytic properties of zinc oxide rods prepared using chemical synthesis in aqueous solutions*. J. Colloid Interf. Sci. 336, 667-674.
- WANG, Y.-M., 1990. *Effect of KOH concentration on the formation and decomposition kinetics of calcium zincate*. J. Electrochem. Soc. 137, 2800-2803.

- WANG, S., YANG, Z., ZENG, L., 2008. *Study of calcium zincate synthesized by solid-phase synthesis method without strong alkali*. Mater. Chem. Phys. 112, 603-606.
- WANG, M., ZHOU, Y., ZHANG, Y., HAHN, S.H., KIM, E.J., 2011. *From Zn(OH)<sub>2</sub> to ZnO: a study on the mechanism of phase transformation*. CrystEngComm 13, 6024-6026.
- WEIR, C.E., LIPPINCOTT, E.R., 1961. *Infrared studies of aragonite, calcite, and vaterite type structures in the borates, carbonates, and nitrates*. J. Res. N.B.S. A Phys. Ch. 65, 173-183.
- WU, D., WEN, S., YANG, J., DENG, J., JIANG, L., 2013. *Dissolution kinetics of smithsonite in sulfamic acid solution*. Asian J. Chem. 25, 10556-10560.
- WU, D.D., WEN, S.M., YANG, J., DENG, J.S., 2015. *Investigation of dissolution kinetics of zinc from smithsonite in 5-sulphosalicylic acid solution*. Can. Metall. Quart. 54, 51-57.
- XIA, Z.M., TANG, M.T., YANG, S.H., 2015. *Materials balance of pilot-scale circulation leaching of low-grade zinc oxide ore to produce cathode zinc*. Can. Metall. Quart. 54, 439-445.
- ZHANG, Y., DENG, J., CHEN, J., YU, R., XING, X., 2013. *Leaching of zinc from calcined smithsonite using sodium hydroxide*. Hydrometallurgy 131&132, 89-92.
- ZHANG, Y., HUA, Y., GAO, X., XU, C., LI, J., LI, Y., ZHANG, Q., XIONG, L., SU, Z., WANG, M., RU, J., 2016. *Recovery of zinc from a low-grade zinc oxide ore with high silicon by sulfuric acid curing and water leaching*. Hydrometallurgy 166, 16-21.
- ZHAO, Y., STANFORTH, R., 2000. *Production of Zn powder by alkaline treatment of smithsonite Zn-Pb ores*. Hydrometallurgy 56, 237-249.