Effect of heating on structure and leaching characteristics of a zinc carbonate ore

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Abstract: In this work, the structural changes occurred in a zinc carbonate (smithsonite) ore sample following heating at temperatures between 523 K and 1173 K were investigated in detail using X-ray diffraction (XRD), thermal (TG/DTA) and Fourier-transform infrared (FT-IR) spectroscopy analyses. Afterwards, the leaching characteristics of zinc from the ore sample and the heated ore samples in sodium hydroxide solutions were determined. While heating at 523 K did not cause any structural change in the ore sample, heating at 723 K completely converted smithsonite (ZnCO₃) in the ore sample to zinc oxide (ZnO), which resulted lower zinc leaching efficiencies of 40.6% and 62.0% for 3 and 4 mol/dm³ NaOH concentrations, respectively, in comparison to zinc leaching efficiencies (67.2% and 70.7%) obtained for the unheated ore sample. On the other hand, due to neoformation of dissolution resistant ZnFe₂O₄, Ca₂ZnSi₅O₁₄ and Zn₂SiO₄ phases during heating and formation of CaZn₁₂(OH)₁₆·2H₂O phase during leaching, the leaching efficiency of zinc further decreased to 22.2% and 31.3%, respectively, in 3 and 4 mol/dm³ NaOH solutions for the ore sample heated at 1173 K. The formation of zinc-containing dissolution resistant phases by high-temperature heating was observed to be the only reason for the reduction in the zinc leaching efficiency (49.4% at 1173 K) at the highest NaOH concentration (8 mol/dm³) studied. In this work, the comparative precipitation studies were also conducted and crystalline zinc oxides with different morphologies could be precipitated at considerably high efficiencies from the selected pregnant solutions obtained following leaching.

Keywords: calcium zincate, smithsonite, sodium hydroxide leaching, zinc carbonate ore, zinc oxide

1. Introduction

One of the most important primary sources of zinc in the world is the nonsulfide zinc ores. Zinc in the smithsonite (ZnCO₃) containing nonsulfide ores can be leached selectively by alkaline reagents, i.e. sodium hydroxide or ammonical solutions, in comparison to the acidic reagents, i.e. sulfuric or organic acids. Therefore, there are many studies in the literature using sodium hydroxide solutions for the leaching of zinc (and lead) from different smithsonite ores in the world (Frenay, 1985; Zhao and Stanforth, 2000a; Abkhoshk et al., 2014; Ghasemi and Azizi, 2018; Ehsani et al., 2019; Kumas et al., 2020).

Other than the direct (without any pre-treatment) leaching in sodium hydroxide solutions, there are only a few studies in the literature on leaching of smithsonite in sodium hydroxide solutions following heating (or thermal pre-treatment) at different temperatures. Zhang et al. (2013) found that after heating at 673 K for 2 hours, smithsonite could be completely converted to zinc oxide and the leaching efficiency of zinc for the heated sample became 93% in 6.25 mol/dm³ NaOH solution at leaching temperature of 373 K (leaching time: 4 h, solid/liquid ratio: 1/80 g/mL), whereas the leaching efficiency of zinc for the (untreated) ore sample (chemical composition: 12.63%ZnO, 25.89%CaO, 15.77%SiO₂, 8.78%Fe₂O₃, 0.66%MgO; gangue components: calcite and quartz; particle size: 150 μm) was 81%. Zhang et al. (2013) indicated that heating of smithsonite produced active zinc oxide and by this way more efficient zinc leaching could be obtained. Zhang et al. (2013) also observed that heating over 973 K produced zinc-
containing ZnFe$_2$O$_4$ and Ca$_2$ZnSi$_2$O$_7$ phases in the heated sample, which are not readily soluble in sodium hydroxide solution, and the leaching efficiency of zinc decreased to 65% and 44% following heating at 1073 K and 1173 K, respectively. Besides, Morgan and Gray (1950) reported that better leaching efficiencies of zinc from oxidized zinc ores with minimized carbonate fouling of the solution and facilitated decantation/filtration properties could be reached when the ore was heated between 623-773 K for 1 h before leaching in sodium hydroxide solution. At this temperature range, zinc carbonate in the ore decomposed whereas the dolomitic gangue does not. Although conducted under different experimental conditions with different nonsulfide zinc ore samples, both Morgan and Gray (1950) and Zhang et al. (2013) concluded that heating converted smithsonite to zinc oxide, increased the leaching efficiency of zinc in sodium hydroxide solution and also some other benefits on solid/liquid separation operations were gained. On the other hand, Baroch et al. (1953) and Mujahed (1966) reported that sodium hydroxide solutions of zinc carbonates contained higher amounts of dissolved zinc in comparison to the similar solutions obtained by using zinc oxide, which means that it may be advantageous to dissolve smithsonite directly in sodium hydroxide solutions without heating pre-treatment. The dissolved carbonate in the pregnant leaching solutions may then be recovered by different methods (Baroch et al., 1953; Ehsani and Obut, 2019). In addition, Zhao and Liu (2011) found that the presence of dissolved carbonate in alkaline pregnant leaching solutions had no significant effect on the electrolytic recovery of zinc.

In this study, the effect of heating at temperatures between 523 K and 1173 K on the structure and the leaching characteristics of a zinc carbonate ore sample was investigated in detail using XRD, TG/DTA, FT-IR and chemical analyses methods. Together with zinc, the leaching characteristic of lead was also presented because of the similarities in their chemical behaviours in sodium hydroxide solutions. In addition, the possibilities of precipitation of dissolved zinc in the pregnant solutions obtained after leaching of unheated and heated ore samples were also studied for comparison purposes.

2. Materials and methods

In the experimental work, a local (Kayseri, Turkey) smithsonite ore sample having 19.46% Zn, 7.54% Fe, 7.21% Ca, 3.85% Mg and 0.62% Pb was used. The sample mainly composed of dolomite and smithsonite (see Figure 1), and also contained quartz, goethite, calcite and clay minerals (kaolinite, illite and smectite group clay minerals (Kumas, 2020)) in lower amounts.

The ground (80% passing 127.1 μm) ore sample was heated for 1 h in a muffle furnace, which was previously brought to the temperatures (523, 673, 723, 823, 923, 1023 and 1173 K) that were selected according to the DTA curve of ore sample (see Figure 2). The leaching of ore sample and the heated ore samples were initiated by the addition of calculated amount of sample (60 g) to aqueous leaching solution (400 mL) inside a Pyrex reactor and continued for 1 h under constant mixing at 298 K. The concentrations of leaching solutions (3, 4 and 8 mol/dm$^3$ NaOH), solid/liquid ratio (0.15 g ore/mL solution), leaching time (1 h) and leaching temperature (298 K) were selected according to a previous study (Kumas et al., 2020). After completion of 1 h, the leaching pulp was centrifuged to obtain clear pregnant solution and the leaching residue, which was washed over filter paper, was dried, weighed and stored in closed glass containers for chemical (AcmeLabs, Bureau Veritas), XRD (Rigaku, by CuKα radiation), TG/DTA (Setaram Labsys, by heating at a rate of 10 degree/minute under air atmosphere) and FT-IR (Perkin Elmer, by KBr pellet technique) analyses. The leaching efficiency of zinc (and lead) was calculated according to Eq. 1:

$$\text{Leaching efficiency of zinc (\%) } = \frac{\text{(amount of zinc in the feed)} - \text{(amount of zinc in the leaching residue)}}{\text{(amount of zinc in the feed)}} \times 100$$

In addition to the characterization and comparative leaching studies, preliminary precipitation tests were also conducted comparatively on the pregnant solutions obtained after leaching of both the ore sample and the heated ore sample in 4 mol/dm$^3$ NaOH solutions. In a representative precipitation test, a fixed volume of pregnant solution (120 mL) was taken into a beaker, which that was placed on a hot plate. Then, a calculated volume (equal for neutralizing the theoretical unreacted sodium hydroxide remained in the solution, i.e. 9 mL) of concentrated sulfuric acid (96% H$_2$SO$_4$) was added dropwise to the pregnant solution under constant magnetic stirring. After 1 h, mixing was stopped. Following solid/liquid separation and drying overnight at 378 K, the obtained white-coloured solid precipitate
was subjected to chemical, XRD and scanning electron microscope (SEM) analyses (FEI-Inspect F50) for characterization.

3. Results and discussion

The XRD patterns, TG/DTA curves and FT-IR spectra of the ore sample and the ore samples heated for one hour at different temperatures were given in Figures 1, 2 and 3, respectively. It can be seen from Figures 1 to 3 that there were no significant structural changes occurred in the main components of ore sample heated at 523 K. Due to the decomposition of smithsonite to zinc oxide phase according to $\text{ZnCO}_3 \rightarrow \text{ZnO} + \text{CO}_2$ reaction, the main smithsonite peaks observed at $2\theta=25.10, 32.60, 38.72, 42.86, 46.68, 51.42, 53.76$ and $62.16^\circ$ in the XRD pattern of ore sample were completely disappeared and new XRD peaks of zinc oxide were appeared at 2θ values of $31.86, 34.48, 36.32, 47.64, 56.66$ and $62.90^\circ$ (Figure 1) in the patterns of ore samples heated at temperatures equal or greater than 723 K. The decomposition of smithsonite in the ore sample by high-temperature heating ($\geq723$ K) could also be followed by the disappearance of the endotherm centered at 660 K and the characteristic doubly degenerate planar bending absorption peak of carbonate group of smithsonite at 744 cm$^{-1}$ in the DTA curve (Figure 2) and the FT-IR spectrum (Figure 3) of the ore sample, respectively (Weir and Lippincott, 1961; Zhang et al., 2013).

Fig. 1. XRD patterns of the ore sample and the ore sample heated at indicated temperatures

The intensity of the XRD peak observed at $2\theta=31.04^\circ$ belonging to major carbonate gangue mineral dolomite in the ore sample reduced by half when the ore sample was heated at 923 K, indicating total decomposition of dolomite to calcium carbonate and magnesium oxide phases according to $\text{CaMg(CO}_3\text{)}_2 \rightarrow \text{CaCO}_3 + \text{MgO} + \text{CO}_2$ reaction (Beck, 1950; Kok and Smykatz-Kloss, 2001). The formation of calcium carbonate and magnesium oxide phases caused by dolomite decomposition could also be followed by the increase in XRD peak intensity of calcite seen at $2\theta=29.46^\circ$ and the newly formed main magnesium oxide peak found at $2\theta=42.94^\circ$ in the pattern of ore sample heated at 1023 K (Figure 1), respectively. The disappearance of characteristic absorption peak of carbonate group of dolomite at 729 cm$^{-1}$ (Huang and Kerr, 1960) in the FT-IR spectrum of the ore sample heated at 1023 K (Figure 3) also substantiated the total dolomite decomposition. On the other hand, the minor carbonate gangue mineral calcite in the ore sample decomposed to calcium oxide phase according to $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$, as revealed by the absence of main calcite peak at 2θ value of $29.46^\circ$ and the presence of
main calcium oxide peak at 2θ=37.44° in the XRD pattern of ore sample heated at 1173 K (Figure 1). In addition, the decomposition of calcite could also be followed by the disappearance of the endotherm between 1000-1100 K (Beck, 1950; Zhang et al., 2013) and the disappearance of characteristic absorption peak for calcite at 714 cm⁻¹ (Huang and Kerr, 1960) in the DTA curve (Figure 2) and the FT-IR spectrum (Figure 3) of the ore sample, respectively.

The minor oxyhydroxide gangue mineral goethite in the ore sample dehydroxylated to form ferric oxide phase according to 2α-FeOOH → α-Fe₂O₃ + H₂O reaction when the ore sample was heated to 673 K. The further increase of heating temperature, i.e. to 1023 K, strengthened the intensities of XRD peaks of ferric oxide found at 20 values of 33.26, 35.62 and 54.22°, as also found in the related literature studies (Goni-Elizalde and Garcia-Clavel, 1988; Liu et al., 2013). The removal of endotherm belonging to goethite at 571 K (Prasad et al., 2006) in the DTA curve of ore sample by heating at 673 K (Figure 2) also showed the dehydroxylation of goethite. On the other hand, the minor planar hydrous phyllosilicates (clay minerals) also affected by heating process and the basal XRD peaks of clay minerals could not be observed in the pattern of ore sample heated to 1173 K.

When heating was conducted at 1023 K, a zinc ferrite phase was observed to neoform, according to ZnO + Fe₂O₃ → ZnFe₂O₄, from the reaction between zinc oxide and ferric oxide phases (Konvicka et al., 2000; Zhang et al., 2013), both were formed in-situ by the decomposition of smithsonite and goethite in the ore sample, respectively. Besides, calcium zinc silicate and zinc silicate phases were also neoformed according to ZnO + 2CaO + 2SiO₂ → Ca₂ZnSi₂O₇ and 2ZnO + SiO₂ → Zn₂SiO₄ reactions, respectively, when the ore sample was heated at 1173 K, as observed in the literature (Takesue et al., 2009; Zhang et al., 2013).

Fig. 2. TG (left) and DTA (right) curves of original and heated ore sample at different temperatures

Fig. 3. FT-IR spectra of original and heated ore sample at different temperatures
The effect of heating temperature on the leaching efficiency of zinc in sodium hydroxide solutions at different concentrations was given in Figure 4. Because no significant structural changes occurred in the main phases of ore sample by heating at 523 K, the leaching efficiency values of zinc became nearly constant for all of the studied solution sodium hydroxide concentrations. With the total decomposition of smithsonite to zinc oxide phase by heating at 723 K, the reduction in the leaching efficiency of zinc was found to be significant (Figure 4) especially for leaching in 3 mol/dm$^3$ NaOH solution (from 67.2% for ore sample to 40.6% for heated sample) due to the very low zinc oxide solubility (Scholder and Hendrich, 1939), which is approximately 16.0 g Zn/L (calculated concentration of zinc in pregnant solution was about 13.1 g Zn/L after leaching in 3 mol/dm$^3$ NaOH solution). With the increase of NaOH concentration to 8 mol/dm$^3$, heating of the ore sample to 723 K had no adverse effect on zinc leaching efficiency (75.5% for ore sample and 76.6% for heated sample) due to the quite high zinc oxide solubility (Scholder and Hendrich, 1939), which is approximately 87.6 g Zn/L (calculated concentration of zinc in pregnant solution was about 24.8 g Zn/L after leaching in 8 mol/dm$^3$ NaOH solution). According to the literature (Baroch et al., 1953; Mujahed, 1966), the maximum zinc solubilities (in g Zn/L) for smithsonite (the zinc-containing phase in the unheated ore sample) in 3 and 8 mol/dm$^3$ NaOH solutions were approximately three and two times higher than that for zinc oxide (the zinc-containing phase in the ore sample heated at 723 K), respectively.

Fig. 4. Effect of heating temperature on leaching efficiencies of zinc (left) and lead (right) in sodium hydroxide solutions at indicated concentrations

The neoformation of difficult-to-leach zinc-containing compounds, i.e. ZnFe$_2$O$_4$, Zn$_2$SiO$_4$ and Ca$_2$ZnSi$_2$O$_7$ (Mujahed, 1966; Zhang et al., 2013; Stefanova et al., 2015; Kaya et al., 2020), in the ore samples heated especially at high temperatures, i.e. 1173 K, the leaching efficiency values of zinc reduced greatly for all of the sodium hydroxide concentrations studied. For example, the leaching
efficiencies of zinc obtained after leaching of the ore sample heated at 1173 K were 22.2%, 31.3% and 49.4% in 3, 4 and 8 mol/dm³ NaOH solutions, respectively. The evaluation of the XRD patterns of leaching residues (see Figure 5) obtained after leaching of the ore sample heated at 1173 K showed that formation of calcium zincate (CaZn₂(OH)₆·2H₂O) phase during leaching in 3 or 4 mol/dm³ NaOH solutions was the probable reason for the considerably lower zinc leaching efficiencies obtained in comparison to 8 mol/dm³ NaOH concentration, for which calcium zincate phase did not form (or decompose) according to the literature studies (Wang, 1990; Ehsani et al., 2019). On the other hand, as seen from Figure 4 that the leaching behaviour of lead component of the ore sample and the heated ore samples was seemed to be quite similar to zinc. But, the leaching efficiency values of lead showed a small increase (peak) only for the samples heated at 823 K. Therefore, a more detailed study should be conducted in future for revealing the cause(s) of ‘peak’ observed in the leaching efficiency of lead.

In the literature studies, it was indicated that dissolved zinc in pregnant sodium hydroxide leaching solutions may be obtained either by electrowinning or by sulfide precipitation (Naybour, 1968; Arouete et al., 1969; St-Pierre and Piron, 1986; Afifi et al., 1991; Liu et al., 2011; Zhang et al., 2014). In addition to these two methods, as also applied in this study (see Materials and methods), it is also possible to obtain dissolved zinc from pregnant sodium hydroxide leaching solutions by precipitation in the form of zinc oxide in accordance with the general Zn(OH)₂⁻ → ZnO + 2OH⁻ + H₂O reaction (Yamabi and Imai, 2002; Zhang and Mu, 2007; Moezzi et al., 2011).

The XRD patterns of the white-coloured solids precipitated from pregnant solutions obtained by leaching of the ore sample and the ore sample heated at 723 K in 4 mol/dm³ NaOH solutions (Figure 6) demonstrated that the obtained precipitates were highly crystalline zinc oxides without any kind of impurity phases. For both of the zinc oxide precipitates, the relative intensities of XRD peak of 002 plane found near 2θ value of 34.4° are higher than the corresponding relative peak intensity given in standard zinc oxide card (JCPDS Card No:36-1451), indicating a preferential growth in c-axis (Oliveira et al., 2003; Wang et al., 2004; Zhang et al., 2008; Kamble et al., 2014; Sanchez et al., 2019). The crystallite sizes of the precipitated zinc oxides prepared by using the ore sample and the ore sample heated at 723 K were calculated using Scherrer equation as 31.2, 53.5 and 29.5 nm, and 36.6, 74.0 and 40.5 nm, respectively, for the 100, 002 and 101 planes (Kumas, 2020).

As shown in Figure 7, the solid zinc oxide precipitated from pregnant solution obtained by leaching of the ore sample in 4 mol/dm³ NaOH solution had a flower-like morphology that formed from

![Figure 5. XRD patterns of heated ore samples and the residues obtained after leaching of the heated samples at indicated NaOH concentrations (mol/dm³) (Only intense peaks are labeled for clarity.)](image-url)
Fig. 6. XRD patterns the solids precipitated from pregnant solutions obtained by leaching of the ore sample (left) and the ore sample heated at 723 K (right) in 4 mol/dm$^3$ NaOH solution

ellipsoid-shaped grains having different diameters and lengths. On the other hand, the zinc oxide precipitated from pregnant solution obtained by leaching of the ore sample heated at 723 K in 4 mol/dm$^3$ NaOH solution had flower-like structure formed from rod-shaped grains having similar diameters and lengths. It is mentioned in the literature that zinc oxides with flower-like morphology may be used in the removal of various contaminants from polluted waters or in photocatalyst applications (Li et al., 2009; Lai et al., 2011; Sun et al., 2016). The several parameters, i.e. the concentration, type, amount and addition rate of the precipitant, the concentration of zinc in pregnant solution, the mixing time, the temperature, the presence of foreign anions/cations in solution etc., were studied in the related literature (Wang et al., 1997; Uekawa et al., 2004; Wang et al., 2004; Kawano and Imai, 2006; Music et al., 2007; Zhang and Mu, 2007; Edalati et al., 2016; Wang et al., 2016; Kumas, 2020; Gudkov et al. 2021; Shaba et al., 2021) because of their effects on the morphology of precipitated zinc oxides. An important difference encountered in this study was the presence dissolved carbonate ion, which may also affect the particle morphology, in the pregnant solution obtained by leaching of the ore sample.

Fig. 7. SEM images of the solids precipitated from pregnant solutions obtained by leaching of the ore sample (left) and the ore sample heated at 723 K (right) in 4 mol/dm$^3$ NaOH solution

The chemical compositions of the precipitates and the precipitation efficiencies of dissolved zinc in the pregnant solutions obtained after leaching of the ore sample and the ore sample heated at 723 K in 4 mol/dm$^3$ NaOH solutions were given in Table 1. According to Table 1, it was seen that the zinc contents of both precipitates were very close to the theoretical amount of zinc (80.3%) in pure zinc oxide. Although the precipitation efficiency of solid zinc oxide obtained from the pregnant solution prepared from the ore sample heated at 723 K (leaching efficiency of zinc/lead was 62.0%/49.5%) was lower
(84.1%), the precipitation efficiency value obtained by using the ore sample (leaching efficiency of zinc/lead was 70.7%/61.2%) was quite high (96.0%), indicating quantitative and very effective zinc precipitation. On the other hand, the precipitated solids contained minor amounts of lead, which may be removed from the pregnant solutions by sulfide precipitation (Zhao and Stanforth, 2000b; Liu et al., 2011).

Table 1. Chemical compositions of the precipitates and the precipitation efficiencies of zinc and lead in pregnant solutions obtained after leaching of the indicated sample in 4 mol/dm³ NaOH solution

| Sample                  | Composition of the precipitate (%) | Precipitation efficiency (%) |
|-------------------------|-----------------------------------|-----------------------------|
|                         | Zn  | Pb | Zn  | Pb |
| Ore sample              | 79.7 | 1.3 | 96.0 | 54.3 |
| Ore sample heated at 723 K | 78.4 | 1.0 | 84.1 | 36.7 |

4. Conclusions

The effect of heating on the structure and the leaching characteristics of a smithsonite ore sample (19.46% Zn) in sodium hydroxide solutions was investigated with the use of different experimental techniques. It was concluded that smithsonite in the ore sample could completely be converted to zinc oxide (ZnO) by heating at 723 K. The heating at higher temperatures, i.e. 1173 K, lead to formation of different zinc-containing phases, i.e. ZnFe₂O₄, Zn₂SiO₄ and Ca₂ZnSi₂O₇, in the heated ore sample. The formation of ZnO phase caused reductions in the leaching efficiencies of zinc only for 3 and 4 mol/dm³ NaOH concentrations whereas the formation of ZnFe₂O₄, Zn₂SiO₄ and Ca₂ZnSi₂O₇ phases caused reductions in the zinc leaching efficiencies for all of the studied (3, 4 and 8 mol/dm³) NaOH concentrations. The formation of calcium zinicate (CaZn₂(OH)₆2H₂O) phase was only observed during leaching in 3 and 4 mol/dm³ NaOH solutions, which resulted further reductions in the leaching efficiencies of zinc. On the other hand, the preliminary precipitation tests conducted on the pregnant solutions obtained after leaching of the ore sample and the ore sample heated at 723 K in 4 mol/dm³ NaOH solutions showed that white-coloured nano-sized crystalline zinc oxide solids having different morphologies could be precipitated with zinc precipitation efficiencies of 96.0% and 84.1%, respectively. In conclusion, although it was disadvantageous to heat smithsonite ore before sodium hydroxide leaching, the efficiencies and the characteristics of downstream operations/processes (i.e. solid/liquid separation, purification of pregnant solution and recovery from pregnant solution) must also be taken under consideration to make a final decision about pre-heating of the smithsonite for the complete zinc extraction/recovery processes.

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References

ABKHOSHKI, E., JORJANI, E., AL-HARAHISHEH, M.S., RASHCHI, F., NAAZERI, M., 2014. Review of the hydrometallurgical processing of non-sulfide zinc ores. Hydrometallurgy 149, 153-167.

AFIFI, S., EBAID, A., HEGAZY, M., DONYA, K., 1991. On the electrowinning of zinc from alkaline zinicate solutions. J. Electrochem. Soc. 138, 1929-1933.

AROUETE, S., BLURTON, K.F., OSWIN H.G., 1969. Controlled current deposition of zinc from alkaline solution J. Electrochem. Soc. 116, 166-169.

BAROCCHI, C.T., HILLIARD, R.V., LANG, R.S., 1953. The caustic electrolytic-zinc process. J. Electrochem. Soc. 100, 165-172.

BECK, C.W., 1950. Differential thermal analysis curves of carbonate minerals. Am. Mineral. 35, 985-1013.
EDALATI, K., SHAKIBA, A., VAHDATI-KHAKI, J., ZEBARJAD, S.M., 2016. Low-temperature hydrothermal synthesis of ZnO nanorods: Effects of zinc salt concentration, various solvents and alkaline mineralizers. Mater. Res. Bull. 74, 374-379.

EHSANI, I., OBUT, A., 2019. Conversion behaviours of Sr- and Ca-containing solids in dissolved carbonate containing alkaline pregnant zinc leaching solutions. Miner. Eng. 135, 9-12.

EHSANI, I., UCYILDIZ, A., OBUT, A., 2019. Leaching behaviour of zinc from a smithsonite ore in sodium hydroxide solutions. Physicochem. Probl. Mi. 55, 407-416.

FRENAY, J., 1985. Leaching of oxidized zinc ores in various media. Hydrometallurgy 15, 243-253.

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.

GONI-ELIZALDE, S., GARCIA-CLAVEL, M.E., 1988. Thermal behavior in air of iron oxyhydroxides obtained from the method of homogeneous precipitation. Part I. Goethite samples of varying crystallinity. Thermochim. Acta 124, 359-369.

GUDKO, A., GONI, A., GHASEMI, S.M.S., AZIZI, A., 2018. Infrared study of the carbonate minerals. J. Therm. Anal. Calorim. 64, 1271-1275.

KONVICKA, T., MOSNER, P., SOLC, Z., 2000. Investigation of the non-isothermal kinetics of the formation of ZnFe₂O₄ and ZnCr₂O₄. J. Therm. Anal. Calorim. 60, 629-640.

KUMAS, C., 2020. Effects of Thermal Pretreatment on Hydrometallurgical Processing of a Zinc Carbonate Ore. PhD Thesis, Hacettepe University (in Turkish).

KUMAS, C., EHSANI, I., OBUT, A., 2020. Leaching properties of a dolomite containing zinc ore in sodium hydroxide solutions. Scientific Mining Journal 59, 93-100.

LI, H., NI, Y., HONG, J., 2009. Ultrasound-assisted preparation, characterization, and properties of flower-like ZnO microstructures. Scr. Mater. 60, 524-527.

LIU, H., CHEN, T., ZOU, X., QING, C., FROST, R.L., 2013. Thermal treatment of natural goethite: Thermal transformation and physical properties. Thermochim. Acta 568, 115-121.

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.

MOEZZI, A., CORTIE, M., MCDONAGH, A., 2011. Aqueous pathways for the formation of zinc oxide nanoparticles. Dalton T. 40, 4871-4878.

MORGAN, H.J., GRAY, J.D., 1950. Low-cost production of zinc dust from oxidized ores. Eng. Min. J. 151, 72-75.

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.

MUSIC, S., DRAGCEVIC, D., POPOVIC, S., 2007. Influence of synthesis route on the formation of ZnO particles and their morphologies. J. Alloys Compd. 429, 242-249.

NAYBOUR, R.D., 1968. Morphologies of zinc electrodeposited from zinc-saturated aqueous alkaline solution. Electrochim. Acta 13, 763-769.

OLIVEIRA, A.P.A., HOCHEPID, J.F., GRILLON, F., BERGER, M.H., 2003. Controlled precipitation of zinc oxide particles at room temperature. Chem. Mater. 15, 3202-3207.

PRASAD, P.S.R., PRASAD, K.S., CHAITANYAB, V.K., BABUA, E.V.S.S.K., SREEDHARC, B., MURTHY, S.R., 2006. In situ FTIR study on the dehydration of natural goethite. J. Aslan Earth Sci. 27, 503-511.
SANCHEZ, L., CASTILLO, C., CRUZ, W., YAUHI, B., SOSA, M., LUYO, C., CANDAL, R., PONCE, S., RODRIGUEZ, J.M., 2019. ZnO (Ag-N) nanorods films optimized for photocatalytic water purification. Coatings 9, 767-782.

SCHOLDER, V.R., HENDRICH, G., 1939. Das system ZnO-Na$_2$O-H$_2$O. Z. Anorg. Allg. Chem. 241, 76-92.

SHABA, E.Y., JACOB, J.O., TIJANI, J.O., SULEIMAN, M.A.T., 2021. A critical review of synthesis parameters affecting the properties of zinc oxide nanoparticle and its application in wastewater treatment. Appl. Water Sci. 11, Article:48.

STEFANOVA, A., AROMAA, J., FORSEN, O., 2015. Alkaline leaching of zinc from stainless steel electric arc furnace dusts. Physicochem. Probl. Miner. Process. 51, 293-302.

ST-PIERRE, J., PIRON, D.L., 1986. Electrowinning of zinc from alkaline solutions. J. Appl. Electrochem. 16, 447-456.

SUN, Y., CHEN, L., BAO, Y., ZHANG, Y., WANG, J., FU, M., WU, J., YE, D., 2016. The applications of morphology controlled ZnO in catalysis. Catalysts 6, 188-232.

TAKESUE, M., HAYASHI, H., SMITH, R. L., 2009. Thermal and chemical methods for producing zinc silicate (willenite): A review. Prog. Cryst. Growth Charact. Mater. 55, 98-124.

UEKAWA, N., YAMASHITA, R., JUN WU, Y., KAKEGAWA, K., 2004. Effect of alkali metal hydroxide on formation processes of zinc oxide crystallites from aqueous solutions containing Zn(OH)$_{4}^{2-}$ ions. Phys. Chem. Chem. Phys. 6, 442-446.

WANG, B.G., SHI, E.W., ZHONG, W.Z., 1997. Understanding and controlling the morphology of ZnO crystallites under hydrothermal conditions. Cryst. Res. Technol. 32, 659-667.

WANG, Y., MA, Q., JIA, H., WANG, Z., 2016. One-step solution synthesis and formation mechanism of flower-like ZnO and its structural and optical characterization. Ceram. Int. 42, 10751-10757.

WANG, Y.-M., 1990. Effect of KOH concentration on the formation and decomposition kinetics of calcium zincate. J. Electrochem. Soc. 137, 2800-2803.

ZHANG, P., LEE, T., XI, F., NAVROTSKY, A., 2008. Energetics of ZnO nanoneedles: surface enthalpy, stability, and growth. J. Mater. Res. 23, 1652-1657.

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., DENG, J., CHEN, J., YU, R., XING, X., 2014. The electrowinning of zinc from sodium hydroxide solutions. Hydrometallurgy 146, 59-63.

ZHANG, Y., MU, J., 2007. Controllable synthesis of flower- and rod-like ZnO nanostructures by simply tuning the ratio of sodium hydroxide to zinc acetate. Nanotechnology 18, 1-6.

ZHAO, G., LIU, Q., 2011. Effects of impurities ions on zinc electrowinning process in alkaline leaching. Int. Conf. Biology, Environment & Chemistry, 28-30 December, Singapore, IACSIT Press, 1, pp.397-400.

ZHAO, Y., STANFORTH, R., 2000a. Production of Zn powder by alkaline treatment of smithsonite Zn-Pb ores. Hydrometallurgy 56, 237-249.

ZHAO, Y., STANFORTH, R., 2000b. Extraction of zinc from zinc ferrites by fusion with caustic soda. Miner. Eng. 13, 1417-1421.