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Preparation of different zinc compounds from a smithsonite ore through ammonia leaching and subsequent heat treatment

Arman Ehsani^{1,2}, İlhan Ehsani^{2,3}, Abdullah Obut²

¹ Adana Alparslan Türkeş Science and Technology University, Mining Engineering Department, Sarıçam, Adana, Turkey

² Hacettepe University, Mining Engineering Department, 06800 Beytepe, Ankara, Turkey

³ Şırnak University, Mining Engineering Department, 73000, Şırnak, Turkey

Corresponding author: aehsani@atu.edu.tr (Arman Ehsani)

Abstract: In this study, firstly, the effects of ammonia concentration, leaching time and solid/liquid ratio on the leaching behaviour of zinc from a smithsonite (ZnCO_3) ore sample in aqueous ammonia solutions were investigated at room temperature by chemical, X-ray diffraction (XRD) and Fourier-transform infrared (FT-IR) spectroscopy analyses. It was found that leaching ratio of zinc steeply increased from 30.1 to 76.2% with increasing ammonia concentration from 1.0 to 4.0 M and maximum zinc leaching ratio of 79.7% was reached after leaching in 13.3 M NH_3 solution. The XRD pattern of the residue obtained after leaching in 4.0 M NH_3 solution for 90 min at solid/liquid ratio of 0.15 g/mL, the optimum condition, showed that smithsonite phase in the ore sample almost completely dissolved whereas the gangue minerals goethite and calcite remained unaffected, confirming the selectivity of ammonia solution for zinc dissolution. Together with zinc, leaching ratios of cadmium were also determined. In second part of the study, precipitation tests (by complete drying at different temperatures) were conducted on dissolved zinc, carbonate and ammonia containing pregnant solutions obtained after selected leaching experiments. By complete drying of the pregnant solutions at low temperatures, i.e. 50°C, relatively pure solid zinc ammine carbonate ($\text{Zn}(\text{NH}_3)\text{CO}_3$) precipitates and at higher temperatures, i.e. 150°C, quite pure solid zinc carbonate hydroxide ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) precipitates could be prepared. High-temperature heating of $\text{Zn}(\text{NH}_3)\text{CO}_3$ and $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ precipitates at 450°C yielded single-phase zinc oxide (ZnO). The chemical compositions, FT-IR spectra and scanning electron microscope (SEM) photographs of some of the precipitates were also presented.

Keywords: ammonia leaching, smithsonite, zinc ammine carbonate, zinc carbonate hydroxide, zinc oxide

1. Introduction

In 2019, the global zinc metal demand (mainly for use in galvanization) and production were about 13.67 and 13.49 million tons, respectively, resulting in a production-to-consumption deficit of refined zinc by 180000 tons (Nayak et al., 2021). Besides, according to Watari et al. (2021), the global demand for zinc metal is expected to show a continuously increasing trend by the end of this century. As the primary resource of zinc metal, zinc ores are generally classified into two: the sulfide and the nonsulfide ores (Mondillo et al., 2018). Because of the rising demand for zinc metal and the decreasing zinc sulfide ore reserves, in recent years, the interest for the processing of nonsulfide zinc ores, and especially smithsonite (ZnCO_3) ores, are increasing (Abkhoshk et al., 2014; Rao et al., 2015; Kaya et al., 2020; Wang et al., 2020). The lower zinc grade, complex nature and the presence of carbonate (e.g., calcite, dolomite) and/or iron (e.g., goethite) containing impurities in smithsonite ores encouraged the use of leaching processes conducted in aqueous sodium hydroxide and ammoniacal solutions, both are selective due to their complexing abilities for zinc (lead and/or cadmium) against the dominant calcium, magnesium and/or iron containing gangue, for their evaluation (Zhao and Stanforth, 2000; Qin et al., 2007; Wang et al., 2008; Rao et al., 2015).

Although there are several studies in the related literature on the leaching of zinc from smithsonite ores in sodium hydroxide solutions under different experimental conditions (Frenay, 1985; Zhao and Stanforth, 2000; Ghasemi and Azizi, 2018; Ehsani et al., 2019; Kumas et al., 2020), the studies that directly leach the ore in ammoniacal solutions including an ammonium salt (Frenay, 1985; Ju et al., 2005; Moghaddam et al., 2005; Feng et al., 2007; Xia et al., 2015) and in only aqueous ammonia solutions (Frenay, 1985; Li et al., 2018) are scarce. Frenay (1985) studied the leaching behaviour of a Belgian smithsonite ore (12.5% Zn) in ammonia solutions (NH_3 concentration: 0.4-4.7 M; 120 min; solid/liquid ratio: 0.088 g/mL; 25°C; ore particle size: $\sim 400 \mu\text{m}$) and obtained zinc leaching ratios changing between 18 and 80%. Using a nonsulfide Chinese zinc ore (15.3% Zn), Li et al. (2018) achieved zinc leaching ratio values of 24.5 and 58.9% after leaching in 3 and 8 M NH_3 solutions (60 min; solid/liquid ratio: 0.33 g/mL; 25°C). In these studies, no experimental work was conducted on the recovery of zinc in any form from the pregnant leaching solutions using any precipitation method.

On the other hand, the studies on the preparation of different zinc carbonate hydroxide compounds from the zinc, carbonate and ammonia containing solutions, either prepared synthetically from reagent grade compounds or by using primary/secondary zinc-containing materials (e.g. Zn-containing natural/calcined/roasted ores, Zn-containing residues, Zn metal, etc.), are generally patent studies, whose details have not been fully disclosed (Harvey, 2006). In these studies, zinc-containing feed materials are dissolved in ammonia solutions, mostly containing ammonium carbonate, under different experimental conditions. Following solid/liquid separation, various zinc carbonate hydroxide compounds, generally in the form of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (hydrozincite), were prepared mostly by heating the zinc, carbonate, and ammonia containing solutions with steam in the absence/presence of vacuum at temperatures about 95°C, where ammonia was recovered for re-leaching (Peters, 1978; Spink and Stein, 1986; Kasai et al., 1987; Spink et al., 1991; Freeman et al., 2005). As explained here, the zinc, carbonate and ammonia containing solutions were heated at higher temperatures for the fast removal/recovery of ammonia from the solution, but no detailed information was given if the heating was conducted at lower temperatures.

There are only a few studies in the related literature on the preparation and/or characterization of zinc ammine carbonate ($\text{Zn}(\text{NH}_3)\text{CO}_3$) compound. In the earlier undetailed studies, Ehret and Greenstone (1943) and Conn and Humphrey (1956) prepared pink-coloured zinc oxide by thermally decomposing a precursor, which was probably zinc ammine carbonate. In the newer studies of Wen et al. (2004) and Khazeni et al. (2016), zinc ammine carbonate was prepared using reagent grade starting materials under solvothermal conditions. In addition, Lopez et al. (2017) prepared zinc ammine carbonate precursor for the synthesis of zinc oxide nanoparticles by leaching of the black mass (ZnO content: 26.88%, zinc in the forms of ZnO and ZnMn_2O_4) obtained during recycling of Zn-C and alkaline batteries in ammoniacal ammonium carbonate solution (1.72 mol/L $(\text{NH}_4)_2\text{CO}_3$ containing 0.1-1.0 mol/L NH_3) at solid/liquid ratio of 0.10 g/mL for 60 min. Following leaching and filtration, the pregnant solution was evaporated under a pressure of 34 bars in an evaporator. The solid precursors obtained in this way were $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and $\text{Zn}(\text{NH}_3)\text{CO}_3$ when leaching was conducted in the presence of 0.1 and 0.5-1 mol/L NH_3 , respectively. As seen from these studies, no study was found in the related literature on the preparation of zinc ammine carbonate by complete drying of the zinc, carbonate and ammonia containing solutions obtained by direct leaching of a smithsonite ore in aqueous ammonia solutions in the absence of any ammonium salt.

Therefore, in this study, the leaching behaviour of zinc from a local smithsonite ore sample containing goethite and calcite as the main gangue minerals was investigated in aqueous ammonia solutions in the absence of any ammonium salt using chemical, XRD and FT-IR analyses methods. In addition, for the first time, the preparation conditions of zinc ammine carbonate and zinc carbonate hydroxide compounds from the pregnant leaching solutions obtained after selected leaching experiments were also determined.

2. Materials and methods

In the experimental studies; analytical grade reagents, classical laboratory equipment, deionized water and a ground smithsonite ore sample (Yahyali-Kayseri/Turkey) having 80% passing size of $124 \mu\text{m}$ were used. The chemical composition (by inductively coupled plasma emission (ICP-OES) spectrometer; AcmeLabs), the XRD pattern (Rigaku Miniflex 600, operated at 15 mA/40 kV using $\text{CuK}\alpha$

radiation at scanning speed of 2°/60 s) and the FT-IR spectrum (Perkin Elmer, KBr pellet method) of the ground sample were determined for sample characterization.

The leaching experiments were conducted in a magnetically stirred closed Pyrex reactor (0.6 L). In a representative leaching experiment, an aqueous solution of ammonia at the selected concentration (1.0, 2.0, 3.0, 4.0, 7.5 and 13.3 mol/L) was transferred into the reactor and then the ground ore sample, whose amount was calculated according to the predetermined solid/liquid (S/L) ratio values (0.075, 0.15, 0.20, 0.30, 0.35 and 0.50 g dry ore/mL solution), was added to the solution. The leaching was continued for the selected leaching time (15, 30, 60, 90 and 120 min) under constant magnetic stirring (700 rpm). The studied ammonia concentrations, S/L ratios and the leaching times were selected according to the preliminary experiments and previous literature studies. All leaching experiments were conducted at room temperature due to the volatility of ammonia and the instability of the zinc ammine complex at high temperatures (Richardson and Lange, 2009). After completion of the leaching time, the undissolved leaching residue was separated by filtration, water-washed, dried at 105±5°C, weighed and stored in closed glass bottles for further analyses by ICP-ES (AcmeLabs). The leaching ratio values (%) of zinc were determined according to Eq. 1. Randomly selected ten of the leaching experiments were conducted at least two replicates, and the difference between the obtained leaching ratio values was always less than ±2%. Besides, together with zinc, the leaching ratio values of cadmium were also determined, because of the similarities in the chemical behaviours of zinc and cadmium in ammoniacal solutions (Hiatt and Huff, 1975; Meng and Han, 1996).

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

The precipitation tests were conducted by complete drying of the pregnant solutions obtained after selected leaching experiments. In a representative precipitation test, a constant volume (100 mL) of zinc, carbonate and ammonia containing pregnant leaching solution was transferred to a Petri dish. Then, the solution-containing Petri dish was placed on a heating plate and heated (or dried) for experimentally determined durations (1440, 180, 135, 60 and 45 min for heating plate temperatures of 50, 75, 100, 125 and 150°C, respectively.) until the solution completely dried and turned into a white precipitate. Finally, the obtained dry zinc-containing solid precipitates were weighed and stored in closed glass bottles for further chemical, XRD, FT-IR and SEM analyses. Also, some of the precipitates were heated (calcined) for 60 min at higher temperatures (in a laboratory oven (Mettler) for temperatures ≤250°C or in a chamber furnace (Protherm) for 450°C) to observe the changes caused by high-temperature heating.

3. Results and discussion

3.1. Characterization of the ore sample

The chemical composition of the ground ore sample was given in Table 1. In addition to the high zinc oxide content, the high carbon and very low sulfur contents (5.34% C and 0.08% S, determined by Leco analyser; AcmeLabs) of the ore sample confirmed that the sample is a nonsulfide zinc ore sample. Besides, the moisture content (at 105°C) and the loss on ignition (at 1000°C) values of the ore sample were determined as 1.4 and 24.2%, respectively.

Table 1. Chemical composition (wt.%) of the ore sample

Component	Amount	Component	Amount	Component	Amount
Zn	23.06	Al	1.67	Mn	0.05
Fe	18.33	Mg	0.30	Na	0.03
Ca	5.12	K	0.28	Cr	0.01
Pb	1.91	Cd	0.12	As	<0.02

The XRD pattern and the FT-IR spectrum of the ground ore sample were given in Fig. 1. The XRD peaks observed at 2θ values of 25.04, 32.54, 38.68, 42.84, 46.64, 51.42 and 53.72° in Fig. 1a indicated that the main zinc ore mineral in the sample is smithsonite (ZnCO₃, JCPDS card no: 8-0449). In addition, Fig. 1a showed that the sample contained goethite (FeOOH, JCPDS card no: 29-0713) and calcite (CaCO₃, JCPDS card no: 5-0586) as the main gangue minerals, and quartz (SiO₂, JCPDS card no: 46-1045), kaolinite (Al₂Si₂O₅(OH)₄, JCPDS card no: 89-6538), cerussite (PbCO₃, JCPDS card no: 47-1734) and

hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$, JCPDS card no: 5-0555) as the minor components. The only absorption peak characteristic for smithsonite in the FT-IR spectrum of the sample (Fig. 1b) was observed at 744 cm^{-1} due to the doubly degenerate planar bending of the carbonate group in smithsonite. On the other hand, the characteristic absorption peak of calcite, the main carbonate impurity, was observed at 711 cm^{-1} (Weir and Lippincott, 1961).

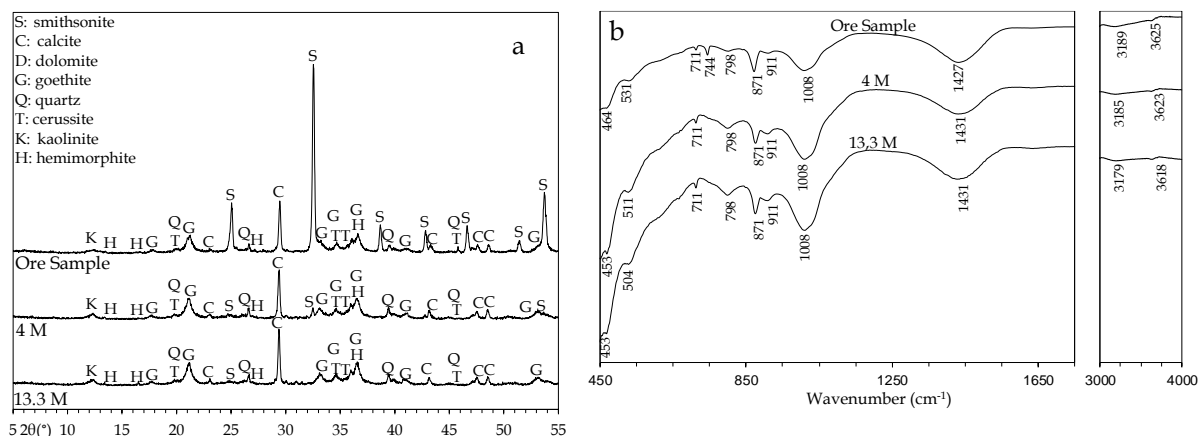


Fig. 1. XRD patterns (a) and FTIR spectra (b) of the ore sample and the residues obtained after leaching at indicated ammonia concentrations

3.2. Leaching experiments

The dissolution reaction of smithsonite in ammonia solutions may be written as $\text{ZnCO}_3 + 4\text{NH}_3 \leftrightarrow \text{Zn}(\text{NH}_3)_4^{2+} + \text{CO}_3^{2-}$ (Bai et al., 2018), where the NH_3/Zn mole ratio is 4. The leaching ratio values of zinc obtained after leaching of the ground ore sample in ammonia solutions of different concentrations for 90 min at S/L ratio of 0.15 g/mL were given in Table 2. As the most important parameter on the leaching of zinc from the sample, the calculated initial NH_3/Zn mole ratio values were also included in Table 2. Table 2 showed that the leaching ratio of zinc was steeply increased from 30.1 to 76.2% when the ammonia concentration of the leaching solution was increased from 1.0 to 4.0 M (about two times the theoretical NH_3/Zn mole ratio), over which the leaching ratio of zinc levelled off and became nearly constant. At the highest workable ammonia concentration (13.3 M NH_3), for which the NH_3/Zn mole ratio is about six times the theoretical, the maximum zinc leaching ratio of 79.7% was achieved. In the literature studies, Frenay (1985) obtained a maximum zinc leaching ratio value of 80% from a Belgian oxidized ore (12.5% Zn) by leaching in 4.7 M NH_3 solution (S/L ratio: 0.088 g/mL, 120 min, 25°C) whereas Li et al. (2018) reported maximum zinc leaching ratio value of 58.9% from a Chinese oxidized ore (15.3% Zn) by leaching in 8 M NH_3 solution (S/L ratio: 0.33 g/mL, 60 min, 25°C). Even in ammonia solutions at very high concentrations (and therefore very high NH_3/Zn mole ratios), zinc leaching ratio values greater than 80% could not be reached. This situation was also encountered in one of our previous studies (Ehsani et al., 2019), which investigated the leaching behaviour of a similar smithsonite ore sample in sodium hydroxide solutions and obtained a maximum zinc leaching ratio of about 80% for 8 M solution NaOH concentration at room temperature. It is thought to be that zinc was not existed only in smithsonite phase of the ore sample but also in goethite and calcite (and also minor hemimor-

Table 2. Effects of NH_3 concentration on the leaching of Zn and Cd

NH_3 concentration (M)	NH_3/Zn mole ratio	Leaching ratio (%)	
		Zn	Cd
1.0	1.88	30.1	20.9
2.0	3.76	53.5	50.5
3.0	5.64	68.3	69.9
4.0	7.52	76.2	80.4
7.5	14.17	79.0	85.9
13.3	25.08	79.7	87.6

phite) components of the sample, all are resistant to dissolution in ammonia solutions (Whittaker and Zabinski, 1981; Santoro et al., 2014; Mondillo et al., 2015).

According to the results given in Table 2, optimum ammonia concentration and more importantly optimum NH_3/Zn mole ratio were selected as 4.0 M and 7.52, respectively. Ding et al. (2013) and Liu et al. (2018) indicated that zinc tetraammine ($\text{Zn}(\text{NH}_3)_4^{2+}$) and zinc monohydroxylamine ($\text{Zn}(\text{NH}_3)_3(\text{OH})^+$) were expected to be the stable soluble zinc containing complex species present in the pregnant leaching solution. On the other hand, as can be seen from Table 2, the leaching behaviour of cadmium was very similar to zinc, as expected (Hiatt and Huff, 1975; Meng and Han, 1996).

The XRD patterns (see Fig. 1a) and the FT-IR spectra (see Fig. 1b) of the residues obtained after leaching in ammonia solutions at optimum (4.0 M) and maximum (13.3 M) concentrations were determined to illustrate the selective zinc leaching from the studied ore sample. The XRD peaks belonging to smithsonite in the pattern of the sample almost completely disappeared in the patterns of the residues (Fig. 1a). On the other hand, the XRD peaks of main gangue minerals, i.e. goethite and calcite, stayed unchanged, indicating the selective dissolution of smithsonite in ammonia solutions against the impurities. Also, the characteristic absorption peak of smithsonite observed at 744 cm^{-1} was almost completely disappeared in the FT-IR spectra of the residues obtained after leaching of 4.0 and 13.3 M NH_3 solutions (Fig. 1b). In addition, the characteristic absorption peaks of goethite (798 cm^{-1}) and calcite (711 cm^{-1}) were stayed unchanged in the spectra of the residues, again showing the selectivity in zinc dissolution.

The effects of leaching time on the dissolution of zinc were investigated for optimally selected 4.0 M NH_3 concentration and S/L ratio of 0.15 g/mL. As shown in Table 3, the leaching of zinc in the 4.0 M NH_3 solution is quite fast (59.7% in 15 min). The leaching ratio of zinc increased to a high level (74.2%) after 60 min and practically became nearly constant (76.2%) after 90 min, which was selected as the optimum leaching time. In a previous study (Talan et al., 2017), the effects of different leaching times (30-720 min) on the leaching of zinc from a smithsonite containing cerussite flotation tailing have been studied. In the study, zinc leaching ratio values of 72.8 and 74.3% were obtained for 5 M and 7 M NH_3 concentrations, respectively, for a leaching time of 360 min. When the leaching time was increased to 720 min, the increase in the zinc leaching ratios decreased and became 75.0 and 76.6% for 5 and 7 M NH_3 concentrations, respectively. On the other hand, as seen from Table 3, the dependence of the leaching ratio of cadmium to leaching time was observed to be very similar to the behaviour of zinc.

Table 3. Effects of leaching time on the leaching of Zn and Cd

Leaching time (min)	Leaching ratio (%)	
	Zn	Cd
15	59.7	64.5
30	69.3	74.1
60	74.2	79.0
90	76.2	80.4
120	76.8	81.2

The effects of the S/L ratio on the leaching of Zn and Cd were investigated in two different modes at optimally selected leaching time of 90 min. In the first mode, the amount of ore sample added to the constant volume ammonia solution was increased by keeping the concentration of ammonia solution constant at an average (2.0 M NH_3) and the optimum (4.0 M NH_3) values. Under these conditions (Table 4), the leaching ratio of Zn (and Cd) decreased with the increase of the S/L ratio, because of the decrease in the initial NH_3/Zn mole ratios. In the second mode, the amount of ore sample added to the constant volume ammonia solution was increased by increasing at the same time NH_3 concentration of the constant volume ammonia solution to keep the initial NH_3/Zn mole ratio constant at an average (3.76) and the optimum (7.52) values. Under these conditions (Table 5), the leaching ratio of Zn (and Cd) increased with the increase of S/L ratio probably due to the increased leaching kinetics of zinc in solutions having increased initial ammonia concentrations and pH, and also the increased stability of zinc ammine complex.

Table 4. Effects of solid/liquid ratio on the leaching ratios (%) of Zn and Cd at constant ammonia concentrations

2.0 M NH ₃				4.0 M NH ₃			
NH ₃ /Zn mole ratio	S/L ratio (g/mL)	Leaching ratio		NH ₃ /Zn mole ratio	S/L ratio (g/mL)	Leaching ratio	
		Zn	Cd			Zn	Cd
7.52	0.075	65.1	67.3	15.04	0.075	75.9	82.3
3.76	0.15	53.5	50.5	7.52	0.15	76.2	80.4
2.82	0.20	46.1	42.9	5.64	0.20	69.0	72.1
1.61	0.35	31.3	25.3	3.22	0.35	58.7	59.0

Table 5. Effects of solid/liquid ratio on the leaching ratios (%) of Zn and Cd at constant NH₃/Zn mole ratios

NH ₃ /Zn mole ratio: 3.76				NH ₃ /Zn mole ratio: 7.52			
NH ₃ conc. (M)	S/L ratio (g/mL)	Leaching ratio		NH ₃ conc. (M)	S/L ratio (g/mL)	Leaching ratio	
		Zn	Cd			Zn	Cd
1.0	0.075	42.4	38.7	2.0	0.075	58.7	60.3
2.0	0.15	53.5	50.5	4.0	0.15	76.2	80.4
2.7	0.20	59.0	59.0	5.3	0.20	76.0	81.7
4.6	0.35	70.9	74.4	9.3	0.35	77.3	84.7

3.3. Precipitation tests

The precipitation tests were conducted by complete drying of the dissolved zinc, carbonate and ammonia containing pregnant solutions obtained after leaching (under optimum NH₃/Zn mole ratio of 7.52 and constant leaching time of 90 min) at different S/L ratios (0.15, 0.30 and 0.50 g/mL) (Table 6) to observe the effect of solution composition on the type of precipitate formed. The very high S/L ratio of 0.50 g/mL was also selected for obtaining highly concentrated zinc pregnant leaching solution and therefore for obtaining a high amount of zinc-containing precipitate.

Table 6. Leaching conditions applied for obtaining pregnant solutions used in the precipitation tests and the properties of these solutions

NH ₃ /Zn mole ratio	NH ₃ conc. (M)	S/L ratio (g/mL)	Leaching ratio		The pregnant leaching solution's		
			Zn (%)	Cd (%)	Code	Zn content	pH
7.52	4.0	0.15	76.2	80.4	N60	26.3 g/L	11.6
7.52	8.0	0.30	77.4	84.1	N120	53.0 g/L	12.3
7.52	13.3	0.50	78.3	84.2	N200	90.3 g/L	12.9

The XRD patterns of the white-coloured solid precipitates obtained by drying of the pregnant leaching solutions (N60, N120 and N200) at temperatures between 50-150°C for different durations (drying durations were presented in Section 2) given in Fig. 2 indicated that all of the formed precipitates were composed of two different phases, zinc ammine carbonate (Zn(NH₃)CO₃, JCPDS card no: 88-2016) and zinc carbonate hydroxide (Zn₅(CO₃)₂(OH)₆, JCPDS card no: 19-1458). The presence of strong XRD peaks observed at 2θ values of 15.2, 19.9, 22.7, 25.3 and 30.2° indicated the dominance of zinc ammine carbonate phase in the precipitates obtained by low-temperature drying (i.e. see Fig 2, patterns N60-50°C, N120-50°C and N200-50°C), whereas the peaks found at 2θ=13.1, 28.2, 31.2, 32.8 and 36.1° indicated the dominance of zinc carbonate hydroxide phase in the precipitates formed after high-temperature drying (i.e. see Fig 2, patterns N60-150°C, N120-150°C and N200-150°C). Considering the intensities of XRD peaks shown in Fig. 2, it can be concluded that the highest purity Zn(NH₃)CO₃ precipitate could be obtained with the lowest amounts of Zn₅(CO₃)₂(OH)₆ impurity by drying of N120 solution at 50°C for 1440 min. On the other hand, quite pure Zn₅(CO₃)₂(OH)₆ precipitates with very low amounts of Zn(NH₃)CO₃ impurity could be prepared by drying of both N60 and N120 solutions at 150°C for 45 min. Although quite pure Zn₅(CO₃)₂(OH)₆ containing precipitates could be obtained by drying both N60 and N120 solutions at 150°C, pure Zn₅(CO₃)₂(OH)₆ precipitate could not be prepared from N200 solution (see Fig.2, compare patterns N60-150°C and N120-150°C with N200-150°C) by drying at 150°C, probably due to its very high zinc and ammonia contents (see Table 6).

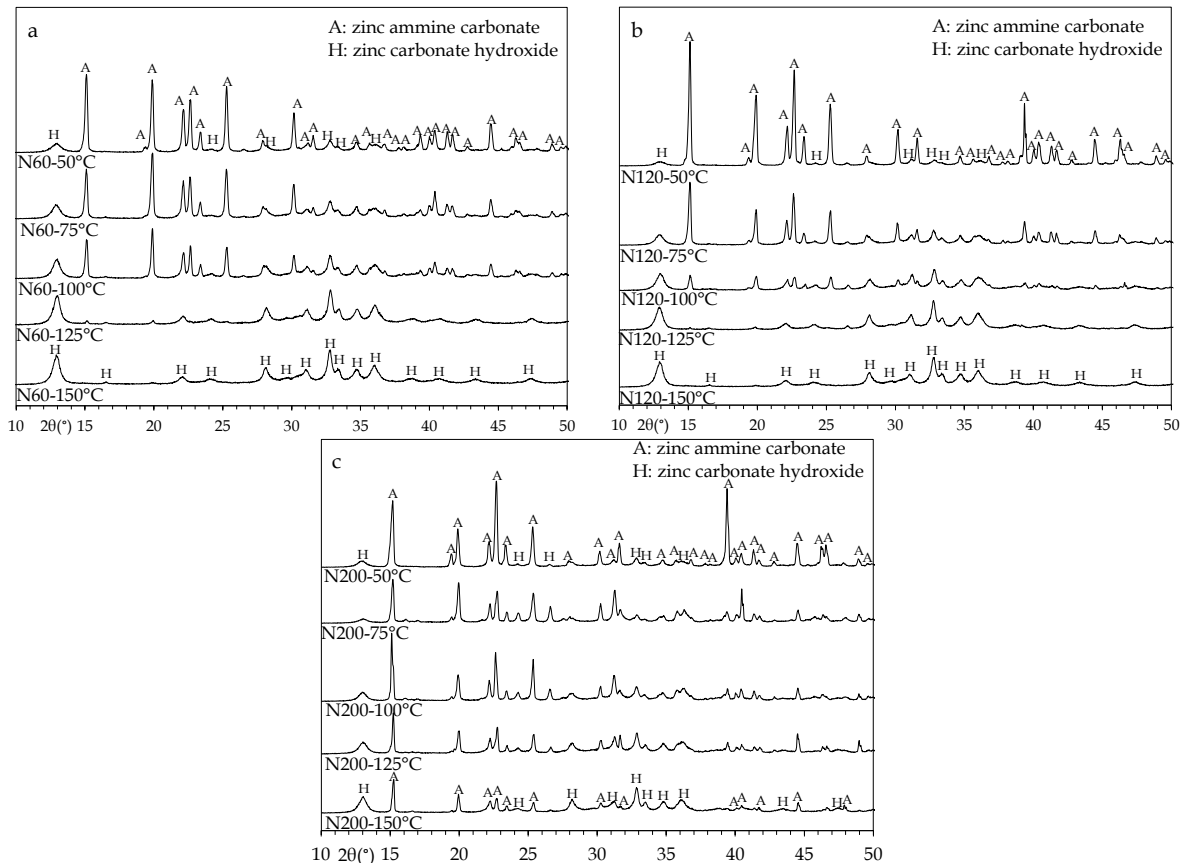


Fig. 2. XRD patterns of the precipitates obtained by complete drying of N60 (a), N120 (b) and N200 (c) solutions at indicated temperatures

In addition to XRD diffraction analyses, the zinc and cadmium contents of the precipitates having the highest amounts of $\text{Zn}(\text{NH}_3)\text{CO}_3$ (theoretical Zn content: 45.92%) and $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ (theoretical Zn content: 59.56%) phases, obtained from N120 solution after drying at 50°C and 150°C, were determined as 49.78% Zn – 0.30% Cd and 57.97% Zn – 0.35% Cd, respectively. Due to the selectivity of ammonia leaching for zinc, the amounts of main ore components (iron, calcium and aluminium) in the precipitates were found to be lower than 0.01%. The FT-IR spectra and SEM (FEI-Inspect F50) photographs of N120-50°C and N120-150°C precipitates were also determined and given in Fig. 3 and Fig. 4, respectively. In the FT-IR spectrum of N120-50°C precipitate, which is a relatively pure zinc ammine carbonate, the absorptions near 3300 and 2900 cm^{-1} may be attributed to the stretching of N-H bond, and the strong band between 1300-1600 cm^{-1} probably be related to the bending of N-H bond and the stretching of CO_3^{2-} group in this sample (Weir and Lippincott, 1961; Erd et al., 1964). In the FT-IR spectrum of the N120-150°C precipitate, all of the observed bands substantiated the presence of Zn-O bond (464 cm^{-1}), CO_3^{2-} group (707, 730, 833, 1390 and 1496 cm^{-1}) and OH group (891, 959, 1047 and 3297 cm^{-1}) in the structure of zinc carbonate hydroxide (or hydrozincite) precipitate (Stoilova et al., 2002; Bucca et al., 2009; Winiarski et al., 2018). The zinc ammine carbonate precipitate showed flat rod-like morphology (Fig. 4a), whereas the zinc carbonate hydroxide precipitate showed flake- or plate-like morphology, as also observed in the previous literature studies (Aversa et al., 2002; Sinhamahapatra et al., 2012).

The effects of high-temperature heating on the phase composition of the selected precipitates were also investigated. The N120-50°C precipitate was heated separately for 60 min at predetermined temperatures of 200, 225, 250 and 450°C and the corresponding XRD diffraction patterns of the heated precipitates (N120-50°C-H200, N120-50°C-H225, N120-50°C-H250 and N120-50°C-H450, respectively) were presented in Fig. 5. Fig. 5 showed that the zinc ammine carbonate phase was stable against heating up to 200°C. Heating at temperatures equal to or greater than 225°C converted zinc ammine carbonate into zinc oxide according to general $\text{Zn}(\text{NH}_3)\text{CO}_3 \rightarrow \text{ZnO} + \text{NH}_3 + \text{CO}_2$ reaction. Besides, the impurity

phase zinc carbonate hydroxide in the precipitate of N120-50°C decomposed into zinc oxide according to $Zn_5(CO_3)_2(OH)_6 \rightarrow 5ZnO + 2CO_2 + 3H_2O$ reaction at 250°C or higher temperature. On the other hand, heating of N60-50°C, N120-50°C and N200-50°C precipitates at 450°C converted them into crystalline single-phase zinc oxides (Fig. 6) with calculated (Ehsani, 2020) approximate crystallite sizes of 27, 28 and 34 nm, respectively. In addition, zinc and cadmium contents of the calcined N120-50°C-H450 zinc oxide (theoretical Zn content: 80.35%) precipitate were determined as 78.34% and 0.49%, respectively.

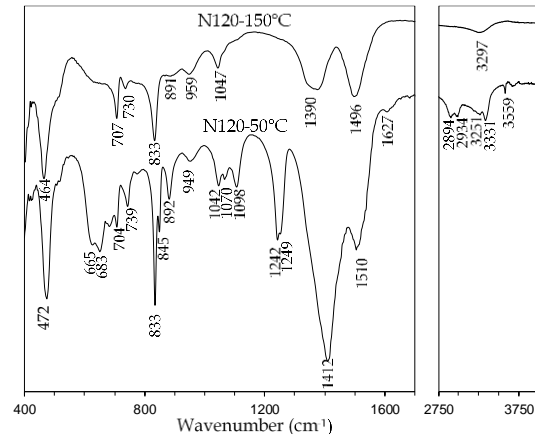


Fig. 3. FT-IR spectra of the precipitates obtained from N120 solution by drying at 50°C (down) and 150°C (up)

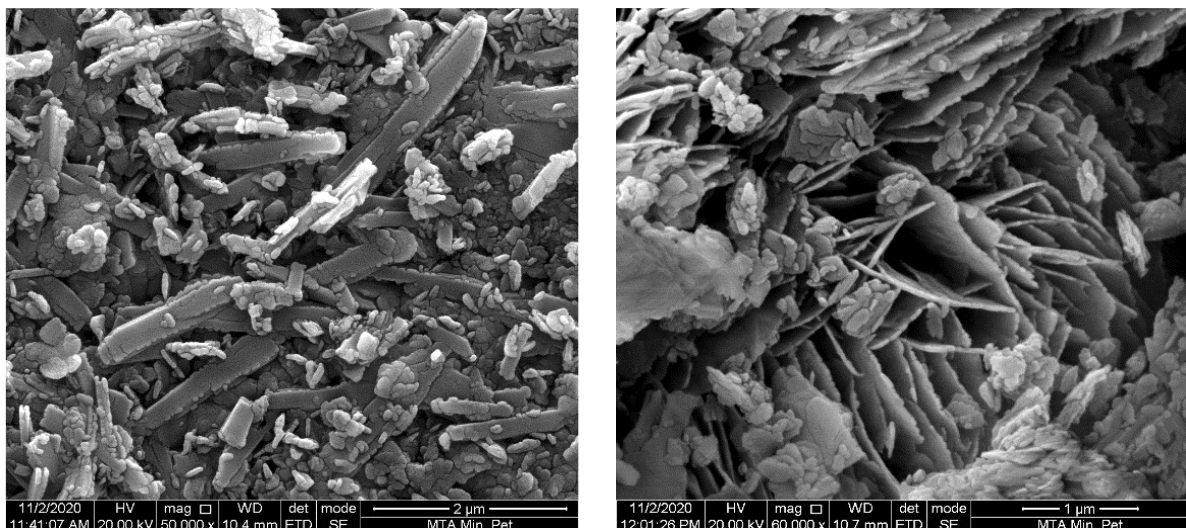


Fig. 4. SEM photographs of the precipitates obtained from N120 solution by drying at 50°C (left) and 150°C (right)

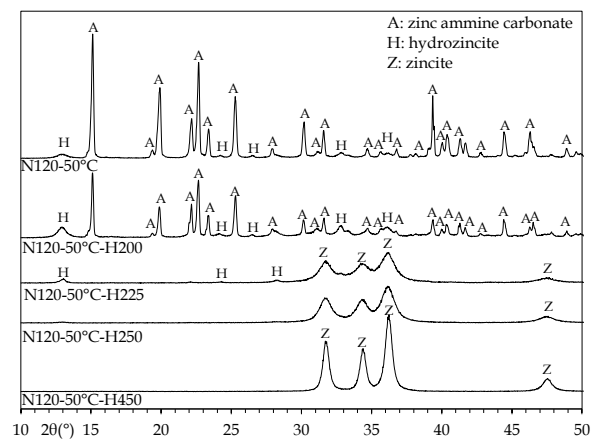


Fig. 5. XRD patterns of N120-50°C precipitate and the solids obtained by heating this precipitate at indicated temperatures

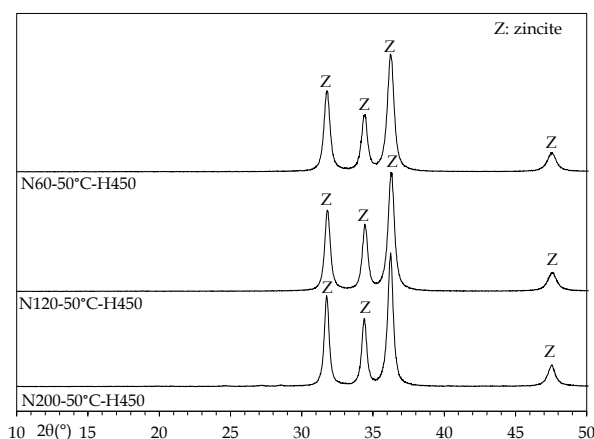


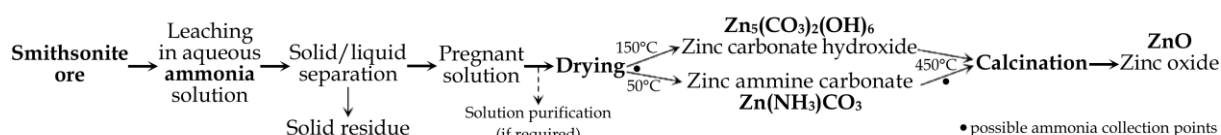
Fig. 6. XRD patterns of the solids obtained by heating of the indicated precipitates at 450°C

4. Conclusions

In this study, zinc-containing $\text{Zn}(\text{NH}_3)\text{CO}_3$ and $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ compounds were prepared from a nonsulfide zinc (smithsonite) ore sample (23.06% Zn) from Yahyali (Kayseri/Turkey) with sequential use of ammonia leaching and precipitation processes. In the leaching step, it was found that smithsonite in the ore sample could be dissolved selectively in ammonia solutions against the dominant goethite and calcite gangue in the ore sample and a high zinc leaching ratio of 76.2% could be achieved under the optimum condition (NH_3 concentration: 4.0 M; leaching time: 90 min; solid/liquid ratio: 0.15 g/mL). The effects of leaching time and solid/liquid ratio on the leaching of zinc were also determined in the study.

The pregnant solutions, containing different amounts of dissolved zinc, obtained after selected leaching experiments were used in the precipitation step. By the complete drying of pregnant solutions at 50 and 150°C, 49.78% Zn-containing $\text{Zn}(\text{NH}_3)\text{CO}_3$ and 57.97% Zn-containing $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ solid precipitates could be prepared, respectively. Optionally, following high-temperature (450°C) processing of both precipitates, crystalline ZnO solids could also be obtained.

In conclusion, considering all of the findings of this study, the following flowsheet is suggested for the preparation of different zinc compounds that may be used in different industries (i.e. chemical, pharmaceutical, pigment, rubber, electronics, etc.) by hydro(pyro)metallurgical processes from smithsonite ores, which have considerable reserves in Turkey.



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