

LEACHING OF HEMIMORPHITE IN NEUTRAL SOLUTION AT HIGH TEMPERATURE

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Abstract

The leaching behavior of hemimorphite in neutral solution ($\text{NH}_4^+ \text{-Cl-H}_2\text{O}$) was investigated at high temperature ($T > 100^\circ\text{C}$) under a range of experimental conditions. Thermodynamic calculations indicate that the tendency of dehydration of silica gel is significantly enhanced with the increasing temperature. It was shown that the temperature, ammonium chloride concentration, or L/S ratio increased resulted in greater leaching efficiency. The following optimized leaching conditions were obtained: stirrer speed 400r/min, NH_4Cl concentration 5.5M, L/S ratio 9mL/g at 160°C for 3h. Under these optimized conditions, the average leaching yield of zinc was 97.82%. The silicon was converted to quartz and remained in the residue. This process can be used to dispose willemite and hemimorphite as it solves the problem of silica gel dehydration.

Keywords: Pressure leaching; Ammonium chloride; Hemimorphite; Silica gel

1. Introduction

Following aluminum and copper, zinc is one of the most commonly used non-ferrous metal in galvanizing and battery manufacturing industries. Currently, zinc sulfide ores are the primary material for the zinc extraction process. Because of the decline of the global reserves of zinc sulfides ores as well as because of the new government mandated sulphur dioxide and particulate emission, extensive investigations turned to the treatment of zinc oxide ores by hydrometallurgical and pyrometallurgical processes [1].

Hydrometallurgical process is used to dispose various zinc oxide ores, such as zincite (ZnO), smithsonite (ZnCO_3), hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), willemite (Zn_2SiO_4), zincsilite ($\text{Zn}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$), and hemimorphite ($\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$) [2, 3]. Sulfuric acid is the most commonly used lixiviant in zinc hydrometallurgical processes [4, 5]. Direct acid leaching systems have been used for a number of years for the treatment of zinc silicate ores (willemite and hemimorphite) [6, 7]. Silica gel is formed in acid leaching of zinc silicate which may not be filterable. A lot of work has been done to precipitate silica effectively and economically. Matthew and Elsnor (1977) developed a continuous process in which silica was dissolved first and then coagulated by controlling

the pH. The pH of the leaching solution was raised to pH 4–5.5 using a neutralizing agent to precipitate and coagulate the colloidal silica [8]. Lots of research work has been done, but there are still a lot of difficulties in industrial applications.

Alkaline treatment of zinc oxide ores or dust has been investigated because Fe cannot be leached and silica gel cannot be formed during the process. Smithsonite can be completely leached but hemimorphite is relatively difficult to leach. Alkaline leaching of hemimorphite requires a mechanochemical process or high temperature, pressure, and alkalinity [9–11]. The silicon may be dissolved as sodium silicate. To avoid the dissolution of silicon, CaO is added to precipitate the silicon, resulting in a large amount of residue which takes away alkali and soluble zinc.

Ammonia with or without ammonium salt is also used to extract zinc from zinc bearing ores or secondary resource [12–14]. Ammonia and ammonium salt have a number of inherent advantages as a leaching agent due to their low cost, low corrosivity and low toxicity. Ions such as Zn(II), Cu(II), Ni(II), and Co(II) form strong ammonia complexes and increase their solubility in ammoniacal solution, while other metals, such as Fe, Pb, Si, Ca, and Mg do not form complexes under the same conditions and precipitate as oxides [15, 16].

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Cementation or solvent extraction can be used to purify the lixivium.

Many investigations show that ZnO can be easily dissolved in ammoniacal solution but the extraction percentage of zinc from willemite is low. To get high extraction percentage of zinc, high L/S or very long leaching time needs to be performed in willemite leaching experiments [17, 18]. Therefore, routine leaching is hard to be practiced in industrial applications. Hemimorphite is one kind of zinc oxide ore and it is a zinc silicate hydroxide hydrate mineral which is commonly associated with smithsonite, sphalerite, and zincate. Hemimorphite is an essential mineral for the extraction of zinc.

The leaching mechanism of hemimorphite in ammonia with or without ammonium salt solution were investigated by many researchers. Yin Zhoulan et al. studied the dissolution of hemimorphite in ammonia-ammonium chloride solution at 25 °C. It was found that the hemimorphite was completely dissolved in ammoniacal solution when the time, the liquid/solid ratio, and the temperature were 1 month, 100/1, and 25 °C; the residue was characteristic of $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ [19] and the coagulation and precipitation speed of $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ was very slow as the solution got close to neutral. Zhiyong Liu et al. studied the dissolution of hemimorphite in ammonia-ammonium sulfate solution. It was found that the residue was characteristic of $\text{H}_2\text{Si}_2\text{O}_5$ or SiO_2 and the extraction percentage of zinc reached 95% when the time, the liquid/solid ratio, and the temperature were 90min, 20g/L, and 35 °C [20]. The dissolution of hemimorphite was limited by the dissolution of Si when the reaction temperature was low.

In the past few years, the investigation of acid leaching under pressure for the processing of zinc-bearing minerals has been performed and put into practice. The treatment of high silica zinc-bearing minerals by acid leaching under pressure has also been investigated [21, 22]. However, little information has been reported concerning the high silica zinc-bearing minerals by ammonium leaching under pressure. In the present work, a process concerning leaching of hemimorphite in ammonium chloride solution at high temperature is performed in order to study a more efficient zinc leaching from hemimorphite process.

2. Materials and Methods

2.1. Materials

The hemimorphite (a gem-grade ore) was obtained from Yunnan Province in China. The hemimorphite sample was ground to a powder of less than 106 μm . The result of the mineralogical analysis of hemimorphite is presented in Table 1. The infrared spectrum of hemimorphite before

leaching is presented by Fig. 8, curve (M). The spectrum of hemimorphite is characterized by peaks at 447.12, 558.86, 602.55, 676.36, 863.79, 933.56, 1086.49, and 1635.09 cm^{-1} and the broad transmittance in the region 3444.79 cm^{-1} is in complete agreement with the literature of Makreski et al. [23]. The X-ray diffraction (XRD) patterns of hemimorphite before leaching is presented by Fig. 3, pattern (M).

2.2. Experimental Setup and Procedure

Leaching experiments were carried out in a 2L autoclave. The temperature and the agitation speed were controlled with a PID controller. Gas was not admitted into the autoclave and the pressure of all experiments was the saturated vapor pressure of the slurry under each temperature. Hemimorphite and NH_4Cl solution were added to the autoclave at room temperature. Agitation did not happen until the temperature reached the desired value. At the end of the experiment the autoclave was rapidly water-cooled.

The effects of several factors such as temperature, leaching time, ammonium chloride concentration, and liquid to solid ratio (L/S) on the extraction percentage of zinc were investigated in batch experiments. All subsequent experiments were performed with a standard agitation speed of 400 rpm. Preliminary experiments had shown that this was sufficient to eliminate the effect of the agitation speed on the extraction percentage of zinc. The experiments were carried out at temperatures from 120 up to 160 °C. All solutions were prepared using deionized water, and the other chemicals used in the experimental part were analytical reagent grade. The residue was separated by vacuum filtration, washed with dilute NH_4Cl solution, and dried at 60 °C. The comprehensive test was repeated four times at optimized leaching conditions (stirrer speed 400r/min, NH_4Cl concentration 5.5M, L/S ratio 9mL/g at 160 °C for 3h). The zinc extraction was determined by analyzing for zinc in the residue by EDTA titration. The mineralogical composition of hemimorphite was provided by Changsha Research Institute of Mining and Metallurgy based upon a selective leaching method metallurgy. XRD measurements were carried out using a RIGAKU-TTRIII instrument (Rigaku Corporation, Tokyo, Japan) with a Cu/ka X-ray source at 40 kV and 250 mA. XRF measurements were carried out using a XRF-1800 instrument (Shimadzu Corporation, Japan). The infrared spectrum was carried out using NICOLET-

Table 1. Mineralogical composition of hemimorphite (wt)%

Phase	ZnSO ₄	Zn ₄ Si ₂ O ₇ (OH) ₂ ·H ₂ O	ZnS	ZnFe ₂ O ₄
Zn%	0.19	99.2	0.47	0.14



6700 instrument (Thermo Nicolet Corporation, USA) with KBr.

3. Results and Discussion

The reaction process is mainly carried out in two stages [24, 25]:

Stage 1: dissolution of hemimorphite

Stage 2: precipitation of silica gel



Thermodynamic calculations indicate that hemimorphite dissolution has a large reaction tendency at 25°C (Table 2), but extraction percentage of zinc was low at routine leaching process in ammonia system. The silicon gel reaches saturation rapidly but the precipitation speed of silicone gel is very slow in the leaching progress of hemimorphite. So the dissolution of silicon is very slow and thereby makes the structure of hemimorphite difficult to destroy. When the silicone gel is dehydrated into silica, the precipitation speed of the silicon can be greatly increased. Therefore, the dissolution of hemimorphite is hindered as the dehydration of silicone gel is very difficult at

routine leaching process. The dehydration of silicone gel is the key to the dissolution of hemimorphite. The $\Delta_r G_m^\theta$ of the dehydration reaction of silica gel decreases with increasing temperature (Fig.1). Negative values begin to appear around 120 °C. The tendency of the dehydration of silica gel is significantly enhanced with increasing temperature.

3.1. Effect of the Temperature

The effect of temperature on the extraction percentage of zinc was performed. It is shown that increasing temperature from 120 °C to 160 °C has a noticeable impact on the extraction percentage of zinc (Fig. 2). The extraction percentage of zinc was increased from 48% to 85%.

The diffraction peak intensity of SiO_2 occurred at 120 °C and enhanced with improving temperature (Fig. 3, pattern (1)-(5)). The XRD patterns revealed that the residue was $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ and SiO_2 . The diffraction peak intensity of $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ was weakened by improving temperature. The diffraction peak intensity of SiO_2 increased with improving temperature.

Table 2. Reaction equation and $\Delta_r G_m^\theta$ (25 °C) of hemimorphite dissolution ($\text{kJ}\cdot\text{mol}^{-1}$)

Reaction equation	$\Delta_r G_m^\theta$	
$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O} + (4-4n)\text{H}^+ + 4n\text{NH}_4^+ = 4\text{Zn}(\text{NH}_3)_n^{2+} + 2\text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O}$	-269.708	1
$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O} + 8\text{NH}_4^+ = 4\text{Zn}(\text{NH}_3)_2^{2+} + 2\text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O}$	-115.595	2
$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O} + 12\text{NH}_4^+ = 4\text{Zn}(\text{NH}_3)_3^{2+} + 2\text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O} + 4\text{H}^+$	37.375	3
$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O} + 16\text{NH}_4^+ = 4\text{Zn}(\text{NH}_3)_4^{2+} + 2\text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O} + 8\text{H}^+$	197.882	4
$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O} + 4\text{NH}_4^+ + 12\text{Cl}^- + 4\text{H}^+ = 4\text{Zn}(\text{NH}_3)\text{Cl}_3^- + 2\text{H}_4\text{SiO}_4 + 2\text{H}_2\text{O}$	-287.29	5

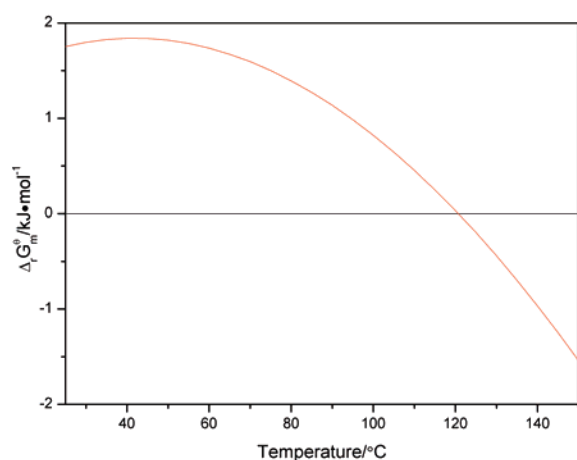


Figure 1. $\Delta_r G_m^\theta$ -T plot of reaction (6)

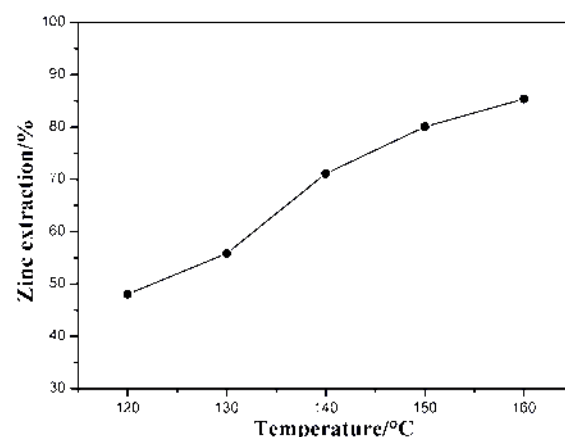


Figure 2. Effect of temperature on zinc extraction: agitation speed 400r/min, concentration of NH_4Cl 5.5mol/L and liquid/solid ratio (L/S) 6mL/g at reaction time 2h



3.2. Effect of L/S

The effect of L/S on the extraction percentage of zinc was investigated. It was shown that the extraction percentage of zinc was increased significantly from 48 % to 90 % (Fig. 4). At a low L/S, the silica was leached out with the dissolution of hemimorphite. The leaching progress of hemimorphite was impeded as silica reach saturation rapidly. The precipitation of silica from the lixivium may be a factor which has an effect on the extraction percentage of zinc.

3.3. Effect of NH_4Cl Concentration

The effect of NH_4Cl concentration on the extraction percentage of zinc was studied. It is shown that the extraction percentage of zinc was increased

significantly from 37 % to 72 % with an increase in NH_4Cl concentration from 4 to 6 mol/L (Fig. 5). A further increase in the NH_4Cl concentration in the range from 5.5 to 6.0 mol/L did not noticeably affect the extraction percentage of zinc. The equipment will corrode more easily at higher Cl^- concentration. Hence, an NH_4Cl concentration of 5.5 mol/L was chosen as an optimum.

3.4. Effect of Time

The effect of time on the extraction percentage of zinc was examined. It was shown that the extraction percentage of zinc was increased from 83 % to 95 % with an increase in the reaction time from 0.5 to 3.5 h (Fig. 6). The extraction percentage of zinc did not increase significantly above 3 h reaction time. For subsequent reactions the reaction time was kept to 3 h.

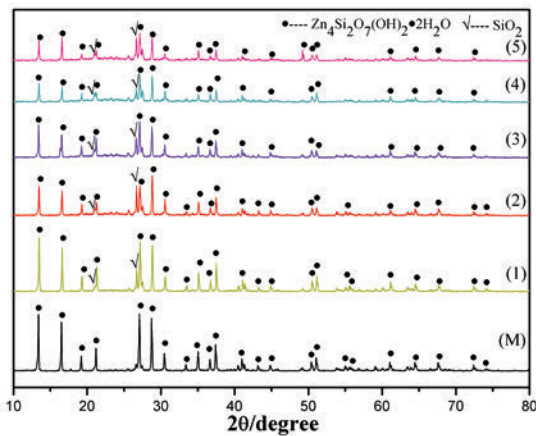


Figure 3. X-ray diffraction pattern of hemimorphite sample and residue: (M) hemimorphite sample; (1), (2), (3), (4), (5) leached under 120 °C, 130 °C, 140 °C, 150 °C, 160 °C respectively

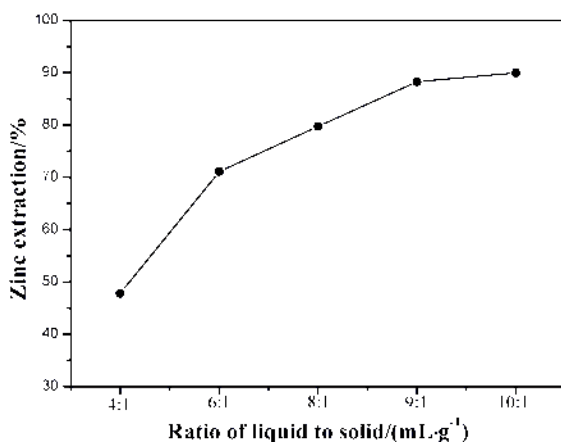


Figure 4. Effect of ratio of liquid to solid on zinc extraction: agitation speed 400 r/min, concentration of NH_4Cl 5.5 mol/L and temperature 140 °C at reaction time 2h

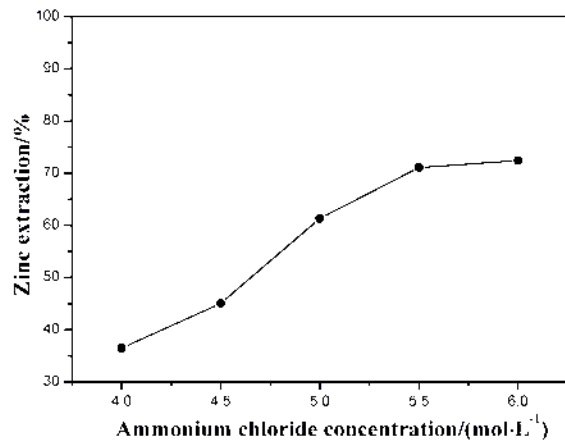


Figure 5. Effect of ammonium chloride concentration on zinc extraction: agitation speed 400r/min, temperature 140 °C and liquid/solid ratio(L/S) 6m L/g at reaction time 2h

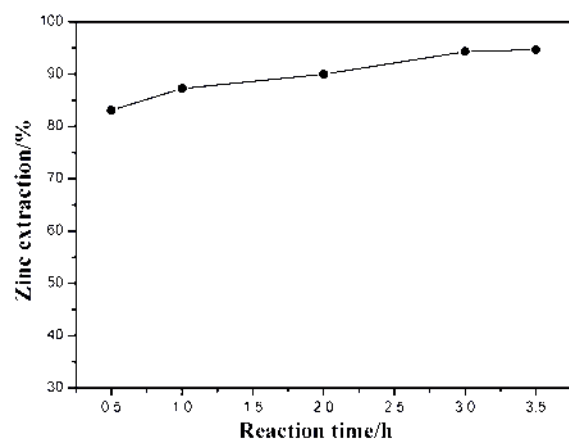


Figure 6. Effect of reaction time on zinc extraction: agitation speed 400 r/min, concentration of NH_4Cl 5.5 mol/L and L/S 10 mL/g at temperature 140 °C

3.5. Comprehensive Experiments

The NH_4Cl concentration, agitation speed, L/S, time, and temperature were kept constant at 5.5 mol/L, 400 r/min, 9 mL/g, 3h, and 160 °C, respectively. Four parallel experiments were carried out. The concentrations of zinc in the solution after the leaching process are 55.42, 55.92, 55.95, and 55.09 g/L, respectively. The average concentration of zinc is 55.88g /L. The results indicated a small variation in the extraction percentage of 97.72 %, 97.89 %, 97.99 %, and 97.68 %. The average leaching yield of zinc was 97.82 %. The zinc remained in residue may be ZnFe_2O_4 or ZnS .

The XRD pattern of the residue in the comprehensive experiment is presented in Fig. 7. The diffraction peak of $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ disappeared. The diffraction peak of SiO_2 is the primary peak and the faint peak at $2\Theta=25^\circ$ which is thought to be the amorphous is not obvious, but the sharp peak appeared obviously. Yang Shenghai etc studied the leaching kinetics of zinc silicate in ammonium chloride solution and found that SiO_2 is the main phase in the residue under 105 °C with XRD pattern analysis [26]. H_4SiO_4 can be transformed spontaneously to SiO_2 under high temperature and improving temperature will make the conversion of H_4SiO_4 into SiO_2 easier to occur. It can be seen that Si

was transformed into SiO_2 in this study. The infrared spectrum of hemimorphite before leaching and the leaching residue in the comprehensive experiment are shown in Fig. 8, curve (1). Both the band at 791.31 cm^{-1} and 950 cm^{-1} which are used to judge the existence of $\text{SiO}_2 \cdot \text{H}_2\text{O}$ are not found [19, 27]. The infrared band observed at 799.15 cm^{-1} is the characteristic infrared band of minerals of the quartz group. The result of the X-ray fluorescence (XRF) analysis of the residue is presented in Table 3. The average molar ratio of O to Si in the comprehensive experiments is 2.005. After a comprehensive analysis of XRD, Infrared spectrum (IR) and XRF, it would seem that Si was precipitated as quartz in the leaching process.

4. Conclusions

The leaching results showed that zinc can be extracted effectively from hemimorphite in a neutral solution at high temperature. The negative values of $\Delta_r G_m^\theta$ begin to appear around 120 °C. The tendency of dehydration of silica gel is significantly enhanced with increasing temperature. The following optimized leaching conditions were obtained: stirrer speed 400r/min, NH_4Cl concentration 5.5M, L/S ratio 9mL/g at 160 °C for 3h. The extraction percentage of zinc was 97.82% under the optimum experimental conditions. The results of XRD, IR, XRF analysis

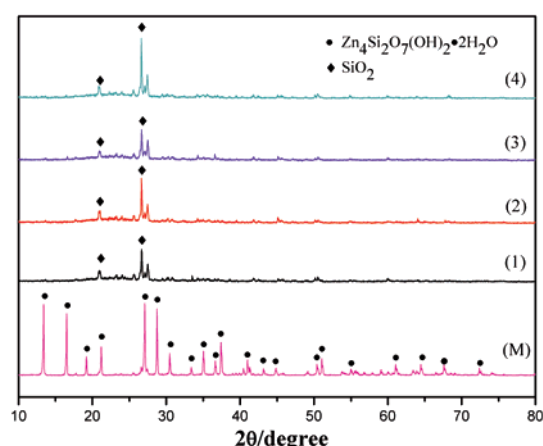


Figure 7. X-ray diffraction pattern of hemimorphite sample and residue: (M) hemimorphite sample; (1), (2), (3), (4) residue of four parallel experiments, respectively

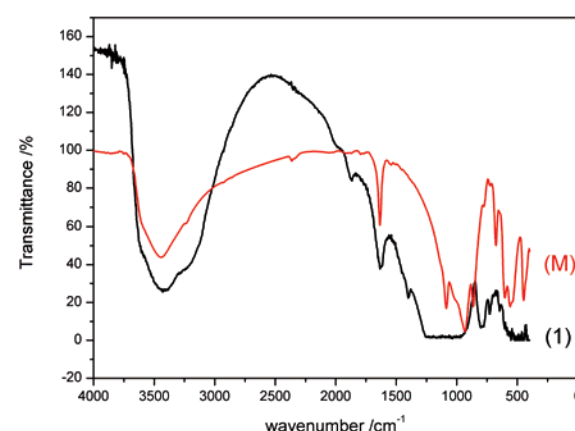


Figure 8. FTIR spectra for material sample and residue: (M) hemimorphite sample (1) mixing residue of four parallel experiments

Table 3. Result of X-ray fluorescence analysis of the residue in comprehensive experiments (wt)%

sample	O	Zn	Si	Mg	Ca	Al	Fe	Cu	Pb	Cl
1	44.91	2.32	40.95	0.62	0.06	2.53	3.01	0.05	0.74	0.57
2	46.61	2.15	39.95	0.57	0.04	2.47	2.9	0.05	0.75	0.64
3	47.29	2.06	39.79	0.59	0.06	2.47	2.78	0.06	0.69	0.43
4	45.59	2.34	40.79	0.59	0.04	2.49	2.94	0.06	0.73	0.58

showed that the silicone gel was converted to quartz and remained in the residue.

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References

- [1] W. Q. Qin, W. Z. Li, Z. Y. Lan, et al., Miner. Eng., 20 (7) (2007) 694-700.
- [2] I. M. Ahmed, A. A. Nayl, J. A. Daoud, J. Saudi Chem. Soc., 20 (2016) 280-285.
- [3] A. H. N. Kashani, F. Rashchi, Min. Eng., 21 (12-14) (2008) 967-972.
- [4] Y. D. Zhang, Y. X. Hua, X. B. Gao, Hydrometallurgy, 166 (2016) 16-21.
- [5] X. Wang, C. Srinivasakannan, X. H. Duan, et al., Sep. Purif. Technol., 115(2) (2013) 66-72.
- [6] B. Terry, A. J. Monhemius, Metall. Mater. Trans. B, 14 (3) (1983) 335-346.
- [7] M. G. Bodas, Hydrometallurgy, 40 (1-2) (1996) 37-49.
- [8] I. G. Matthew, D. Elsner, Metall. Trans. B, 8 (1) (1977) 73-83.
- [9] M. O. Fabiano, S. Pablo, P. Rodrigo, et al., Hydrometallurgy, 102 (1-4) (2010) 43-49.
- [10] A. Chen, Z. W. Zhao, X. Jia, Hydrometallurgy, 97(3-4) (2009) 228-232.
- [11] Z. Zhao, S. Long A. Chen, et al., Hydrometallurgy, 99(3) (2009) 255-258.
- [12] S. Rao, D. C. Zhang, T. Z. Yang, et al., Hydrometallurgy, 169 (2017) 508-514.
- [13] T. G. Harvey, Min. Process. Extr. M. Rev., 27 (4) (2006) 231-279.
- [14] C. A. Nogueira, F. Margarido, Hydrometallurgy, 157 (2015) 13-21.
- [15] S. Amer, A. Luis, Rev. Meta. Madrid., 31 (6) (1995) 351-360.
- [16] S. A. Mitra, G. M. Acosta, J. Khan, et al., J. Environ. Sci. Health, A32 (2) (1997) 497-515.
- [17] Z. Liu, Z. Liu, Q. Li, et al., Hydrometallurgy, 125-126 (2012) 137-143.
- [18] Z. Ding, Z. Yin, H.P. Hu, et al., Hydrometallurgy, 104 (2) (2010) 201-206.
- [19] Z. Yin, Z. Ding, H. P. Hu, et al., Hydrometallurgy, 103 (1-4) (2010) 215-220.
- [20] Z. Liu, Z. Liu, Q. Li, et al., Hydrometallurgy, 125-126 (2012) 50-54.
- [21] S. He, J. Wang, J. Yan, Hydrometallurgy, 108 (3-4) (2011) 171-176.
- [22] H. Xu, C. Wei, C. Li, et al., Hydrometallurgy, 105 (1-2) (2010) 186-190.
- [23] P. Makreski, G. Jovanovski, B. Kaitner, Vib. Spectrosc., 44 (1) (2007) 162-170.
- [24] A. Roine, HSC Chemistry Ver.6.0 [CP]. Pori: Outokumpu Research Oy, 2006.
- [25] X. Yin, C. Q. Liu, Q. Y. Chen, et al., J. Cent. South Univ. T., 43 (2012) 2054-2058.
- [26] S. H. Yang, H. Li, Y. W. Sun, et al., T. Nonferr. Metal. Soc. 26 (6) (2016) 1688-1695.
- [27] V.C. Farmer, The Infrared Spectra of Minerals. Science Press., Beijing, 1982 P. 289.

LUŽENJE HEMIMORFITA U NEUTRALNOM RASTVORU NA VISOKOJ TEMPERATURI

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Apstrakt

Pod različitim eksperimentalnim uslovima istraživano je ponašanje hemimorfita pri luženju u neutralnom rastvoru ($\text{NH}_4^+ - \text{Cl}^- / \text{H}_2\text{O}$) na visokoj temperaturi ($T > 100^\circ\text{C}$). Termodinamički proračuni ukazuju na to da je tendencija dehidratacije silikagela značajno povećana sa povećanjem temperature. Pokazano je da su veća temperatura, koncentracija amonijum hlorida ili L/S odnos rezultirali većom efikasnošću luženja. Postignuti su sledeći optimizirani uslovi luženja: brzina mešalice 400r/min, koncentracija NH_4Cl 5.5M, L/S odnos 9mL/g, pri temperaturi od 160°C u trajanju od 3h. Pod ovim optimiziranim uslovima, prosečan prinos cinka tokom luženja bio je 97.82%. Silicijum je pretvoren u kvarc i ostao je u talogu. Ovaj proces se može koristiti za uklanjanje vlemita i hemimorfita jer to rešava problem dehidratacije silikagela.

ključne reči: Luženje pod pritiskom; Amonijum hlorid; Hemimorfit; Silikagel

