Leaching of Hemimorphite in Neutral Solution at High Temperature

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Abstract: The leaching behavior of hemimorphite in neutral solution (NH₄⁺-Cl–H₂O) was investigated at high temperature (T > 100 °C) under a range of experimental conditions. Thermodynamic calculations indicate that the tendency of dehydration of silica gel is significantly enhanced with increasing temperature. It is 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, NH₄Cl 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
Zinc is one of the most commonly used non-ferrous metal after aluminum and copper as its consumption in galvanizing and battery manufacturing industries. Currently, zinc sulfide ores are the primary material for the zinc extraction process. With declining of global reserves of zinc sulfides ores as well as new government mandated sulphur dioxide and particulate emission, extensive investigations have been turned to the treatment of zinc oxide ores by hydrometallurgical and pyrometallurgical [1].

Hydrometallurgical process is used to dispose various of zinc oxide ores, such as zincite(ZnO), smithsonite (ZnCO₃), hydrozincite (Zn₅(CO₃)₂(OH)₆), willemite (Zn₂SiO₄), zinccsilite (Zn₃Si₆O₁₆(OH)₂·4H₂O) and hemimorphite (Zn₄Si₂O₇(OH)₂·H₂O) [2,3]. Sulfuric acid is the most commonly used lixiviant in zinc hydrometallurgical process [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. Much work has been done to precipitate silica effectively and economically. Matthew and Elsner (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 industrial applications are still very difficult.

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 mechanochemical 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 are 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 its low cost, low corrosivity and low toxicity. Ions such as \( \text{Zn(II)}, \text{Cu(II)}, \text{Ni(II)} \) and \( \text{Co(II)} \) form strong ammonia complexes and increase their solubility in ammoniacal solution, while other metals, such as \( \text{Fe}, \text{Pb}, \text{Si}, \text{Ca} \) and \( \text{Mg} \), do not form complexes under the same conditions and precipitate as oxides \([15,16]\). Cementation or solvent extraction can be used to purify the lixivium.

Many investigations show that \( \text{ZnO} \) 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 \([17,18]\). So routine leaching is hard to be practiced in industrial applications. Hemimorphite is one kind of zinc oxide ores 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, etc. studied the dissolution of hemimorphite in ammonia-ammonium chloride solution at 25°C. They find that the hemimorphite was completely dissolved in ammoniacal solution when the time, liquid/solid ratio and temperature were 1 month, 100/1 and 25°C and the residue is characteristic of \( \text{SiO}_2 \cdot n\text{H}_2\text{O} \) \([19]\) and the coagulation and precipitation speed of \( \text{SiO}_2 \cdot n\text{H}_2\text{O} \) is very slow as the solution got close to neutral. Zhiyong Liu, etc. studied the dissolution of hemimorphite in ammonia-ammonium sulfate solution. They find that the residue was characteristic of \( \text{H}_2\text{Si}_2\text{O}_5 \) or \( \text{SiO}_2 \) and the extraction percentage of zinc reached 95% when the time, liquid/solid ratio and 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 also has 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 for studying a more efficient zinc leaching from hemimorphite process.

2. Materials and Methods

2.1. Materials

The hemimorphite (a gem-grade ore) obtained from Yunnan Province in China. The hemimorphite sample was ground to a powder of less than 106 μm. The mineralogical analysis result of hemimorphite is presented in Table 1. The infrared spectrum of hemimorphite before leached 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 leached is presented by Fig. 3, pattern (M).

2.2. Experimental Setup and Procedure.

Leaching experiments were carried out in a 2L autoclave. Temperature and agitation speed were controlled with a PID controller. Gas was not admitted into the autoclave and the pressure of all experiments were the saturated vapor pressure of the slurry under each temperature. Hemimorphite and NH₄Cl 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 agitation speed on the extraction percentage of zinc. Experiments were carried out at temperature from 120 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 NH₄Cl solution and dried at 60°C. The comprehensive was repeated four times at optimized leaching conditions (stirrer speed 400 r/min, NH₄Cl concentration 5.5M, L/S ratio 9mL/g at 160°C for 3h). The zinc extraction was determined by analyzing for zinc in residue by EDTA titration. The mineralogical composition of hemimorphite were 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-6700 instrument (Thermo Nicolet Corporation, USA) with KBr.

Table 1. Mineralogical composition of hemimorphite (wt)%.

| Phase          | ZnSO₄ | Zn₄Si₂O₇(OH)₂·H₂O | ZnS   | ZnFe₂O₄ |
|----------------|-------|-------------------|-------|---------|
| Zn%            | 0.19  | 99.20             | 0.47  | 0.14    |

3. Results and Discussion

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

Stage 1: dissolution of hemimorphite
Table 2. Reaction equation and $\Delta G_m^0$ (25 °C) of hemimorphite dissolution (kJ·mol$^{-1}$).

| Reaction equation                                                                 | $\Delta G_m^0$ (kJ·mol$^{-1}$) |
|-----------------------------------------------------------------------------------|---------------------------------|
| $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}+ (4-4n)\text{H}^++4n\text{NH}_4^+ = 4\text{Zn(NH}_3)_2^{2+}$+2H$_4$SiO$_4$+2H$_2$O | -269.708                        |
| $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}+8\text{NH}_4^+ = 4\text{Zn(NH}_3)_2^{2+}$+2H$_4$SiO$_4$+2H$_2$O | -115.595                        |
| $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}+12\text{NH}_4^+ = 4\text{Zn(NH}_3)_2^{2+}$+2H$_4$SiO$_4$+2H$_2$O+4H$^+$ | 37.375                           |
| $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}+16\text{NH}_4^+ = 4\text{Zn(NH}_3)_2^{2+}$+2H$_4$SiO$_4$+2H$_2$O+8H$^+$ | 197.882                          |
| $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}+4\text{NH}_4^+ + 12\text{Cl}^- + 4\text{H}^+ = 4\text{Zn(NH}_3)\text{Cl}_4^{-}$+2H$_4$SiO$_4$+2H$_2$O | -287.290                         |

Stage 2: precipitation of silica gel

$$\text{H}_4\text{SiO}_4 \rightarrow \text{SiO}_2+2\text{H}_2\text{O}$$

Figure 1. $\Delta G_m^0$-Tplot of reaction (6).

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 silicon 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 is difficult to be destroyed. When the silicon gel is dehydrated into silica, the precipitation speed of the silicon can be greatly increased. Therefore, Dissolution of hemimorphite is
hindered as dehydration of silicon gel is very difficult at routine leaching process. The dehydration of silicon gel is the key to the dissolution of hemimorphite. The $\Delta rG_m^0$ of dehydration reaction of silica gel decreases with increasing temperature (Fig.1). Negative values begin to appear around 120 °C. The tendency of 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). 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 Zn$_4$Si$_2$O$_7$(OH)$_2$·H$_2$O and SiO$_2$. The diffraction peak intensity of Zn$_4$Si$_2$O$_7$(OH)$_2$·H$_2$O was weakened by improving temperature. The diffraction peak intensity of SiO$_2$ increased with improving temperature.

![Figure 2. Effect of temperature on zinc extraction: agitation speed 400r/min, concentration of NH$_4$Cl 5.5mol/L and liquid/solid ratio(L/S) 6mL/g at reaction time 2h.](image-url)
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.

3.2. Effect of L/S

The effect of L/S on the extraction percentage of zinc was investigated. It is 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 of infecting the extraction percentage of zinc.

Figure 4. Effect of ratio of liquid to solid on zinc extraction: agitation speed 400r/min, concentration of NH₄Cl 5.5mol/L and temperature 140°C at reaction time 2h.

3.3. Effect of NH₄Cl Concentration
The effect of \(\text{NH}_4\text{Cl}\) 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 \(\text{NH}_4\text{Cl}\) concentration from 4 to 6mol/L (Fig. 5). A further increase in the \(\text{NH}_4\text{Cl}\) concentration in the range from 5.5 to 6.0mol/L did not noticeably affect the extraction percentage of zinc. The equipment will be corroded more easily at higher Cl\(^-\) concentration. Hence, an \(\text{NH}_4\text{Cl}\) concentration of 5.5mol/L was chosen as optimum.

![Graph showing effect of ammonium chloride concentration on zinc extraction](image)

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

3.4. **Effect of Time**

The effect of time on the extraction percentage of zinc was examined. It is shown that the extraction percentage of zinc was increased from 83% to 95% with an increase in reaction time from 0.5 to 3.5h (Fig. 6). The extraction percentage of zinc did not increase significantly above 3h reaction time. For subsequent reactions the reaction time was kept to 3h.
Figure 6. Effect of reaction time on zinc extraction: agitation speed 400r/min, concentration of NH₄Cl 5.5mol/L and L/S 10mL/g at temperature 140℃.

3.5. Comprehensive Experiments

The NH₄Cl concentration, agitation speed, L/S, time and temperature were kept constant at 5.5mol/L, 400r/min, 9mL/g, 3h and 160℃, respectively. Four parallel experiments were carried out. The concentration of zinc in the solution after leaching process are 55.42, 55.92, 55.95 and 55.09g/L, respectively. The average concentration of zinc is 55.88g/L. 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 ZnFe₂O₄ or ZnS.

The XRD pattern of the residue in the comprehensive experiment is presented in Fig. 7. The diffraction peak of Zn₄Si₂O₇(OH)₂·H₂O is disappeared. The diffraction peak of SiO₂ is the primary peak and the faint peak at 2θ=25° which is thought to be the amorphous is not obvious, but the sharp peak is appeared obviously. Yang Shenghai. etc studied the Leaching kinetics of zinc silicate in ammonium chloride solution and found that SiO₂ is the main phase in the residue under 105℃ with XRD pattern analysis [26]. H₄SiO₄ can be transformed spontaneously to SiO₂ under high temperature and improving temperature will make the conversion of H₄SiO₄ into SiO₂ easier to occur. It can be seen that Si was transformed into SiO₂ in this study. The infrared spectrum of hemimorphite before leaching and the leaching residue in comprehensive experiment are shown by Fig. 8, curve (1). Both the band at 791.31 cm⁻¹ and 950 cm⁻¹ which are used to judge the existence of SiO₂·H₂O are not found [19,27]. The infrared band observed at 799.15 cm⁻¹ is the characterized infrared band of minerals of the quartz group. The result of X-ray fluorescence (XRF) analysis of the residue is presented in Table 3. The average molar ratio of O to Si in comprehensive experiments is 2.005. After
comprehensive analysis of XRD, Infrared spectrum (IR) and XRF we think that Si was precipitated as quartz in the leaching process.

**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 | 2.90 | 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 |

**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.

4. Conclusions

The leaching results showed that zinc can be extracted effectively from hemimorphite in neutral solution at high temperature. Negative values of $\Delta r G_m^0$ 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, NH₄Cl concentration 5.5M, L/S ratio 9mL/g at 160 °C for 3h. The extraction percentage of zinc was 97.82% under the optimum experiment condition. The results of XRD, IR, XRF analysis showed that the silicon gel was converted to quartz and remained in the residue.

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