

## Solubility of hemimorphite in ammonium sulfate solution at 25 °C

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**Abstract:** The solubility of natural hemimorphite in ammonium sulfate solution was measured by isothermal solution method at 25 °C and the dissolved residue of hemimorphite was investigated by X-ray powder diffraction (XRD), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) methods. The results show that zinc and silica in hemimorphite simultaneously dissolve in ammonium sulfate solution. The solubility of zinc in solution increases rapidly from 4.5381 mmol/kg in 0.5469 mol/kg ammonium sulfate solution to 11.5083 mmol/kg in 3.7038 mol/kg ammonium sulfate solution. The solubility of silica in solution increases slowly from 2.5509 mmol/kg in 0.5469 mol/kg ammonium sulfate solution to 7.2891 mmol/kg in 3.7038 mol/kg ammonium sulfate solution. The dissolved residue is the characteristic of hemimorphite  $Zn_4Si_2O_7(OH)_2 \cdot H_2O$  based on the results of the XRD, SEM and FTIR. Thus, no phase transition occurs in the dissolution process of hemimorphite in ammonium sulfate solution.

**Key words:** hemimorphite; ammonium sulfate; silicic acid; solubility

### 1 Introduction

As the primary source of zinc, oxidized zinc ores are the main source of zinc metal after nature sulfide ores are steadily getting depleted. Oxidized zinc ores are generally found in the form of silicates or carbonates such as smithsonite ( $ZnCO_3$ ), hydrozincite ( $2ZnCO_3 \cdot 3Zn(OH)_2$ ), zincite ( $ZnO$ ), willemite ( $Zn_2SiO_4$ ) and hemimorphite ( $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ ) in different regions of the world. As zinc silicate, hemimorphite is becoming increasingly attractive as one of most spread minerals of the oxidation zone of zinc-bearing ores.

Extensive work has been carried out on the treatment of zinc silicate ores by hydrometallurgical and pyrometallurgical methods. Sulfuric acid has been used to be a leaching reagent in hydrometallurgy process [1,2]. However, the high quantity of silica in zinc silicate ores results in the introduction of silica gel with Zn into the solution. The formation of silica gel adds difficulties to the filtration.

Recently, ammonia has attracted immense attention as a leaching agent for it has a number of inherent advantages due to its low cost, low toxicity, good complexes ability and easy regeneration. The first account of zinc extraction by ammoniacal leaching was

published as “the Schnabel Process” in 1880, which pre-dated the better-known applications of ammoniacal leaching to copper and nickel by 30 years or more [3]. Extensive works have studied on the application to a specific feedstock, mainly non-silica minerals such as zinc dust [4], high grade zinc ores containing smithsonite [5] and sphalerite [6].

Hemimorphite is a zinc silicate hydroxide hydrate mineral. Mineralogical studies show that hemimorphite is relatively refractory to leaching with sulfuric and with caustic soda [7–9]. To inhibit the leaching of silica, some processes were developed for extracting zinc from hemimorphite in sodium hydroxide solution [10,11]. However, these processes needed the extreme operating conditions such as high temperature, pressure and alkalinity or adding calcium oxide. Based on these works, we studied the dissolution kinetics of hemimorphite in ammonia/ammonium chloride systems [12,13]. The experimental data indicate that the ammonia/ammonium chloride system is appropriate for the leaching of complex zinc ores of both oxide and sulfide types. Unexpectedly, chloride ions can interact with most metal ions, and their use would introduce metal ion impurities into the solution. Furthermore, chloride ions can corrode equipment. To solve these problems, the system of ammonia/ammonium sulfate

was chose to leach hemimorphite [14]. The results show that zinc rapidly dissolved in ammonia/ ammonium sulfate system and the leaching efficiency of zinc reached 95%. Despite its extensive history and works, however, there is limited investigation about the thermodynamics of hemimorphite. In the present study, the solubility of hemimorphite in ammonium sulfate system at 25 °C was measured, and the dissolved residue was investigated in detail. The results may be used to provide the foundation data for studying the thermodynamic properties for zinc silicate ores in hydrometallurgy process.

## 2 Experimental

### 2.1 Experimental materials

Natural hemimorphite in this study was provided by Lanping Town in Yunnan Province in China. The hemimorphite sample was ground with an agate mortar and a pestle into 39  $\mu\text{m}$  and then 6 g of hemimorphite was put into 150 mL ammonium sulfate solution with different concentrations from 0.5469 to 3.7038 mol/kg. The flask was put into a temperature-controlled water bath set at (25 $\pm$ 0.05) °C and stirred for three months. Analytically pure ammonium sulfate was supplied by Sinopharm Chemical Reagent Company Limited. The concentrations of zinc and silica in solution were measured respectively by zinc-complexometric titration and silica–molybdenum blue methods. After dissolution, the residue was filtered and dried in an oven at 60 °C.

### 2.2 X-ray powder diffraction (XRD)

X-ray powder diffraction (XRD) measurement of the samples was determined by a Rigaku D/max 2550VB<sup>+</sup>18 kW powder diffractometer with a Cu/K $\alpha$  X-ray source at 40 kV and 300 mA. The XRD results were recorded with a scan rate of 0.075 (°)/s and sampling interval of 0.02° and compared with the PDF-4/Mineral powder diffraction file.

### 2.3 Fourier transform infrared spectroscopy (FTIR)

IR spectra analyses were obtained using an American Nicolet 6700 spectrometer with a smart endurance single-bounce diamond ATR cell. The samples were prepared using the KBr pellet method. The spectra over the 4000  $\text{cm}^{-1}$  to  $-400 \text{ cm}^{-1}$  range were obtained with a resolution of 4  $\text{cm}^{-1}$  and mirror velocity of 0.6329  $\text{cm/s}$ .

### 2.4 Scanning electron microscopy (SEM)

The surface morphology of crude and dissolved residues was examined by SEM using a Japan Jeol

JSM–6360 instrument at 20 kV. The grains mounted on a stub were coated with Au/Pd for SEM observation.

## 3 Results and discussion

### 3.1 Characterization of natural hemimorphite

The mineralogical data obtained from chemical phase are presented in Table 1. The mineralogical analysis shows that the sample contained hemimorphite (99.76 %) as the major oxide mineral, with only small amounts of zinc carbonate (0.19 %), franklinite (0.04 %) and trace amount of zinc sulfide and zinc sulfate. From the XRD analysis, the major minerals present in the ore are hemimorphite ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$ ), exhibiting sharp diffraction peaks; no other material diffraction peaks are observed, indicating a high level of purity for hemimorphite.

**Table 1** Mineralogical composition of hemimorphite

Phase	Zinc content/%	Occupancy/%
Hemimorphite	53.80	99.76
Franklinite	0.02	0.04
Zinc carbonate	0.10	0.19
Zinc sulfide	Trace amount	–
Zinc sulfate	Trace amount	–
Total Zn	53.93	100

The IR spectrum of hemimorphite is characterized in agreement with the spectrum in Ref. [15], very strong band around 3453.77  $\text{cm}^{-1}$  frequency side, together with an overtone of the bending  $\text{H}_2\text{O}$  mode around 1634  $\text{cm}^{-1}$ , which are main characteristic of —OH stretching region of hemimorphite. The bands at 1086.53 and 676.70  $\text{cm}^{-1}$  could be assigned as  $\nu_{\text{as}}(\text{Si}-\text{O}_b-\text{Si})$  modes ( $\text{O}_b$  denotes bridging oxygen). The remaining stretching vibrations of the  $\text{SiO}_3$  groups, manifested by the strong peaks at 933.35 and 864.75  $\text{cm}^{-1}$  are also positioned lower than  $\nu_{\text{as}}(\text{Si}-\text{O}_b-\text{Si})$  mode. The number of the bands of the lower-frequencies at 603.88, 557.20 and 448.63  $\text{cm}^{-1}$  should be attributed to the  $\delta(\text{Si}-\text{O}_b-\text{Si})$  modes.

The surface morphology of hemimorphite shows that the section of natural ore appears regular, blocky and smooth.

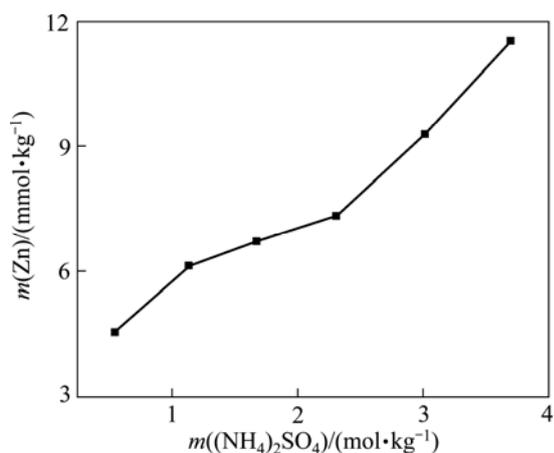
### 3.2 Solubility of hemimorphite in ammonium sulfate solution

Solubilities of hemimorphite in ammonium sulfate solution at (25 $\pm$ 0.05) °C are listed in Table 2. Figure 1 and Table 2 show that the solubility of zinc in the hemimorphite – ammonium sulfate – water system increases with the increase of ammonium sulfate

**Table 2** Solubility of hemimorphite in ammonium sulfate solution at (25±0.05) °C

Composition of liquid phase			pH <sup>b</sup>	pH <sup>a</sup>	Characteristic of solid phase
$m((\text{NH}_4)_2\text{SO}_4)/(\text{mol}\cdot\text{kg}^{-1})$	$m(\text{Zn})/(\text{mmol}\cdot\text{kg}^{-1})$	$m(\text{Si})/(\text{mmol}\cdot\text{kg}^{-1})$			
0.5469	4.5381	2.5509	5.14	7.15	$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$
1.1358	6.1125	4.2603	5.22	7.01	$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$
1.6776	6.7125	5.2180	5.31	6.99	$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$
2.3131	7.3276	5.8045	5.71	6.88	$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$
3.0135	9.2866	6.8547	5.48	6.85	$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$
3.7038	11.5083	7.2891	5.11	6.75	$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$

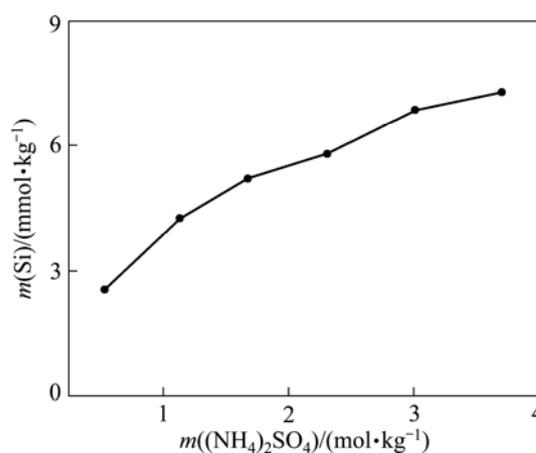
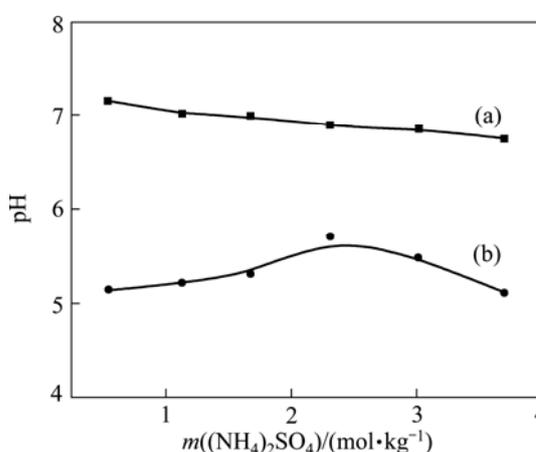
pH<sup>b</sup> represents pH of ammonium sulfate solution; pH<sup>a</sup> represents pH of hemimorphite–ammonium sulfate–water system.

**Fig. 1** Solubility of zinc in hemimorphite–ammonium sulfate–water system at (25±0.05) °C

concentration, which shows monotonically increasing from  $m(\text{Zn})=4.5381$  mmol/kg in 0.5469 mol/kg ammonium sulfate solution to  $m(\text{Zn})=11.5083$  mmol/kg in 3.7038 mol/kg ammonium sulfate solution. It is interpreted that the ammonia by ionization extracted zinc from the hemimorphite to form stable metal ammine complexes, leading to higher solubility.

Figure 2 displays the solubility of silicon in hemimorphite–ammonium sulfate–water system at (25±0.05) °C. It is easily shown that solubility of silicon in solution slowly increases with the ammonium sulfate concentration up to 3.7038 mol/kg. According to Ref. [16], the probable reason is that a protonation process of the bonds is involved between the divalent metals and oxygen, bonds between silicon and oxygen are relatively un-reactive and the silicate anion is probably released intact from the mineral surface as silicic acid.

Figure 3 reveals the pH of ammonium sulfate solution (curve (b)) and the pH of hemimorphite–ammonium sulfate–water system (curve (a)). It can be seen that the pH of hemimorphite–ammonium sulfate–water system is higher than the pH of ammonium sulfate solution. It may be interpreted that protonation processes were also involved in silicic acid, which always were in the dynamic balance depending on the pH. The

**Fig. 2** Solubility of Si in hemimorphite–ammonium sulfate–water system at (25±0.05) °C**Fig. 3** Comparison of pH of ammonium sulfate solution and system of hemimorphite–ammonium sulfate–water at (25±0.05) °C: (a) pH of hemimorphite–ammonium sulfate–water system; (b) pH of ammonium sulfate solution

polymerization of silicic acid to form a gel process is explained by two different mechanisms [17]: in alkaline and slightly acid solution, it is the condensation of  $\text{H}_4\text{SiO}_4$  and  $\text{H}_3\text{SiO}_4^-$ ; in the acid side, it is the polymerization of  $\text{H}_4\text{SiO}_4$  and  $\text{H}_5\text{SiO}_4^+$ . In this study, the range of pH is 5–8, in which the forms of silica in solution are mainly  $\text{H}_4\text{SiO}_4$  and  $\text{H}_3\text{SiO}_4^-$ . The polymerization mechanism in solution expressed by the

following reaction [18]:



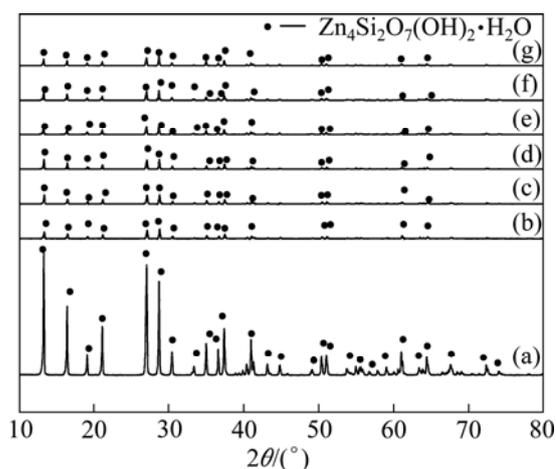
Combining Fig. 3 with the above reaction, the reason that pH value of hemimorphite–ammonium sulfate–water system is greater than the ammonium sulfate solution could be explained.

### 3.3 Characterizations of dissolved residues

The dissolved residue of hemimorphite in ammonium sulfate solutions was characterized via XRD, FTIR and SEM. The XRD, FTIR and SEM results of dissolved residues are shown in Figs. 4–6, respectively.

After hemimorphite dissolved in ammonium sulfate solution for 3 months, the intensity of the characteristic peak weakens and its peak height decreases as shown in Fig. 4. All the residues have the characteristic of  $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ .

A number of infrared bands of dissolved residues of hemimorphite in ammonium sulfate solutions are shown in Fig. 5. The characteristic bands appear at 449, 559, 603, 677, 864, 933, 1087, 1635 and  $3445 \text{ cm}^{-1}$ , which obviously coincide with the infrared spectra of hemimorphite [15]. According to Fig. 5, it can be seen that the characteristic O—H structural band in water at  $3453 \text{ cm}^{-1}$  appears red shift, which means the O—H group in water of hemimorphite tends to be unstable after hemimorphite dissolved in ammonium sulfate solutions. In contrast, the stretching vibrations of the — $\text{SiO}_3$  group manifested as strong peak at  $931 \text{ cm}^{-1}$  appears blue shift, which means that the — $\text{SiO}_3$  group of hemimorphite becomes more stable after hemimorphite was dissolved in ammonium sulfate solutions.

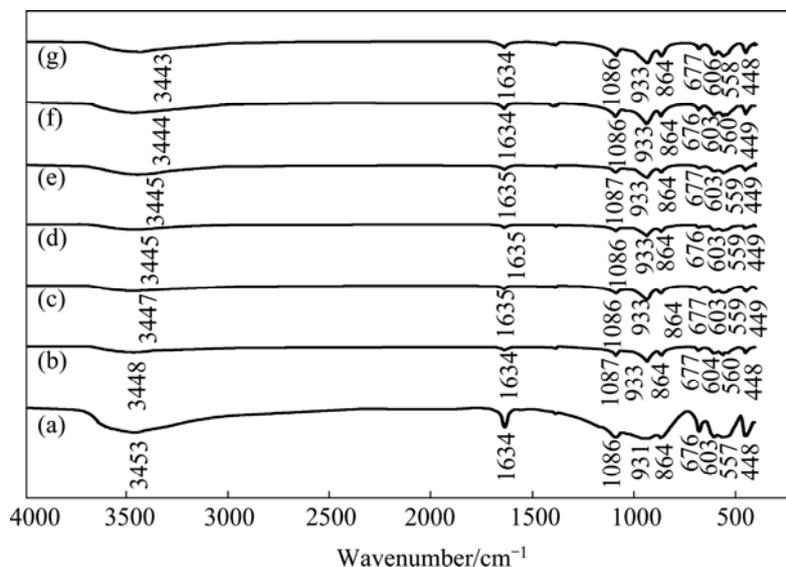


**Fig. 4** XTD patterns of hemimorphite samples: (a) Natural ore; (b) In 0.5469 mol/kg ammonium sulfate solution; (c) In 1.1358 mol/kg ammonium sulfate solution; (d) In 1.6776 mol/kg ammonium sulfate solution; (e) In 2.3131 mol/kg ammonium sulfate solution; (f) In 3.0135 mol/kg ammonium sulfate solution; (g) In 3.7038 mol/kg ammonium sulfate solution

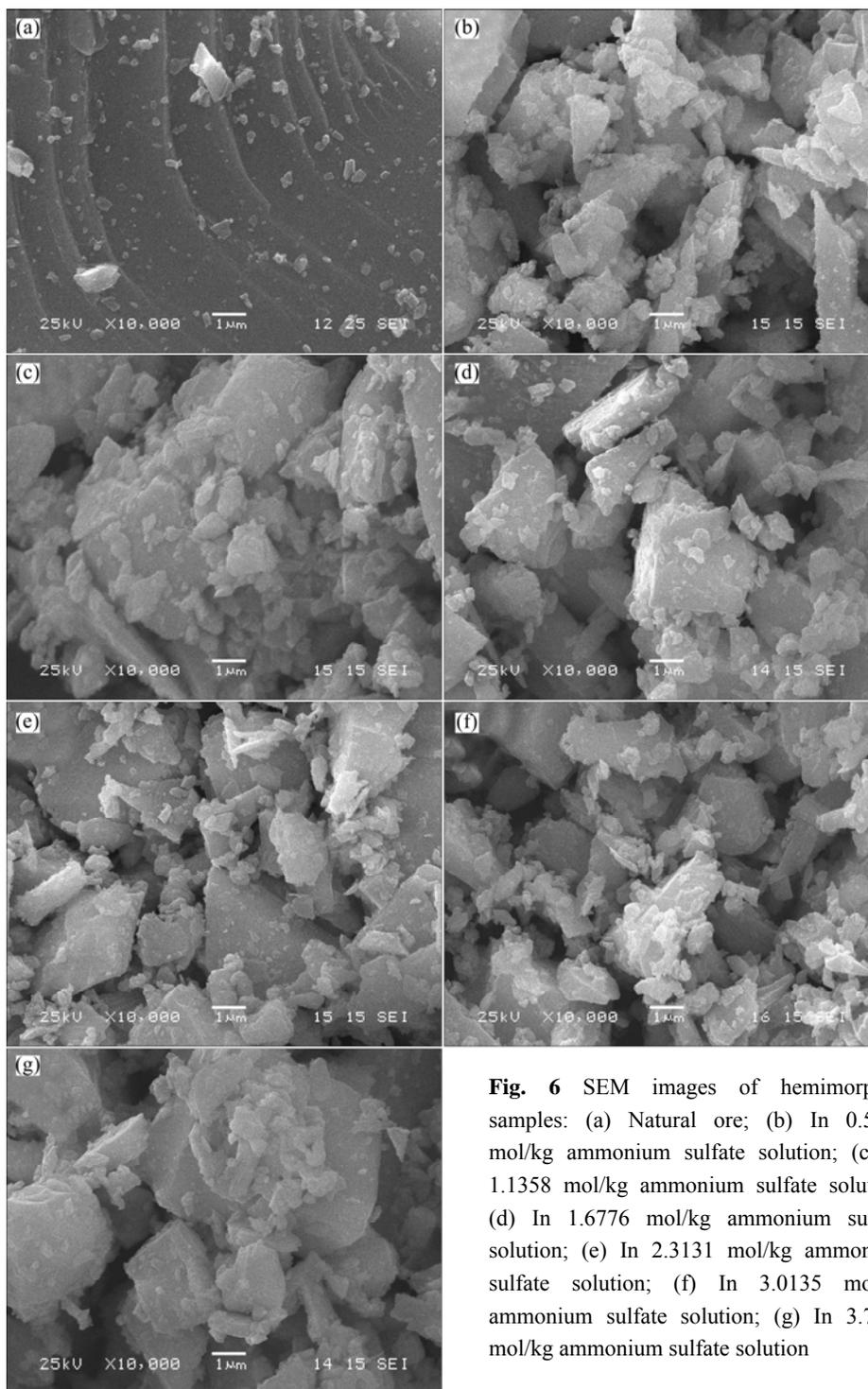
Figure 6 shows the morphologies of hemimorphite in several ammonium sulfate concentrations. It can be seen that the residue is corroded to be tiny and irregular particles after dissolving in ammonium sulfate.

### 4 Conclusions

The solubility of hemimorphite in ammonium sulfate solution was measured by isothermal solution method at  $(25 \pm 0.05) \text{ }^\circ\text{C}$ . The result reveals that the solubility of zinc increases with the increase of the ammonium sulfate concentration. It can be interpreted



**Fig. 5** IR spectra of hemimorphite samples: (a) Natural ore; (b) In 0.5469 mol/kg ammonium sulfate solution; (c) In 1.1358 mol/kg ammonium sulfate solution; (d) In 1.6776 mol/kg ammonium sulfate solution; (e) In 2.3131 mol/kg ammonium sulfate solution; (f) In 3.0135 mol/kg ammonium sulfate solution; (g) In 3.7038 mol/kg ammonium sulfate solution



**Fig. 6** SEM images of hemimorphite samples: (a) Natural ore; (b) In 0.5469 mol/kg ammonium sulfate solution; (c) In 1.1358 mol/kg ammonium sulfate solution; (d) In 1.6776 mol/kg ammonium sulfate solution; (e) In 2.3131 mol/kg ammonium sulfate solution; (f) In 3.0135 mol/kg ammonium sulfate solution; (g) In 3.7038 mol/kg ammonium sulfate solution

that the zinc was extracted from hemimorphite by ammonia to form stable zinc ammine complexes. The solubility of silicon also increases with the increase of ammonium sulfate concentration and the silicon in solution is mainly in forms of  $\text{H}_3\text{SiO}_4^-$  and  $\text{H}_4\text{SiO}_4$ . Data on the dissolution residue of hemimorphite in ammonium sulfate at  $(25 \pm 0.05)^\circ\text{C}$  was obtained by XRD, FTIR and SEM analysis. The results indicate that the residue is characteristic of  $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ .

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## 25 °C 时异极矿在硫酸铵溶液中的溶解度

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**摘要:** 采用等温法测定了 25 °C 时异极矿在硫酸铵溶液中的溶解度, 并利用 X 射线衍射、傅里叶转换红外光谱及扫描电子显微镜分析了溶解湿渣的性质。结果表明: 异极矿中的锌、硅同时溶解在硫酸铵溶液中且随着硫酸铵浓度的增加, 溶液中锌的浓度从 4.5381 mmol/kg 迅速增加到 11.5083 mmol/kg, 硅的浓度从 2.5509 mmol/kg 缓慢增加到 7.2891 mmol/kg。结合 X 射线衍射、傅里叶转换红外光谱以及扫描电子显微镜的结果, 证实了在溶解过程中无相变发生, 湿渣的组成仍为异极矿。

**关键词:** 异极矿; 硫酸铵; 硅酸; 溶解度

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