Leaching Kinetics of Hemimorphite in Ammonium Chloride Solution

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Abstract: The leaching kinetics of hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) in ammonium chloride solution was presented in detail. Effects of stirring speed (150–350 rpm), leaching temperature (75–108 °C), particle size of hemimorphite (45–150 μm), and the concentration of ammonium chloride (3.5–5.5 mol/L) on the zinc extraction rate were studied. The zinc extraction rate enhanced slightly with the increase in stirring speed, but increased significantly with an increase in the leaching temperature and ammonium chloride concentration. Zinc extraction was enhanced significantly in the first 60 min with decreasing particle size, but had little effect on the leaching process after 60 min. Scanning electron microscopy (SEM) analysis showed that some silica gel formed in the leaching process was not separated from the hemimorphite surface, but covered some of the active particle surface. The Elovich equation successfully described the leaching kinetics of hemimorphite in ammonium chloride solution with an apparent activation energy of 405.14 kJ/mol at temperatures of 75–90 °C and 239.61 kJ/mol at temperatures of 95–108 °C, which is characteristic for a chemically-controlled process. Silica gel is generated at temperatures of 75–90 °C and decomposed into silica at temperatures of 95–108 °C.

Keywords: hemimorphite; ammonium chloride; leaching kinetics; Elovich equation

1. Introduction

Zinc oxide ores are difficult to use, as these ores are difficult to separate by flotation. With the consumption of zinc sulfide resources and environmental protection requirements, studies are paying more and more attention to zinc oxide ores. Zinc oxide ores are generally found in the form of carbonates and silicates, such as smithsonite, hydrozincite, zincite, willemite, and hemimorphite, etc. [1,2]. High-silicon zinc ore (willemite and hemimorphite) resources are very difficult to use because silicon is hard to dispose of in the current process [3]. To treat high-silicon zinc ores, a large amount of research has been carried out in recent years in pyrometallurgical and hydrometallurgical methods. The hydrometallurgical process is more economically attractive, as the pyrometallurgical method suffers from high energy consumption and capital investment. Acids [4,5], sodium hydroxide [6,7], and ammoniacal solutions are often used as leaching agents [8,9].

Hemimorphite (one kind of high silicon zinc ore) is blended with smithsonite, sphalerite, and zincite in the oxidized zone. Hemimorphite has a high commercial value for zinc recovery from zinc oxidized ore, as zinc sulfide is consumed in large quantities.

The dissolution kinetics of high-silicon zinc ores have been researched in acid, alkali, and ammoniacal leaching systems in recent years. He et al. studied the dissolution kinetics of zinc silicate in acidic systems [10]. The research shows that the pressure leaching kinetics were controlled by diffusion, and the apparent activation energy was 16.39 kJ/mol. Santos et al. studied the dissolution kinetics of zinc silicate ores in sodium hydroxide solutions. The research showed that the leaching kinetics

were controlled by chemical reaction, and the apparent activation energy was 67.8 ± 9 kJ/mol [11]. Yang et al. studied the dissolution kinetics of zinc silicate in NH_4Cl solution. They found that the leaching kinetics were controlled by porous diffusion, and the apparent activation energy was 161.26 kJ/mol [12].

In recent years, the extraction of zinc from zinc oxide ores with ammoniacal solution is a hotspot in the zinc recovery process. The extraction process in ammonia—with or without ammonium—has been researched a great deal [13–16]. However, the leaching kinetics of hemimorphite in ammonium chloride have never been studied. Ammonium chloride solution is a nearly neutral solution, which makes the calcium, magnesium, silicon, iron, and other minor elements (such as As, Sb, and Bi) contained in the minerals remain in the residues in the leaching process [17]. The working environment is good, with little ammonia released to the air. To develop this efficient process, it is necessary to have a detailed knowledge of the leaching kinetics of hemimorphite in ammonium chloride. The effects of stirring speed, leaching temperature, particle size, and the concentration of NH_4Cl on zinc extraction were investigated in detail, and the kinetic model was discussed. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies were also conducted.

2. Material and Methods

2.1. Materials

The hemimorphite, from Yunnan Province in China, was ground and wet-sieved to yield a particle size distribution between 45 and 150 μm. The mineralogical composition of hemimorphite was analyzed by powder X-ray diffraction (XRD) (Figure 1) and chemical methods. The mineralogical composition is presented in Table 1. Analytical-grade ammonium chloride and deionized water were used in the experiments.
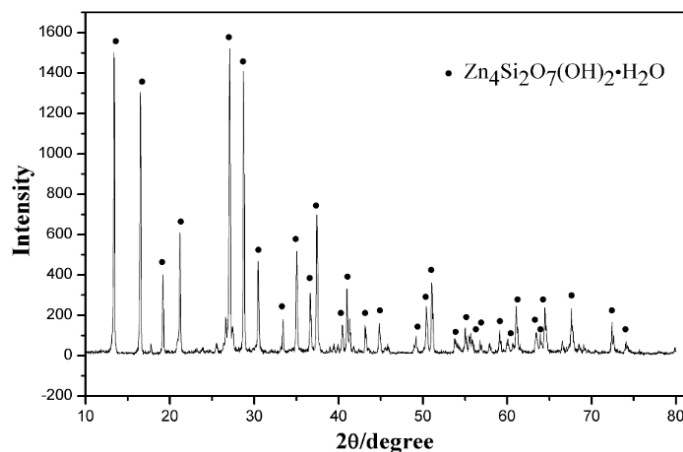

Figure 1. X-ray diffraction (XRD) patterns of the hemimorphite.

Table 1. Mineralogical analysis of hemimorphite.

Phase	$ZnSO_4$	$Zn_4Si_2O_7(OH)_2 \cdot H_2O$	ZnS	$ZnFe_2O_4$	Zn (total)
Content (%) [1]	0.08	41.90	0.20	0.06	42.24
Occupancy (%) [2]	0.19	99.20	0.47	0.14	100

[1] Content : $\frac{\text{the mass of zinc in each phase}}{\text{the mass of ore}} \times 100\%$; [2] Occupancy : $\frac{\text{the mass of zinc in each phase}}{\text{the mass of total zinc}} \times 100\%$.

2.2. Leaching Methods

The leaching experiments were carried out in a three-necked flask (2000 mL total volume) which was equipped with a mercury thermometer and a condenser device. The leaching temperature changed within ±0.5 degrees. A magnetic stirrer (DF-101S, Gongyi, China) was used to confuse the ore particles and the solution. The particle size distribution in the experiments was 45–61 μm, except for the particle size experiments. The leaching temperatures in the experiments were 75, 80, 85, 90, 95, 100, 104, and 108 °C, and the stirring speeds were 150, 200, 250, 300, and 350 rpm. The concentrations of NH_4Cl were 3.5, 4.0, 4.5, 5.0, and 5.5 mol/L. Typically, 5 g of solid was added into 1000 mL NH_4Cl solution. Five milliliters of slurry was withdrawn by the sampling port at a preset time and filtered quickly. Atomic absorption spectrometry (TAS-990, Persee, Peking, China) was used to analyze the concentration of zinc in solution.

The extraction percentage of zinc, α, is defined by:

$$\alpha = \frac{CV}{WM} \times 100\% \tag{1}$$

where *C*, *V*, *W*, and *M* are the zinc concentration in filtration, the volume (we assumed it to be constant), weight, and zinc content of the added material, respectively.

The hemimorphite and leaching residues were analyzed by XRD (TTRIII, Rigaku, Tokyo, Japan), SEM (JSM-6360LV, Jeol, Tokyo, Japan), and back-scattered electron micrographs (BEM, JSM-6360LV, Jeol, Tokyo, Japan).

3. Results

3.1. Effect of Leaching Temperature

The effect of the leaching temperature from 75 to 108 °C on zinc extraction is presented in Figure 2. This shows that elevated temperature had a noticeable enhanced effect on the percentage of extracted zinc. The increasing rates of zinc extraction at temperatures of 95–108 °C were quicker than at temperatures of 75–90 °C over 30 min. The leaching process changed obviously when the temperature was higher than 90 °C. Figure 3 shows the XRD patterns of the leaching residues obtained at different leaching temperatures. As the leaching temperature increased, the hemimorphite constantly dissolved and Si precipitated as SiO_2.
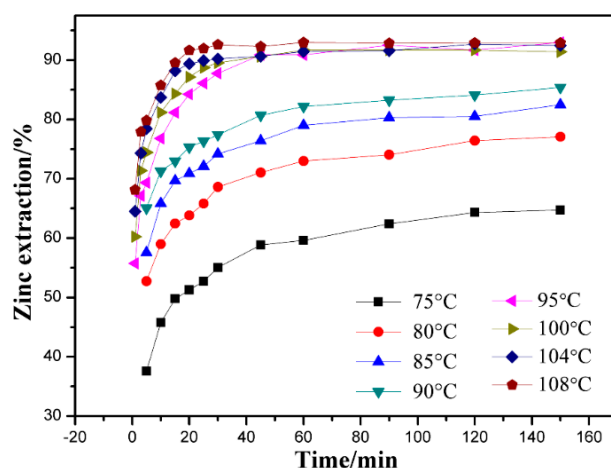

Figure 2. The effect of leaching temperature on zinc extraction (5.0 mol/L NH_4Cl; solid/liquid ratio, 5 g/L; stirring speed, 350 rpm; and particle size, 45–61 μm).
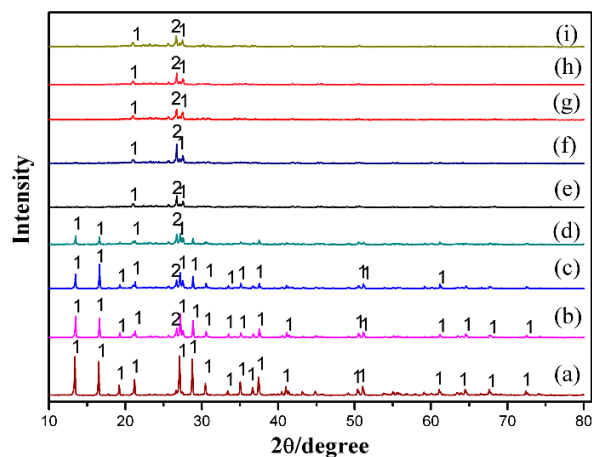
Figure 3. XRD patterns of the leaching residues at different temperatures. 1: $Zn_4Si_2O_7(OH)_2 \cdot H_2O$; 2: SiO_2; (**a**): material; (**b**): 75 °C; (**c**): 80 °C; (**d**): 85 °C; (**e**): 90 °C; (**f**): 95 °C; (**g**): 100 °C; (**h**): 104 °C; and (**i**): 108 °C.

3.2. Effect of Stirring Speed

Experiments were carried out using four stirring speeds of 150, 250, 300, and 350 rpm, respectively. The mass transfer can be enhanced by increasing the stirring speed. The results, as presented in Figure 4, show that the stirring speed had a small effect on zinc extraction. Therefore, mass transfer is not the main reason affecting the leaching process when the stirring speed is higher than 350 rpm. The stirring speed was kept at 350 rpm in other experiments, unless otherwise stated in this paper.
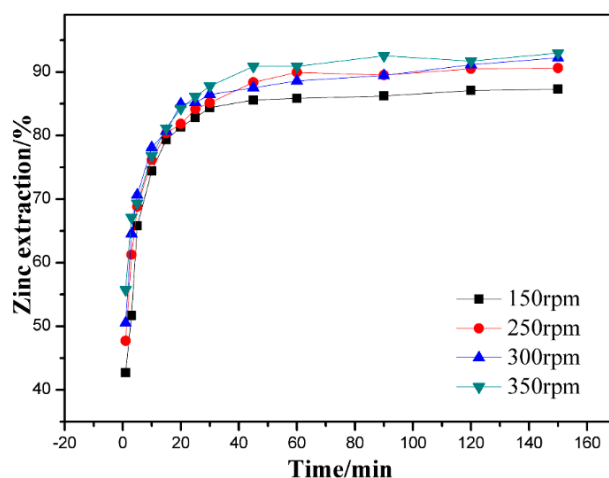

Figure 4. Effect of stirring speed on zinc extraction (5.0 mol/L NH_4Cl; solid/liquid ratio, 5 g/L; temperature, 95 °C; and particle size, 45–61 μm).

3.3. Effect of Ammonium Chloride Concentration

The effect of ammonium chloride concentration on zinc extraction is presented in Figure 5. This shows that the rate of zinc extraction increased significantly with the increase in the ammonium chloride concentration. The concentration of Zn^{2+} was very small, as $Zn(NH_3)_i^{2+}$ is the main species in the solution. This is one reason why zinc extraction was significantly affected by the ammonium chloride concentration. About 92.95% of zinc was extracted in 5.0 mol/L of ammonium chloride solution after 150 min, but only 47.28% of zinc was extracted in 3.5 mol/L of ammonium chloride solution.
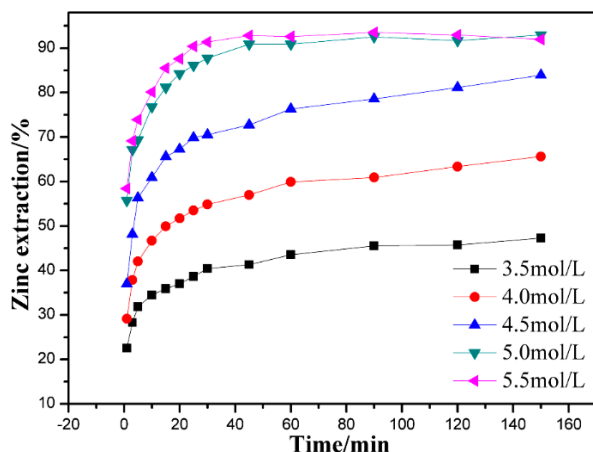
Figure 5. Effect of ammonia chloride concentration on zinc extraction (temperature, 95 °C; solid/liquid ratio, 5 g/L; stirring speed, 350 rpm; and particle size, 45–61 μm).

3.4. Effect of Particle Size

The effect of particle size on zinc extraction is presented in Figure 6. It shows that the decrease in particle size had a noticeably enhanced effect on the percentage of extracted zinc in 60 min. This is because decreasing the particle size improves the reaction area and surface activity. However, the particle size had a small effect on zinc extraction after 60 min.
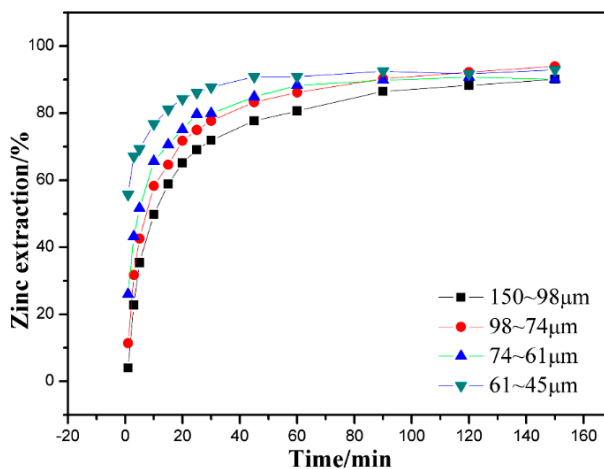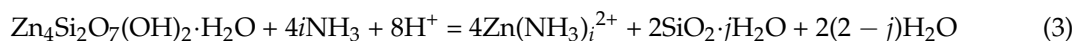

Figure 6. Effect of particle size on zinc extraction (5.0 mol/L NH$_4$Cl; solid/liquid ratio, 5 g/L; stirring speed, 350 rpm; and temperature, 95 °C).

3.5. Kinetic Discussion

The dissolution of hemimorphite in ammonium chloride solution may include vapor–fluid–solid three-phase reaction, as free NH$_3$ is an important reaction species. The main chemical reactions can expressed in Equations (2) and (3):

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \tag{2}$$

$$Zn_4Si_2O_7(OH)_2 \cdot H_2O + 4iNH_3 + 8H^+ = 4Zn(NH_3)_i^{2+} + 2SiO_2 \cdot jH_2O + 2(2-j)H_2O \tag{3}$$

The ammoniacal system shrinking core model is the most used mathematical model for ammonical leaching kinetics [18–20], but it cannot explain the leaching progress in this work. Figures 2, 3, 5 and 6

show that the zinc extraction rate is more than 50% after a few minutes, so a logarithmic equation is needed to describe the kinetics.

The empirical Elovich equation is used in this work. It is commonly used in chemisorption, but it also can describe leaching progress [21]. The Elovich equation can be expressed as:

$$d\alpha/dt = \delta\exp(-\beta\alpha) \tag{4}$$

where t is time; β and δ are constant; α is zinc extraction.

After integration and simplification, Equation (4) becomes:

$$\alpha = (1/\beta)\ln(\beta\delta) + (1/\beta)\ln t \tag{5}$$

Thus, it predicts a linear dependence of α with $\ln t$. The experimental data were linearly fitted with Equation (5), and the results are shown in Figures 7–9. The values of β and δ can be calculated by the slope and intercept of the lines in Figures 7–9, which are used to predict α using Equation (5). Figure 10 presents the predicted α (line) against the experimental α (points) at different temperatures, where they fit very well with each other. Similar plots were also calculated for other variables (Figures 7–9), and they also fit equally well, which strongly supports the application of the Elovich equation to describe the dissolution kinetics of hemimorphite in ammonium chloride solution.
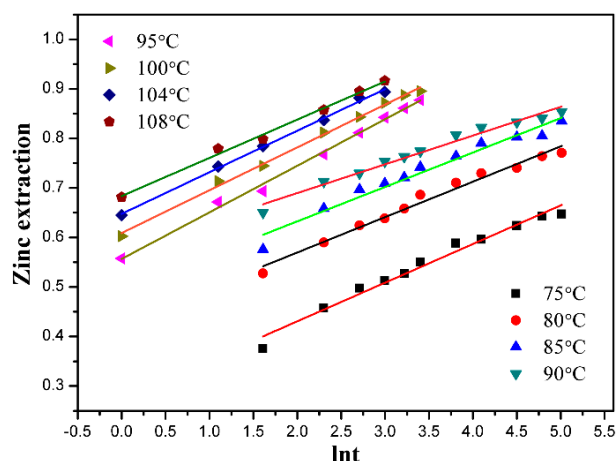

Figure 7. Plot of zinc extraction versus ln$t$ for different temperature.
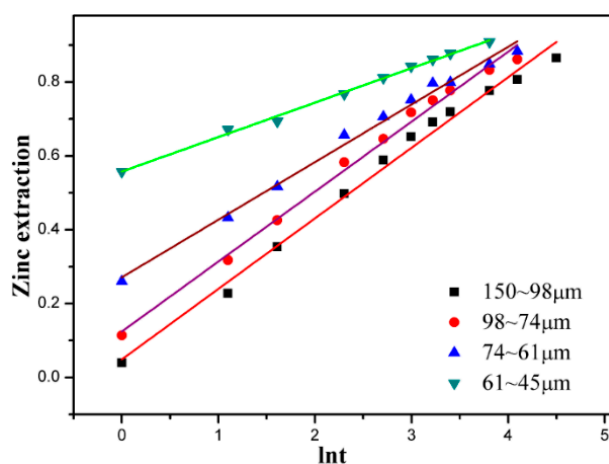

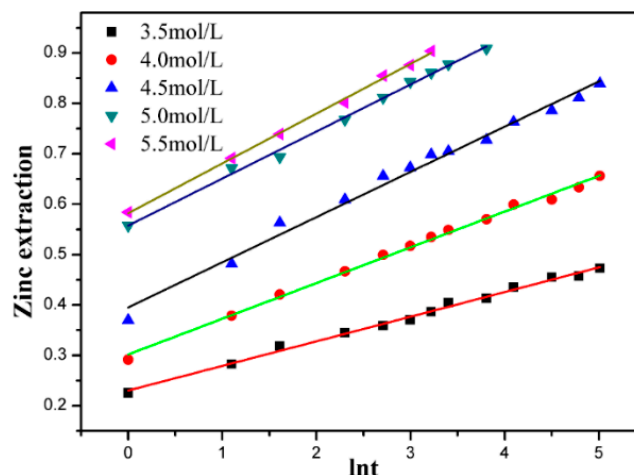**Figure 8.** Plot of zinc extraction versus ln$t$ for different particle sizes.

Figure 9. Plot of zinc extraction versus ln$t$ for different NH_4Cl concentrations.
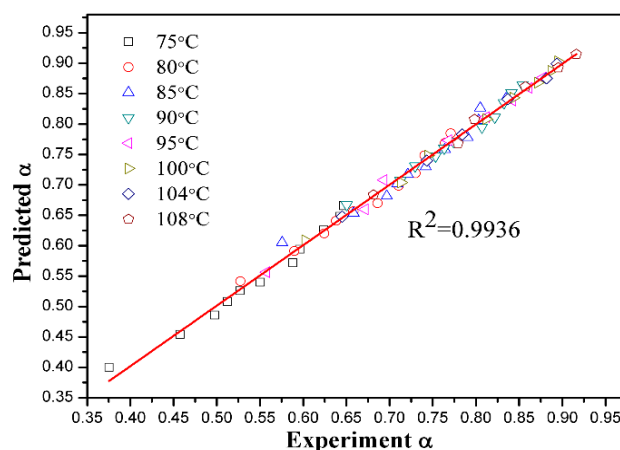

Figure 10. Predicted α against experimental α.

The Arrhenius equation is used to calculate the apparent activation energy to explain the effect of temperature on the leaching process. The Arrhenius equation is as follows:

$$\delta = C\theta \exp(-E_a/RT) \tag{6}$$

where E_a is the initial apparent activation energy; C and θ are constants relating to the surface area and the number of active sites per unit area; R is the gas constant; and T is the absolute temperature.

The value of $(-E_a/R)$ is the slope of curve of lnδ against $1/T$, as shown in Figure 11. After calculation, the value of E_a was 405.14 kJ/mol at a temperature of 75–90 °C and 239.61 kJ/mol at a temperature of 95–108 °C. Chemical control appears to represent the mechanism of hemimorphite leaching kinetics with ammonium chloride.
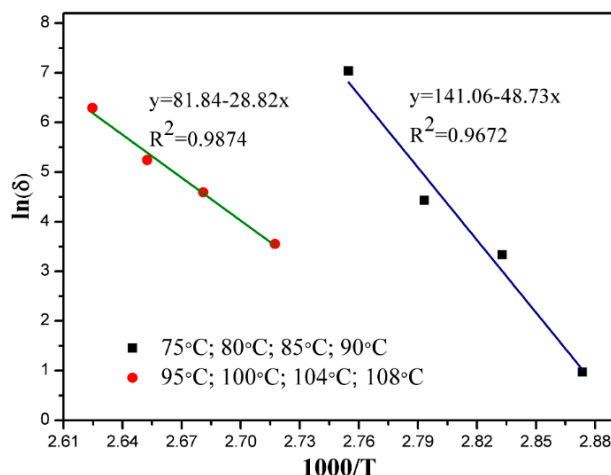
Figure 11. Arrhenius curve for the dissolution of hemimorphite.

3.6. Characterization of the Leaching Residues

Figure 12a,b shows the SEM images of hemimorphite and the leaching residue. Figure 12b shows that the silica—one kind of product in the leaching process—was adsorbed on the certain surface of the hemimorphite particle, blocking the surface-active sites and reducing the reactivity. Figure 12c,d are the BEM of hemimorphite and the leaching residue (polished section), which show smooth and flat profiles. The reticulate structure did not appear, and no reaction product layer occurred on the particle surface.
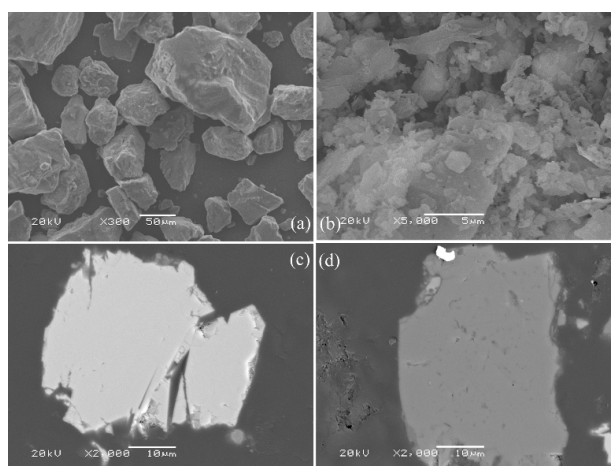

Figure 12. Scanning electron microscopy (SEM) and back-scattered electron micrograph (BEM, polished section) of hemimorphite and the leaching residue. (**a**) material, (**b**) temperature, 100 °C; solid/liquid ratio, 5 g/L; stirring speed, 350 rpm, (**c**) material, (**d**) temperature, 100 °C; solid/liquid ratio, 5 g/L; stirring speed, 350 rpm; zinc extraction rate 93%.

Figure 13 shows the Fourier transform infrared (FT-IR) spectra of the hemimorphite and the leaching residues at different temperatures. Farmer and Wen et al. have shown that the IR spectra of quartz, tridymite, cristobalite, silica glass, and opal in the 1250 to 400 cm^{-1} range are similar [22,23]. Aside from the four-coordinated typical characteristic bands of SiO_2 at 1094, 800, and 470 cm^{-1}, the Si–O stretching vibration peak from the Si–OH groups of the newly-precipitated silica also appeared at 950 cm^{-1}, as shown in Figure 13b,c. However, increasing the temperature made the Si–OH groups polymerize and form Si–O–Si, and the characteristic bands disappear at 950 cm^{-1}, as shown in Figure 13d,e.
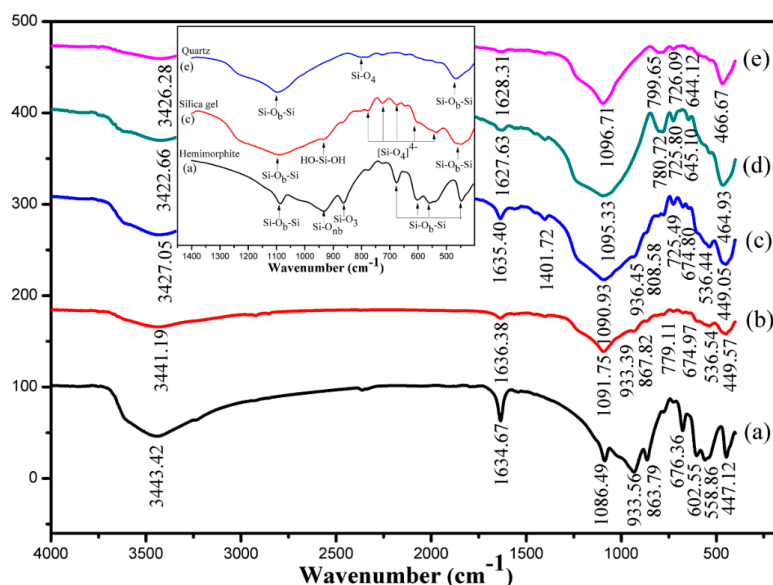
Figure 13. Fourier transform infrared (FT-IR) spectra of the hemimorphite and the residues. (**a**) Hemimorphite; (**b**) 75 °C; (**c**) 80 °C; (**d**) 100 °C; and (**e**) 108 °C.

Based on the above analysis, silica gel was generated at temperatures of 75–90 °C and decomposed into silica at temperatures of 95–108 °C. The silica gel is produced and adsorbed on the surface-active sites of the hemimorphite particles. This is the reason for the high apparent activation energy (405.14 kJ/mol) at temperatures of 75–90 °C. However, with the decomposition of silica gel at temperatures of 95–108 °C, the apparent activation energy reduced to 239.61 kJ/mol.

4. Conclusions

The main parameters for ammonical dissolution for hemimorphite are determined as stirring speed, temperature, particle size, and ammonium chloride concentration. The zinc extraction rate enhanced slightly with the increase in stirring speed, decrease in particle size, raising leaching temperature, and ammonium chloride concentration. The Elovich equation successfully describes the leaching kinetics of hemimorphite in ammonium chloride solution with an apparent activation energy of 405.14 kJ/mol at temperatures of 75–90 °C and 239.61 kJ/mol at temperatures of 95–108 °C, which is characteristic for a chemically-controlled process.

Author Contributions: Duoqiang Zhao, writing and data analysis, Shenhai Yang, data analysis and study design, Yongmin Chen, data analysis and collection, Chaobo Tang, literature search, Jing He, study design and figures, Hao Li, data collection.

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Shirin, E.; Fereshteh, R.; Sadrnezhaad, S.K. Hydrometallurgical treatment of tailings with high zinc content. *Hydrometallurgy* **2006**, *82*, 54–62.
2. Navidi Kashani, A.H.; Rashchi, F. Separation of oxidized zinc minerals from tailings: Influence of flotation reagents. *Miner. Eng.* **2008**, *21*, 967–972. [CrossRef]
3. Xu, H.S.; Wei, C.; Li, C.X.; Deng, Z.G.; Li, X.B. Sulfuric acid leaching of zinc silicate ore under pressure. *Hydrometallurgy* **2010**, *105*, 186–190. [CrossRef]
4. Souza, A.D.; Pina, P.S.; Lima, E.V.O.; Silva, C.A.; Leao, V.A. Kinetics of sulphuric acid leaching of a zinc silicate calcine. *Hydrometallurgy* **2007**, *89*, 337–345. [CrossRef]

5. Ahmed, I.M.; Nayl, A.A.; Daoud, J.A. Leaching and recovery of zinc and copper from brass slag by sulfuric acid. *J. Saudi Chem. Soc.* **2016**, *20*, 280–285. [CrossRef]

6. Chen, A.L.; Zhao, Z.W.; Jia, X.J.; Long, S.; Huo, G.S.; Chen, X.Y. Alkaline leaching Zn and its concomitant metals from refractory hemimorphite zinc oxide ore. *Hydrometallurgy* **2009**, *97*, 228–232. [CrossRef]

7. Zhao, Z.; Long, S.; Chen, A.; Huo, G.; Li, H.; Jia, X.; Chen, X. Mechanochemical leaching of refractory zinc silicate (hemimorphite) in alkaline solution. *Hydrometallurgy* **2009**, *99*, 255–258. [CrossRef]

8. Harvey, T.G. The hydrometallurgical extraction of zinc by ammonium carbonate: A review of the Schnabel process. *Miner. Process. Extr. Metall. Rev.* **2006**, *27*, 231–279. [CrossRef]

9. Rao, S.; Yang, T.Z.; Zhang, D.C.; Liu, W.F.; Chen, L. Leaching of low grade zinc oxide ores in NH$_4$Cl-NH$_3$ solution with nitrilotriacetic acid as complexing agents. *Hydrometallurgy* **2015**, *158*, 101–106. [CrossRef]

10. He, S.M.; Wang, J.K.; Yang, J.F. Pressure leaching of synthetic zinc silicate in sulfuric acid medium. *Hydrometallurgy* **2011**, *108*, 171–176. [CrossRef]

11. Santos, F.M.F.; Pina, P.S.; Porcaro, R.; Oliveira, V.A.; Silva, C.A.; Leão, V.A. The kinetics of zinc silicate leaching in sodium hydroxide. *Hydrometallurgy* **2010**, *102*, 43–49. [CrossRef]

12. Yang, S.H.; Li, H.; Sun, Y.W.; Chen, Y.M.; Tang, C.B.; He, J. Leaching kinetics of zinc silicate in ammonium chloride solution. *Trans. Nonferrous Met. Soc. China* **2016**, *26*, 1688–1695. [CrossRef]

13. Miki, T.; Chairaksa-Fujimoto, R.; Maruyama, K.; Nagasaka, T. Hydrometallurgical extraction of zinc from Cao treated EAF dust in ammonium chloride solution. *J. Hazard. Mater.* **2016**, *302*, 90–96. [CrossRef] [PubMed]

14. Nogueira, C.A.; Margarido, F. Selective process of zinc extraction from spent Zn-MnO$_2$ batteries by ammonium chloride leaching. *Hydrometallurgy* **2015**, *157*, 13–21. [CrossRef]

15. Tang, F.L.; Li, X.B.; Wei, C. Synergistic extraction of zinc from ammoniacal/ammonia sulfate solution by a mixture of β-diketone and 2-hydroxy-5-nonylacetophenone oxime. *Hydrometallurgy* **2016**, *162*, 42–48. [CrossRef]

16. Liu, Z.Y.; Liu, Z.H.; Li, Q.H.; Yang, T.Z.; Zhang, X. Leaching of hemimorphite in NH$_3$-(NH$_4$)$_2$SO$_4$-H$_2$O system and its mechanism. *Hydrometallurgy* **2012**, *8*, 137–143. [CrossRef]

17. Limpo, J.L.; Figueiredo, J.M.; Amer, S.; Luis, A. The CENIM-LNETI process: A new process for the hydrometallurgical treatment of complex sulphides in ammonium chloride solutions. *Hydrometallurgy* **1992**, *28*, 149–161. [CrossRef]

18. Alafara, A.B.; Ayo, F.B.; Daud, T.O.; Rafiu, B.B.; Folahan, A.A.; Abdul, G.G.A. Leaching kinetics of a Nigerian complex covellite ore by the ammonia-ammonium sulfate solution. *Korean J. Chem. Eng.* **2017**, *34*, 1133–1140.

19. Baba, A.A.; Ghosh, M.K.; Pradhan, S.R.; Rao, D.S.; Baral, A.; Adekola, F.A. Characterization and kinetic study on ammonia leaching of complex copper ore. *Trans. Nonferrous Met. Soc. China* **2014**, *24*, 1587–1595. [CrossRef]

20. Ekmekyapar, A.; Demirk1ran, N.; Kunkul, A.; Aktas, E. Leahcing of malachite ore in ammonium sulfate solutions and production of copper oxide. *Braz. J. Chem. Eng.* **2015**, *32*, 155–165. [CrossRef]

21. Ding, Z.Y.; Yin, Z.L.; Hu, H.P.; Chen, Q.Y. Dissolution kinetics of zinc silicate (hemimorphite) in ammoniacal solution. *Hydrometallurgy* **2010**, *104*, 201–206. [CrossRef]

22. Farmer, V.C. *The Infrared Spectra of Minerals*; Ying, Y.P., Wang, S.T., Li, C.G., Han, X.L., Li, Z., Li, Y.Q., Translators; Science Press: Beijing, China, 1982; p. 428.

23. Wen, L.; Liang, W.; Zhang, Z.; Huang, J. *The Infrared Spectroscopy of Minerals*; Chongqing University Press: Chongqing, China, 1989; p. 190.