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Selective Extraction of Zinc from Refractory Hemimorphite Using Iminodiacetic Acid as a Complexing Agent

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An environmentally friendly process for the selective extraction of zinc from refractory hemimorphite using iminodiacetic acid (H_2Ida) as a complexing agent was investigated. Thermodynamic simulations demonstrated that the partially dissociated protons and amino carboxylate anions synergistically affect the dissolution of hemimorphite. The experimental results were consistent with the theoretical analyses. Under optimal conditions, the leaching extraction of zinc was above 88% and that of iron was below 4%. Furthermore, the complexing agent could be recovered from the leaching solution at the isoelectric point by adding dilute sulfuric acid.

INTRODUCTION

Zinc is an important nonferrous metal that has been widely used to produce brass and zinc compounds.[1] Currently, zinc is mainly produced by hydrometallurgical processes using sphalerite as raw materials.[2] Nevertheless, with the rising demand for zinc in the industry, the grades of zinc sulfide ores have lowered significantly. Therefore, zinc oxide ores have been increasingly used as potential zinc resources in recent years.[3]

Leaching of zinc oxide ores using sulfuric acid is the most common method for the recovery of zinc.[4–7] Yet, this process is not selective, and alkaline gangue minerals such as $CaCO_3$, MgO, and Fe_2O_3, which are soluble in sulfuric acid solutions, make the purification process difficult.[1,5,8] Moreover, it may also lead to the formation of silica gel, causing a serious filtration problem.[9,10] To overcome these limitations, ammonia and sodium hydroxide have been proposed as leaching agents owing to their high selectivity.[11–17] Nonetheless, these leaching agents are more suitable for zinc carbonate minerals; the leaching extraction is relatively low for zinc silicate minerals.[11]

Recently, organic reagents have been explored to dissolve zinc oxide minerals and secondary resources.[18] Hursit et al.[19] studied the leaching of smithsonite in gluconic acid solutions. Compared with conventional acidic or alkaline leaching processes, it was possible to recover zinc directly in the form of available zinc gluconate compounds. Under optimal conditions, the leaching extraction of zinc was close to 100%. Steer et al.[20] used carboxylic acids and nonaqueous solvents as leaching agents to extract zinc from blast furnace dust slurry. The results indicated that the dissociated substituent group played a significant role in the zinc extraction, whereas the iron extraction was more dependent on the pH of the leaching solution. Yet, the previously mentioned studies mainly focus on the zinc carbonate minerals, which can be dissolved completely in ammoniacal solutions. There are hardly any reports on the leaching of refractory zinc silicate minerals.

The objective of the present work is to provide an alternative method for the dissolution of insoluble zinc silicate minerals. In this study, a novel complexing agent, iminodiacetic acid, is used to dissolve the refractory hemimorphite. The leaching mechanism is studied by using a thermodynamic model. In addition, the effects of the concentration of the complexing agent and the pH of the leaching solution on the dissolution efficiency of refractory hemimorphite are studied in detail. Finally, a method for the regeneration of the complexing agent is proposed.

EXPERIMENTAL

Materials and Methods

The material used in this study was a low-grade zinc oxide ore, obtained from Lanping city, Yunnan province of China. The contents (wt.%) of zinc and iron in the ore were analyzed quantitatively by titration using ethylenediaminetetraacetic acid (EDTA) and potassium dichromate, and they were estimated as 9.23% and 6.53%, respectively. The mineralogical composition of the material sample was determined by chemical phase analysis.[21] The result is shown in Table I, indicating that hemimorphite is the main phase of zinc in the ore.

To study the mechanism of the leaching process, the effects of main influential factors, including the concentration of the leaching agent and the pH of the leaching solution, on the leaching extraction of zinc were investigated in detail. The other leaching conditions were fixed as follows: leaching temperature 313 K, solid-to-liquid ratio 100 g/L, stirring speed 400 r/min, and leaching time 2 h. After the leaching process, the complexing agent was regenerated by adding dilute sulfuric acid.

Thermodynamic Model

As a result of a relatively high pH of the leaching solution, it is expected that silicon precipitates in the leaching residue in a more filterable silica phase. Therefore, the solubility equilibrium equation of hemimorphite is expressed as:

$$\begin{aligned} &Zn_4Si_2O_7(OH)_2 \cdot H_2O + 2H_2O \\ &\rightleftarrows 4Zn^{2+} + 8OH^- + 2SiO_2 \downarrow \end{aligned} \tag{1}$$

The solubility product constant (K_{sp}) was calculated using Outokumpu HSC Chemistry 6.0 and is expressed as:

$$K_{sp} = [Zn^{2+}][OH^-]^2 = 10^{-19.71} \tag{2}$$

In the leaching solution, both iminodiacetate anion (Ida^{2-}) and OH^- can be viewed as leaching ligands to coordinate with Zn^{2+} to form soluble $ZnIda_i^{2-2i}$ (i = 1–2) complexes and $Zn(OH)_i^{2-i}$ (i = 1–4) complexes, respectively. The complexation reaction equations and the stability constants of various zinc complexes are listed in Table II.[22] Therefore, the total concentration of zinc ions ($[Zn^{2+}]_T$) can be obtained using the following equation:

$$\begin{aligned} \left[Zn^{2+}\right]_T = \left[Zn^{2+}\right] + \sum_{i=1\sim2}\left[ZnIda_i^{2-2i}\right] \\ + \sum_{j=1\sim4}\left[Zn(OH)_j^{2-j}\right] \end{aligned} \tag{3}$$

Besides the complexation reaction of Zn^{2+} with Ida^{2-}, the protonation of Ida^{2-} must be taken into account. The protonation reaction equations and the protonation constants of Ida^{2-} are listed in Table III.[22] Therefore, the total ligand concentration ($[Ida^{2-}]_T$) is expressed as:

$$\begin{aligned} \left[Ida^{2-}\right]_T = \left[Ida^{2-}\right] + \sum_{i=1\sim2} i\cdot\left[ZnIda_i^{2-2i}\right] \\ + \sum_{j=0\sim3}\left[H_jIda^{j-2}\right] \end{aligned} \tag{4}$$

Based on the thermodynamic data given in Tables II and III, there are five unknowns in Eqs. 2, 3, and 4, which are $[Zn^{2+}]_T$, $[Zn^{2+}]$, $[Ida^{2-}]_T$, $[Ida^{2-}]$, and $[H^+]$. During the practical leaching process, the total concentration of the leaching agent can be determined from the leaching condition. The concentration of H^+ can be measured by a pH meter. Therefore, the remaining three unknowns can be calculated theoretically using MATLAB software. The development of the mathematical model will provide theoretical guidance for the dissolution of refractory hemimorphite.

RESULTS AND DISCUSSION

Theoretical Analyses

The leaching agent used in this study can be considered to be a partially dissociated weak acid. The partially dissociated protons can react with OH^-, decreasing the concentration of free OH^- and promoting the equilibrium reaction Eq. 1 to the right. Moreover, the partially dissociated Ida^{2-} can coordinate with Zn^{2+} to form the soluble zinc complexes, reducing the concentration of free Zn^{2+} and further facilitating the dissolution of hemimorphite.

Based on the previously mentioned mathematical model, the variation in the $[Zn^{2+}]_T$ with the pH and $[Ida^{2-}]_T$ is presented in Fig. 1. It can be seen that both the $[Ida^{2-}]_T$ and the pH affect the $[Zn^{2+}]_T$ significantly. An increase in the $[Ida^{2-}]_T$ enhances the $[Zn^{2+}]_T$, whereas a higher pH leads to a reduction in the $[Zn^{2+}]_T$. These results suggest that the partially dissociated protons and the amino carboxylate anions have a synergetic effect on the dissolution of the refractory hemimorphite.

Table I. Mineralogical composition of the material sample

Phase	Zinc sulfate	Zinc oxide	Hemimorphite	Zinc sulfide	Franklinite	Total zinc
Content, wt.%	< 0.1%	< 0.1%	9.18	0.03	0.02	9.23

Table II. Complexation reaction equations and the stability constants of zinc complexes

Ligand	Formula	Equation	Stability constant (lg β)
OH^-	–	$Zn^{2+} + OH^- = ZnOH^+$	4.4
		$Zn^{2+} + 2OH^- = Zn(OH)_2$	11.3
		$Zn^{2+} + 3OH^- = Zn(OH)_3^-$	14.14
		$Zn^{2+} + 4OH^- = Zn(OH)_4^{2-}$	17.66
Ida^{2-}	$[HN(CH_2COO)_2]^{2-}$	$Zn^{2+} + Ida^{2-} = ZnIda$	7.24
		$Zn^{2+} + 2Ida^{2-} = ZnIda_2^{2-}$	12.52

Table III. Protonation reaction equations and the protonation constants of Ida^{2-}

Ligand	Formula	Equation	Protonation constant (lg β)
Ida^{2-}	$[HN(CH_2COO)_2]^{2-}$	$H^+ + Ida^{2-} = HIda^-$	9.34
		$2H^+ + Ida^{2-} = H_2Ida$	11.95
		$3H^+ + Ida^{2-} = H_3Ida^+$	13.77

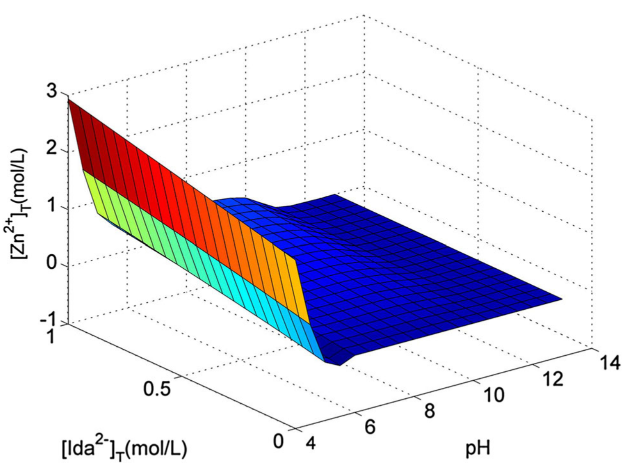

Fig. 1. Variation in the $[Zn^{2+}]_T$ with the pH and the $[Ida^{2-}]_T$.

To elucidate the results presented in Fig. 1, the distribution of the Zn^{2+} and Ida^{2-} species as a function of the pH (when the $[Ida^{2-}]_T$ is 1 mol/L) was studied, and the results are shown in Fig. 2a and b, respectively. As shown in Fig. 2a, when the pH of the leaching solution is 4.0, the distribution of free Zn^{2+} is larger than that of the ZnIda complex. With the increase of the pH, the distribution of free Zn^{2+} decreases owing to the formation of the $ZnIda_2^{2-}$ complex. The $ZnIda_2^{2-}$ complex becomes the predominant species in the pH range from 7.0 to 12.0. But the $Zn(OH)_4^{2-}$ complex predominates in the leaching solution at pH 13.0. From Fig. 2b, it can be observed that more than 99.0% of Ida^{2-} is ZnIda or $ZnIda_2^{2-}$ complexes in the pH range from 4.0 to 8.0, showing an adequate complex reaction

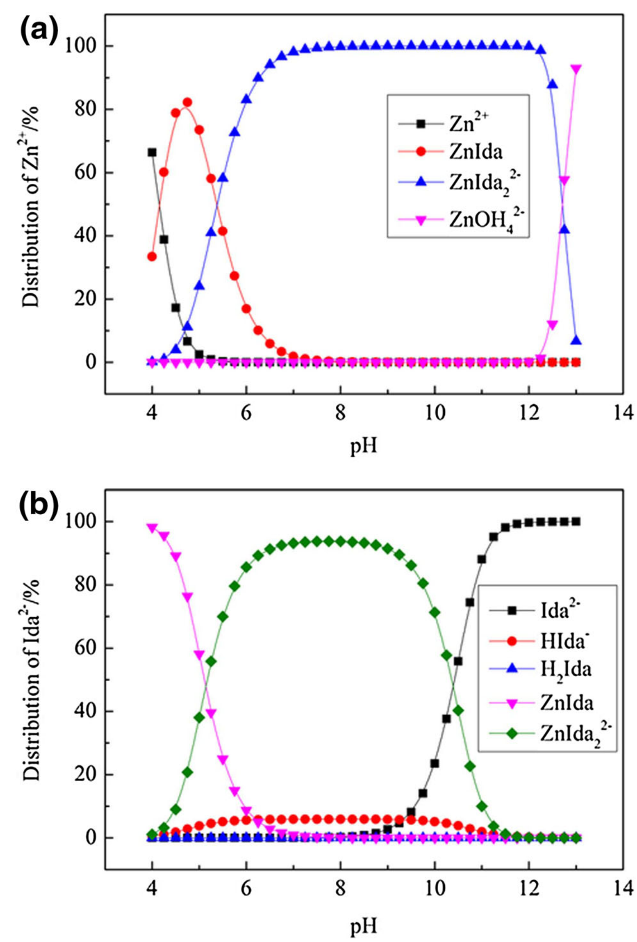

Fig. 2. Distribution of the Zn^{2+} and the Ida^{2-} species as a function of the pH: (a) Zn^{2+} and (b) Ida^{2-}.

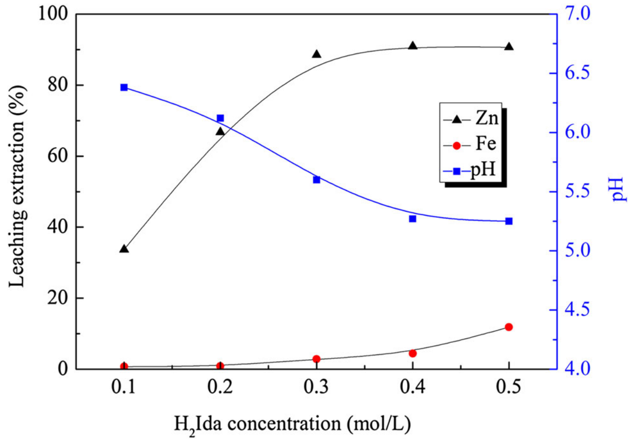

Fig. 3. Effect of the concentration of the leaching agent on the leaching extraction of zinc and iron.

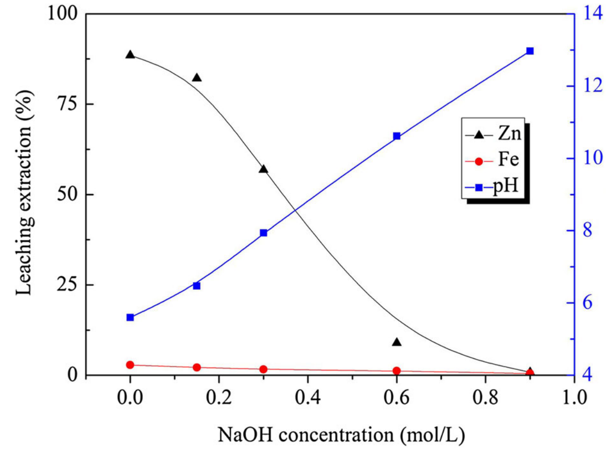

Fig. 4. Effect of the concentration of sodium hydroxide on the leaching extraction of zinc and iron.

between Ida^{2-} and Zn^{2+}. The distribution of free Ida^{2-} increases gradually at the pH above 8.0, which is adverse for the leaching process.

Leaching Experiments

To verify the accuracy and the reliability of the thermodynamic simulation, a series of leaching experiments was conducted. The effects of the concentration of the leaching agent and the pH of the leaching solution on the dissolution efficiency of hemimorphite were mainly studied. In addition, the leaching extraction of iron is discussed to study the selectivity of the leaching process compared with that of conventional sulfuric acid leaching.

Effect of the Leaching Agent Concentration

The effects of the concentration of the leaching agent on the leaching extraction of zinc and iron are shown in Fig. 3. It is evident that the zinc leaching extraction is strongly dependent on the concentration of the complexing agent. An increase in the H_2Ida concentration improves the leaching extraction of zinc significantly. For example, the leaching extraction of zinc reaches 90.9% when the H_2Ida concentration increases to 0.5 mol/L. A higher H_2Ida concentration provides more H^+ and Ida^{2-}, promoting the solubility equilibrium equation (Eq. 1) to the right. It is worth noting that the dissolution of iron is very low when the concentration of the leaching agent varies from 0.1 mol/L to 0.3 mol/L. Further increase in the concentration of the leaching agent to 0.5 mol/L leads to a sharp increase in the leaching extraction of iron. The results suggest that, apart from the preferential leaching of zinc in the H_2Ida solution, a proportion of iron can be dissolved using higher concentrations of the complexing agent.

Effect of the pH of the Leaching Solution

The pH of the leaching solution was adjusted by adding various amounts of sodium hydroxide. As shown in Fig. 4, an increase in the pH is observed with an increase in the concentration of NaOH. Nevertheless, a higher pH leads to a reduction in the leaching extraction of zinc, indicating that the addition of NaOH adversely affects the leaching process. The leaching extraction of zinc is below 1.0% in a 0.3-mol/L H_2Ida–0.9-mol/L NaOH solution. The results are consistent with the theoretical analyses. A higher pH promotes the dissociation of H_2Ida but weakens the formation reaction of the zinc complexes. These results confirm the synergetic effect of the partially dissociated protons and the amino carboxylate anions in the dissolution of hemimorphite.

The Comparison for the Different Leaching Process

To confirm the selective extraction of zinc using iminodiacetic acid as a complexing agent, the leaching experiments also were conducted at “standard” acidic and ammonicial conditions, including 1-mol/L H_2SO_4 solution and 1-mol/L NH_4Cl–1-mol/L NH_3 solution. The experimental results, given in Table IV, indicate that a high zinc extraction is obtained in 1-mol/L H_2SO_4 solution, whereas the iron leaching extraction is above 35%. In 1-mol/L NH_4Cl–1-mol/L NH_3 solution, although iron is almost not dissolved in the leaching solution, the zinc leaching extraction is relatively low owing to the weaker complexation ability between NH_3 and Zn^{2+}. Compared with sulfuric acid and ammoniacal leaching processes, iminodiacetic acid can be considered to be a suitable leaching agent owing to its high selectivity.

Table IV. Comparison for the different leaching process

Leaching agent	1-mol/L H_2SO_4 (%)	1-mol/L NH_4Cl–1-mol/L NH_3 (%)	0.3-mol/L H_2Ida (%)
Zinc leaching extraction	90.64	28.35	88.51
Iron leaching extraction	35.30	<0.10	2.82

Regeneration of the Leaching Agent

Based on the thermodynamic simulations and on the results of leaching experiments, it can be concluded that H_2Ida can be used as a suitable complexing agent to dissolve hemimorphite. Considering that the zinc complex in the leaching solution is very stable with a large formation constant, it is difficult to recover zinc directly from the solution by solvent extraction or electro-winning methods. Moreover, H_2Ida is an unconventional and expensive reagent. Therefore, from an economic perspective, it is necessary to recover the complexing agent for sustainable hydrometallurgical extraction of zinc from refractory hemimorphite.

It is well known that amino carboxylic acid can be separated from aqueous solutions owing to its lowest solubility at the pH corresponding to its isoelectric point (pI). The pI of amino carboxylic acid can be calculated according to the equation:

$$pI = (pK_1 + pK_2)/2 \tag{5}$$

where K_1 and K_2 are the protonation constant of the amino group and the dissociation constant of the carboxyl group, respectively. According to Table III, the pI of iminodiacetic acid is calculated to be 2.40. Therefore, the complexing agent can be recovered from the leaching solution in the form of white precipitates by adding dilute sulfuric acid to attain a pH of 2.40. At the same time, the $ZnIda_2^{2-}$ complex is transformed into free Zn^{2+} in the leaching solution and can be processed by the conventional hydrometallurgical methods.

CONCLUSION

Based on thermodynamic simulations and leaching experiments, the following conclusions were drawn from this investigation:

1. The partially dissociated protons and amino carboxylate anions have a synergic effect on the dissolution of hemimorphite.
2. Zinc can be dissolved in the leaching solution selectively and efficiently using iminodiacetic acid as a complexing agent. Under optimal conditions, the leaching extraction of zinc and iron are 88.51% and 2.82%, respectively.
3. Recovery of the complexing agent is possible at the isoelectric point of iminodiacetic acid by adding dilute sulfuric acid.

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