

Thermodynamics of solubility of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ in ammonia-ammonium chloride-ethylenediamine(En)-water system

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Received 6 July 2009; accepted 25 December 2009

Abstract: In order to decrease the evaporating rate of ammonia and increase the solubility of copper in the solution, ethylenediamine was added into the ammonia-ammonium chloride system to leach the copper-containing oxide ores. The thermodynamic model was constructed and the solubility of malachite $\text{Cu}_2(\text{OH})_2\text{CO}_3$ in the ammonia-ammonium chloride-ethylenediamine(En)-water system was calculated using the exponential computation method based on both mass balance and charge balance. It is found that the solubility of copper can be increased and the free ammonia concentration can be decreased by submitting partial ammonia with ethylenediamine. The lower free ammonia concentration in the solution is a guarantee to the lower evaporating rate of ammonia. The conditions of malachite $\text{Cu}_2(\text{OH})_2\text{CO}_3$ converting to atacamite $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ were also studied. A group of experiments were designed to validate the veracity of the results of the thermodynamic calculation. It is found that the thermodynamic model is reliable and it can guide the leaching process.

Key words: thermodynamics; solubility; malachite; ammonia; ammonium chloride; ethylenediamine(En)

1 Introduction

Ammonia is a good selective reagent for copper extraction. Many researches have been focused on the leaching of copper oxide ore with ammoniac solution especially when the gangue is composed of carbonates [1–4].

The thermodynamic and kinetic characteristics of dissolving of copper oxide ore in ammoniac solution have been widely studied [5–7]. However, the volatilization of ammonia during operation always makes the working environment very terrible. In order to overcome this shortcoming, the ethylenediamine(En), which has a higher boiling point, is used to substitute partial ammonia [8]. RAMDANE [9], SERDAR and FIONA [10] investigated the ϕ -pH diagrams of the Cu-En- H_2O system. But the dissolving characteristics of the copper oxide ores in ammonia-ammonium chloride-ethylenediamine(En)-water solution was not yet illustrated clearly. In this work, an attempt is made to study the solubility of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ in the ammonia-

ammonium chloride-ethylenediamine(En) solution. The calculations, based on both mass balance and charge balance equations, are made to express equilibrium relations between solid phase and associated solution in terms of total concentrations of the actual lixiviants ammonia, ammonium chloride and ethylenediamine(En). Furthermore, the solution composition for keeping $\text{Cu}_2(\text{OH})_2\text{CO}_3$ stable is also established.

2 Thermodynamic model

2.1 Data selection

Considering that the activity of each ion is approximated by its mole concentration in this work and the concentration of each ion is in relatively high level, the data determined at the highest ionic intensity are selected from the literature. The stability constants are listed in Tables 1–3.

2.2 Calculation method

As mentioned by TANG et al [11–13] in their studies, all the concentrations of ions in the solution can

Table 1 Cumulative formation constants of copper complexes at 298 K

Species	lg β	I	Ref.
CuCl ⁺	0.09	2	[14]
Cu(NH ₃) ²⁺	4.24	2	[14]
Cu(NH ₃) ₂ ²⁺	7.83	2	[14]
Cu(NH ₃) ₃ ²⁺	10.8	2	[14]
Cu(NH ₃) ₄ ²⁺	13.0	2	[14]
Cu(NH ₃) ₅ ²⁺	12.43	2	[14]
Cu(OH) ⁺	6.30	0	[14]
Cu(OH) ₂ (aq)	12.8	1	[14]
Cu(OH) ₃ ⁻	14.5	1	[14]
Cu(OH) ₄ ²⁻	15.6	1	[14]
Cu ₂ (OH) ₂ ²⁺	17.28	1	[14]
CuNH ₃ (OH) ⁺	14.9	0.5	[14]
CuNH ₃ (OH) ₃ ⁻	16.3	0.5	[14]
Cu(NH ₃) ₂ (OH) ₂ (aq)	15.7	0.5	[14]
CuEn ²⁺	11.02	2.15	[14]
CuEn ₂ ²⁺	20.61	2.15	[14]
CuEn ₃ ²⁺	19.71	1	[15]
CuOHEn ⁺	0.73	0.5	[14]

Table 2 Constants of addition proton at 298 K

Species	lg β_i	I	Ref.
OH ⁻ +H ⁺ ==H ₂ O	14.18	3.0	[14]
NH ₃ +H ⁺ ==NH ₄ ⁺	9.80	5.0	[14]
CO ₃ ²⁻ +H ⁺ ==HCO ₃ ⁻	9.56	3.0	[14]
CO ₃ ²⁻ +2H ⁺ ==H ₂ CO ₃	15.89	3.0	[14]
En+H ⁺ ==HEn ⁺	10.21	0.5	[14]
En+2H ⁺ ==H ₂ En ²⁺	17.48	0.5	[14]

Table 3 Solubility-product constants (K_{sp})

Species	lg K_{sp}	I	Ref.
Cu(OH) ₂ ==Cu ²⁺ +2OH ⁻	-18.90	1.0	[14]
CuO+H ₂ O==Cu ²⁺ +2OH ⁻	-19.51	0.5	[14]
CuCO ₃ ==Cu ²⁺ +CO ₃ ²⁻	-9.63	0	[14]
Cu ₂ (OH) ₂ CO ₃ ==2Cu ²⁺ +2OH ⁻ +CO ₃ ²⁻	-33.78	0	[14]
Cu ₃ (OH) ₂ (CO ₃) ₂ ==3Cu ²⁺ +2OH ⁻ +2CO ₃ ²⁻	-45.96	0	[14]
Cu(OH) _{1.5} Cl _{0.5} ==Cu ²⁺ +1.5OH ⁻ +0.5Cl ⁻	-17.30	0	[14]

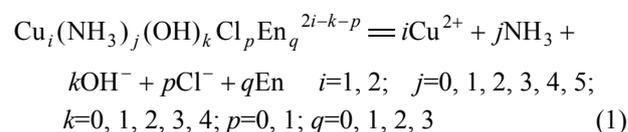
be expressed as $[X]=\exp(a+b\text{pH}+c\varphi+e\ln[L_1]+f\ln[L_2]+\dots)$, where a , b , c , e and f are coefficients; φ is the value of potential which is only needed when redox reactions

exist; L_1 , L_2 , \dots are the free ions including free metal ion, free ligands and other free ions besides H⁺ and OH⁻.

After substituting the concentration of each ion with the above expression, the variables can be greatly decreased when the thermodynamic model is established based on both mass balance and charge balance equations, which makes solving the nonlinear equations on a computer more convenient and easy. TANG et al defined the whole process as the exponential computation method. The exponential computation method is also used in this research.

2.3 Dissolving characteristic of Cu₂(OH)₂CO₃

The equilibrium among the copper-containing species dissolved in the solution and the simple ions (Cu²⁺, NH₃, OH⁻, H⁺, Cl⁻, CO₃²⁻) can be expressed as the following equation:

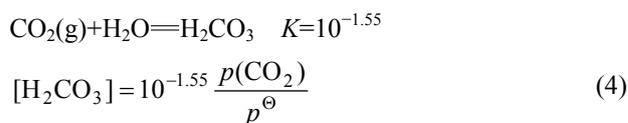


$$\frac{[\text{Cu}_i(\text{NH}_3)_j(\text{OH})_k\text{Cl}_p\text{En}_q^{2i-k-p}]}{[\text{Cu}^{2+}]^i[\text{NH}_3]^j[\text{OH}^-]^k[\text{Cl}^-]^p[\text{En}]^q} = \beta_{i,j,k,p,q} \quad (2)$$

$$[\text{Cu}_i(\text{NH}_3)_j(\text{OH})_k\text{Cl}_p\text{En}_q^{2i-k-p}] = \beta_{i,j,k,p,q} [\text{Cu}^{2+}]^i [\text{NH}_3]^j [\text{OH}^-]^k [\text{Cl}^-]^p [\text{En}]^q \quad (3)$$

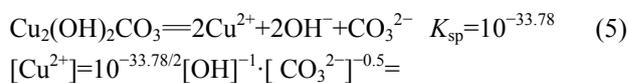
where $[x]$ is the concentration of the species in the solution.

When the solid of Cu₂(OH)₂CO₃ is in equilibrium with the solution, H₂CO₃ will be formed and will be in equilibrium with CO₂ in the air:



The partial pressure of CO₂ in the atmosphere is $p(\text{CO}_2)=1.01 \times 10^{2.5}$ MPa. The concentration of H₂CO₃ in solution is calculated to be $10^{-5.05}$ from Eq.(4). CO₃²⁻ and HCO₃⁻ are also in equilibrium with H₂CO₃ and their concentrations are calculated to be $[\text{CO}_3^{2-}]=10^{-20.94}[\text{H}^+]^{-2}$ and $[\text{HCO}_3^-]=10^{-11.38}[\text{H}^+]^{-1}$, respectively.

The dissolution equation of Cu₂(OH)₂CO₃ can be written as



$$10^{-16.89} \times 10^{14.18} [\text{H}^+] \cdot [\text{CO}_3^{2-}]^{-0.5} \quad (6)$$

Substituting $[\text{CO}_3^{2-}]=10^{-20.94}[\text{H}^+]^{-2}$ into Eq.(6) yields $[\text{Cu}^{2+}]=10^{7.76}[\text{H}^+]^2 \quad (7)$

Substituting Eq.(7) into Eq.(3) yields

$$\begin{aligned}
 & [\text{Cu}_i(\text{NH}_3)_j(\text{OH})_k\text{Cl}_p\text{En}_q^{2i-k-p}] = \\
 & \beta_{i,j,k,p,q} 10^{7.76i} [\text{H}^+]^{2i} [\text{NH}_3]^j [\text{OH}^-]^k [\text{Cl}^-]^p [\text{En}]^q = \\
 & \exp(\ln(\beta_{i,j,k,p,q} 10^{7.76i}) + j \ln[\text{NH}_3] + (k-2i) \ln 10 \text{pH} + \\
 & \quad k \ln 10 \text{p}K_w + p \ln[\text{Cl}^-] + q \ln[\text{En}]) = \\
 & \exp((\ln(\beta_{i,j,k,p,q} 10^{7.76i}) + k \ln 10 \text{p}K_w) + j \ln[\text{NH}_3] + \\
 & \quad (k-2i) \ln 10 \text{pH} + p \ln[\text{Cl}^-] + q \ln[\text{En}]) = \\
 & \exp(A + B \ln[\text{NH}_3] + C \text{pH} + D \ln[\text{Cl}^-] + E \ln[\text{En}])
 \end{aligned}$$

where $A = \ln(\beta_{i,j,k,p,q} 10^{7.76i}) + k \ln 10 \text{p}K_w$; $B = j$; $C = (k-2i) \ln 10$; $D = p$ and $E = q$. K_w is the ion product of water.

The coefficients of A , B , C , D and E of each species are listed in Table 4.

The mass balance equations of copper, total ammonia, chloride and ethylenediamine can be expressed as

$$\begin{aligned}
 c(\text{Cu}^{2+})_{\text{T}} &= [\text{Cu}^{2+}] + [\text{CuCl}^+] + \sum_{i=1}^5 [\text{Cu}(\text{NH}_3)_i^{2+}] + \\
 & \sum_{j=1}^4 [\text{Cu}(\text{OH})_j^{2-j}] + 2[\text{Cu}_2(\text{OH})_2^{2+}] + [\text{CuNH}_3\text{OH}^+] + \\
 & [\text{CuNH}_3(\text{OH})_3^-] + [\text{Cu}(\text{NH}_3)_2(\text{OH})_{2(\text{aq})}] + \\
 & \sum_{i=1}^3 [\text{Cu}(\text{En})_i^{2+}] + [\text{Cu}(\text{OH})\text{En}^+] \quad (8)
 \end{aligned}$$

$$\begin{aligned}
 c(\text{NH}_3)_{\text{T}} &= c(\text{NH}_3 \cdot \text{H}_2\text{O}) + c(\text{NH}_4\text{Cl}) = \\
 & [\text{NH}_4^+] + [\text{NH}_3] + \sum_{i=1}^5 i \cdot [\text{Cu}(\text{NH}_3)_i^{2+}] + [\text{CuNH}_3\text{OH}^+] + \\
 & [\text{CuNH}_3(\text{OH})_3^-] + 2[\text{Cu}(\text{NH}_3)_2(\text{OH})_{2(\text{aq})}] \quad (9)
 \end{aligned}$$

$$c(\text{Cl}^-)_{\text{T}} = c(\text{NH}_4\text{Cl}) = [\text{Cl}^-] + [\text{CuCl}^+] \quad (10)$$

$$\begin{aligned}
 c(\text{En})_{\text{T}} &= [\text{En}] + i \cdot \sum_{i=1}^3 [\text{Cu}(\text{En})_i^{2+}] + [\text{Cu}(\text{OH})\text{En}^+] + \\
 & [\text{HEn}^+] + [\text{H}_2\text{En}^{2+}] \quad (11)
 \end{aligned}$$

where $c(\text{Cu}^{2+})_{\text{T}}$, $c(\text{NH}_3)_{\text{T}}$, $c(\text{Cl}^-)_{\text{T}}$ and $c(\text{En})_{\text{T}}$ are the total concentration of copper, ammonia, chloride and ethylenediamine in the solution, respectively. The total concentration of ammonia in the solution equals the concentration of ammonia $c(\text{NH}_3 \cdot \text{H}_2\text{O})$ plus ammonium chloride $c(\text{NH}_4\text{Cl})$ added into the solution. And the total concentration of chloride equals the concentration of ammonium chloride.

The charge balance equation can be written as

$$\sum m \cdot [X] = 0 \quad (12)$$

where m and $[X]$ mean the charge and the concentration of the ions in the solution, respectively.

After introducing the expression of $[X] = \exp(A + B \ln[\text{NH}_3] + C \text{pH} + D \ln[\text{Cl}^-] + E \ln[\text{En}])$ into Eqs.(11)–(12) and giving the concentration of ammonia $c(\text{NH}_3 \cdot \text{H}_2\text{O})$, ammonium chloride $c(\text{NH}_4\text{Cl})$ and ethylenediamine $c(\text{En})_{\text{T}}$ as the operating conditions and varying from 0 to 5 mol/L, only five variables remain namely $c(\text{Cu}^{2+})_{\text{T}}$, $[\text{NH}_3]$, pH , $[\text{Cl}^-]$ and $[\text{En}]$. The equation groups are solved with the soft ware of Matlab using the function of “fsolve()”. The concentration of each species $[X]$ is obtained from $[X] = \exp(A + B \ln[\text{NH}_3] + C \text{pH} + D \ln[\text{Cl}^-] + E \ln[\text{En}])$.

Table 4 Coefficients of each species

Species	A	B	C	D	E	Species	A	B	C	D	E
NH_3	0	1	0	0	0	$\text{Cu}(\text{OH})_3^-$	-46.696	0	2.303	0	0
* NH_4^+	22.565	1	-2.303	0	0	$\text{Cu}(\text{OH})_4^{2-}$	-76.814	0	4.605	0	0
* H^+	0	0	-2.303	0	0	$\text{Cu}_2(\text{OH})_2^{2+}$	10.223	0	-4.605	0	0
* OH^-	-32.651	0	2.303	0	0	$\text{CuNH}_3(\text{OH})^+$	19.526	1	-2.303	0	0
Cl^-	0	0	0	1	0	$\text{CuNH}_3(\text{OH})_3^-$	-42.552	1	2.303	0	0
Cu^{2+}	17.868	0	-4.605	0	0	$\text{Cu}(\text{NH}_3)_2(\text{OH})_{2(\text{aq})}$	-11.283	2	0	0	0
CuCl^+	18.075	0	-4.605	1	0	CO_3^{2-}	-48.216	0	4.605	0	0
$\text{Cu}(\text{NH}_3)^{2+}$	27.631	1	-4.605	0	0	HCO_3^-	-26.203	0	2.302	0	0
$\text{Cu}(\text{NH}_3)_2^{2+}$	35.897	2	-4.605	0	0	CuEn^{2+}	43.243	0	-4.605	0	1
$\text{Cu}(\text{NH}_3)_3^{2+}$	42.736	3	-4.605	0	0	CuEn_2^{2+}	65.324	0	-4.605	0	2
$\text{Cu}(\text{NH}_3)_4^{2+}$	47.802	4	-4.605	0	0	CuEn_3^{2+}	63.252	0	-4.605	0	3
$\text{Cu}(\text{NH}_3)_5^{2+}$	46.489	5	-4.605	0	0	CuOHEn^+	52.200	0	-2.303	0	1
$\text{Cu}(\text{OH})^+$	-0.184	0	-2.303	0	0	HEn^+	23.509	0	-2.303	0	1
$\text{Cu}(\text{OH})_{2(\text{aq})}$	-17.960	0	0	0	0	H_2En^{2+}	40.249	0	-4.605	0	1

* $[\text{H}^+] = \exp(-\ln 10 \text{pH})$; $[\text{NH}_4^+] = 10^{9.8} [\text{NH}_3] [\text{H}^+] = \exp(9.8 \ln 10 + \ln[\text{NH}_3] - \ln 10 \text{pH})$; $[\text{OH}^-] = 10^{-14.18} [\text{H}^+]^{-1} = \exp(-14.18 \ln 10 + \ln 10 \text{pH})$

3 Experimental

The verifying tests of solubility of each solid phase in the solution with different ammonia, ammonium chloride and ethylenediamine concentrations were carried out by adding 15 g pure $\text{Cu}_2(\text{OH})_2\text{CO}_3$ into 50 mL solution in bottles. The bottles were exposed to the atmosphere for many days to ensure CO_2 saturation. All the bottles were placed on a constant-temperature shaking table and held at 298 K. The reagents used for preparing the solutions were all of analytical quality. The concentration of copper in the solution was analyzed by titration method and the solid undissolved in the solution

was dried and weighed, and the phase composition was detected by X-ray diffraction.

4 Results and discussion

4.1 Thermodynamic characteristic of $\text{Cu}_2(\text{OH})_2\text{CO}_3\text{-NH}_3\text{-NH}_4\text{Cl-En-H}_2\text{O}$ system

The equation group of the thermodynamic model of $\text{Cu}_2(\text{OH})_2\text{CO}_3\text{-NH}_3\text{-NH}_4\text{Cl-En-H}_2\text{O}$ system was solved and the results of $c(\text{Cu}^{2+})_{\text{T}}$, $[\text{NH}_3]$, $[\text{En}]$, $[\text{Cl}^-]$, pH are shown in Fig.1. It can be seen that the total copper concentration dissolved in the solution increases with the increasing concentration of ethylenediamine. A low concentration of free ammonia, which is the guarantee to

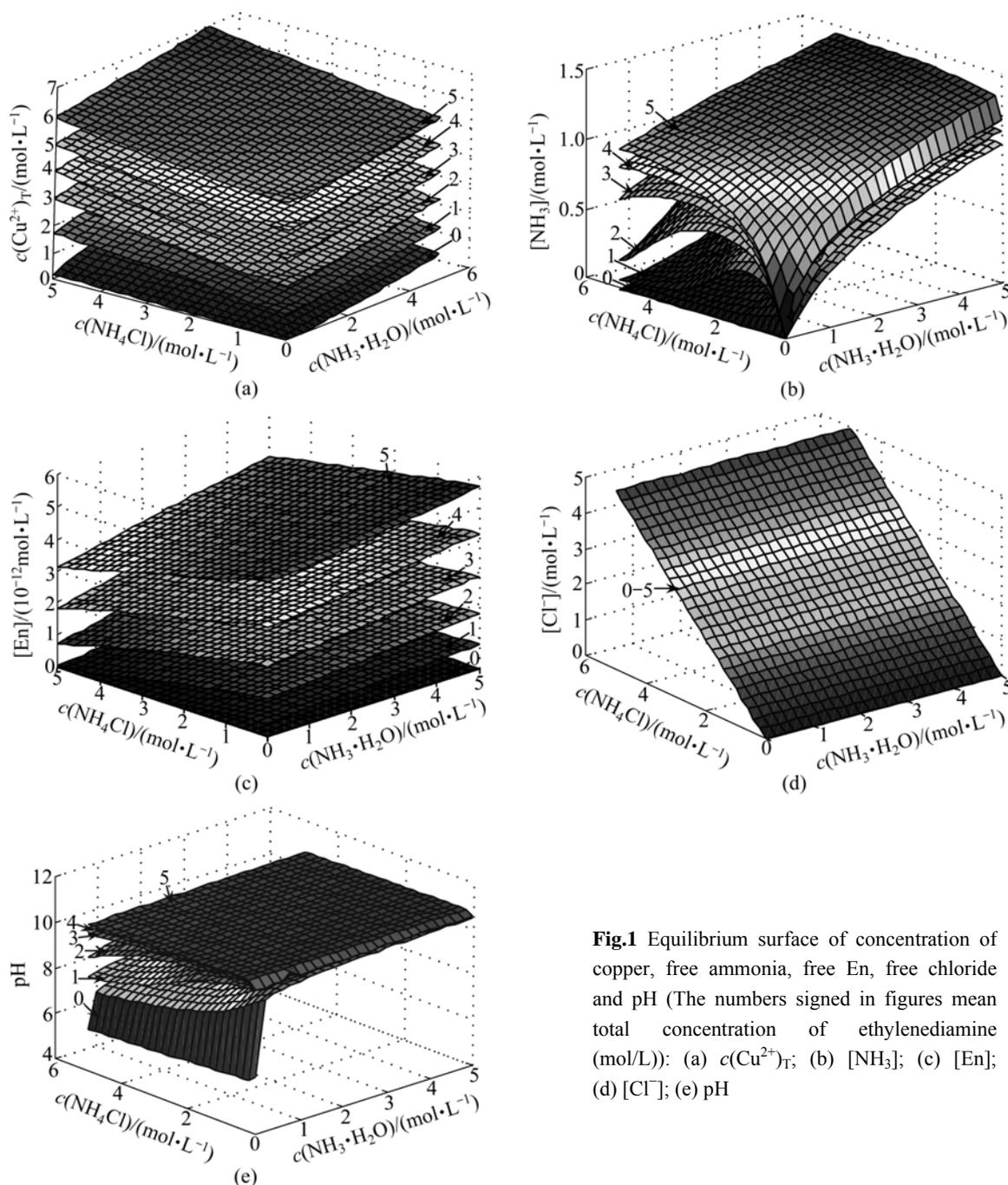


Fig.1 Equilibrium surface of concentration of copper, free ammonia, free En, free chloride and pH (The numbers signed in figures mean total concentration of ethylenediamine (mol/L)): (a) $c(\text{Cu}^{2+})_{\text{T}}$; (b) $[\text{NH}_3]$; (c) $[\text{En}]$; (d) $[\text{Cl}^-]$; (e) pH

the decreasing evaporation rate of the ammonia to the air, can be kept when the concentration of ammonia added into solution is very low. However, a satisfactory solubility of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ can also be attained by submitting ammonia with ethylenediamine.

The solid of CuO , CuCO_3 , $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ and $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ may be formed in the system of $\text{Cu}_2(\text{OH})_2\text{CO}_3\text{-NH}_3\text{-NH}_4\text{Cl-En-H}_2\text{O}$. It is necessary to validate the possibility by comparing the concentration-product of each solid phase (J_{sp}) and the solubility-product constants (K_{sp}) of each solid phase.

The J_{sp} of CuO is calculated as

$$J_{\text{sp}}(\text{CuO})=[\text{Cu}^{2+}]\cdot[\text{OH}]^2 \quad (13)$$

Introducing Eq.(7) into Eq.(13), there is

$$J_{\text{sp}}(\text{CuO})=[\text{Cu}^{2+}]\cdot[\text{OH}]^2=10^{7.76}[\text{H}^+]^2\cdot[\text{OH}]^2=10^{7.76}\cdot K_{\text{w}}^2=10^{-20.6}$$

The J_{sp} of CuO is smaller than its K_{sp} (K_{sp} of CuO is $10^{-19.51}$).

The J_{sp} of CuCO_3 is calculated as

$$J_{\text{sp}}(\text{CuCO}_3)=[\text{Cu}^{2+}][\text{CO}_3^{2-}]=10^{7.76}[\text{H}^+]^2\cdot 10^{-20.94}[\text{H}^+]^{-2}=10^{-13.18}$$

It is apparent that J_{sp} of CuCO_3 is smaller than its K_{sp} (K_{sp} of CuCO_3 is $10^{-9.63}$).

The J_{sp} of $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ is calculated as

$$J_{\text{sp}}(\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2)=[\text{Cu}^{2+}]^3[\text{OH}^-]^2[\text{CO}_3^{2-}]^2=10^{23.28}[\text{H}^+]^6[\text{OH}^-]^2\cdot 10^{-41.88}[\text{H}^+]^{-4}=10^{-18.6}[\text{H}^+]^2[\text{OH}^-]^2=10^{-46.96}$$

J_{sp} of $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ is also smaller than its K_{sp} (K_{sp} of $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ is $10^{-45.96}$).

From the above discussion, the J_{sp} of CuO , CuCO_3 and $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ are all smaller than their K_{sp} , which means that the formation of the solid of CuO , CuCO_3 and $\text{Cu}_3(\text{OH})_2(\text{CO}_3)_2$ is impossible in the system of $\text{Cu}_2(\text{OH})_2\text{CO}_3\text{-NH}_3\text{-NH}_4\text{Cl-En-H}_2\text{O}$.

Another solid phase that may be formed is $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$. Fig.2 shows the comparison between J_{sp} and K_{sp} of $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ in the system of $\text{Cu}_2(\text{OH})_2\text{CO}_3\text{-NH}_3\text{-NH}_4\text{Cl-En-H}_2\text{O}$. It can be seen that, when the concentration of ethylenediamine is smaller than 2 mol/L, the concentration of ammonium chloride is relatively high and the concentration of ammonia is relatively low. The J_{sp} of $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ is larger than its K_{sp} , which means that in these areas $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ is formed. The stable areas of $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ and $\text{Cu}_2(\text{OH})_2\text{CO}_3$ are shown in Fig.3. The lines dividing these areas were fitted as Eqs.(14) and (15), respectively:

$$\begin{aligned} c(\text{En})_{\text{T}} &= 0 \text{ mol/L} \\ c(\text{NH}_4\text{Cl}) &= 1.707\ 06 + 0.991\ 73 \cdot c(\text{NH}_3 \cdot \text{H}_2\text{O}) \text{ mol/L} \\ R^2 &= 0.997\ 66 \end{aligned} \quad (14)$$

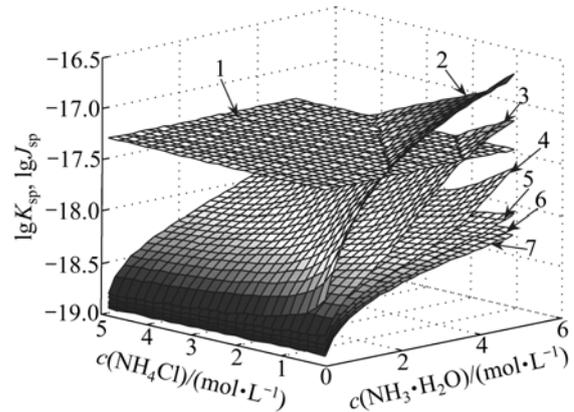


Fig.2 Comparison between $\lg J_{\text{sp}}$ and $\lg K_{\text{sp}}$ of $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$: 1— $\lg K_{\text{sp}}$; 2— $\lg J_{\text{sp}}(c(\text{En})=0)$; 3— $\lg J_{\text{sp}}(c(\text{En})=1 \text{ mol/L})$; 4— $\lg J_{\text{sp}}(c(\text{En})=2 \text{ mol/L})$; 5— $\lg J_{\text{sp}}(c(\text{En})=3 \text{ mol/L})$; 6— $\lg J_{\text{sp}}(c(\text{En})=4 \text{ mol/L})$; 7— $\lg J_{\text{sp}}(c(\text{En})=5 \text{ mol/L})$

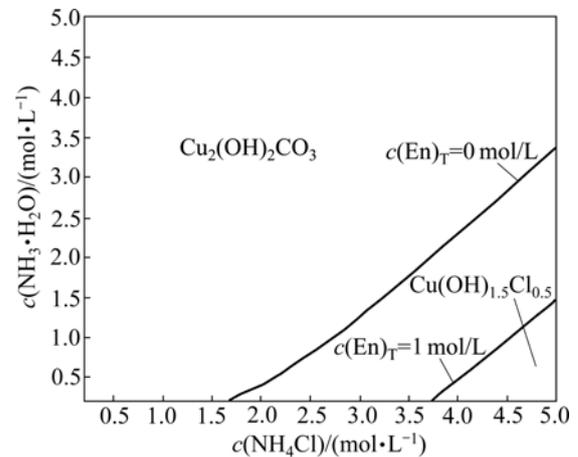


Fig.3 Stable area of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$

$$\begin{aligned} c(\text{En})_{\text{T}} &= 1 \text{ mol/L} \\ c(\text{NH}_4\text{Cl}) &= 3.512\ 17 + 1.006\ 49 \cdot c(\text{NH}_3 \cdot \text{H}_2\text{O}) \text{ mol/L} \\ R^2 &= 0.999\ 57 \end{aligned} \quad (15)$$

4.2 Verifying tests

The X-ray diffraction patterns of the final solid, after being brought to equilibrium with solution of specific concentration of ammonia, ammonium chloride and ethylenediamine, are shown in Figs.4 and 5.

Figs.6–7 show the distributions of each tested final solid on the stable area images. And the final solid phase compositions are listed in Table 5. It is apparent that the experimental results are very coincident with the forecast by the thermodynamics model. A phenomenon must be especially explained. Using the f point in Fig.6 as an example, the final solid phase of this point is the mixture of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ and $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ but not the pure $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ when the original $c(\text{NH}_3 \cdot \text{H}_2\text{O})$ and $c(\text{NH}_4\text{Cl})$ are located at the $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ stable area. The reason is that the decreased concentration of ammonium chloride, which results from the decreased

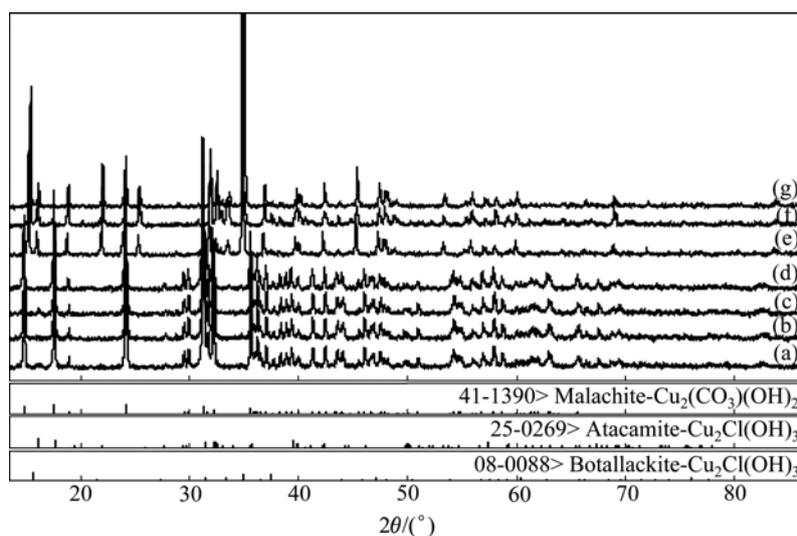


Fig.4 XRD patterns of final solid of different $c(\text{NH}_3\cdot\text{H}_2\text{O})$ and $c(\text{NH}_4\text{Cl})$ when $c(\text{En})_1=0$ mol/L: (a) Original $\text{Cu}_2(\text{OH})_2\text{CO}_3$; $c(\text{NH}_3\cdot\text{H}_2\text{O})$ and $c(\text{NH}_4\text{Cl})$ of (b)–(g) are 3, 2; 3, 4; 1, 2; 3, 5; 1, 3; 0, 5 mol/L, respectively

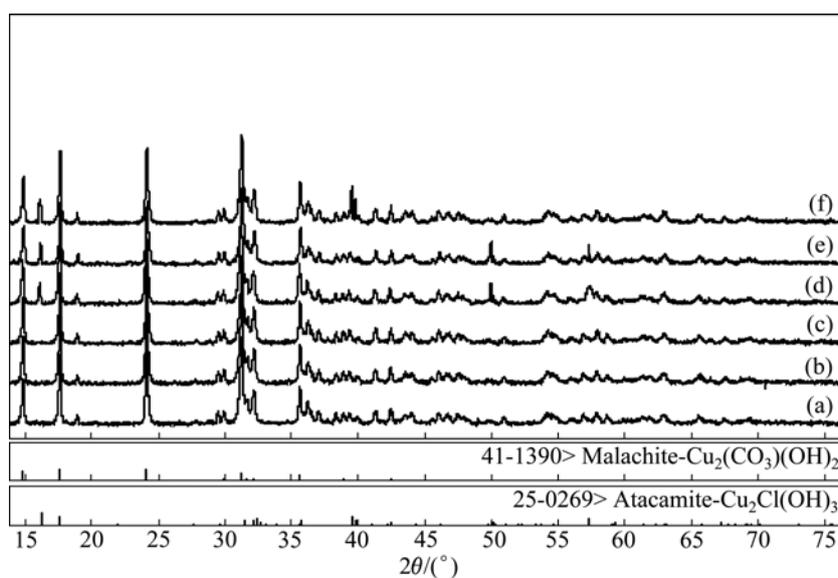


Fig.5 XRD patterns of final solid of different $c(\text{NH}_3\cdot\text{H}_2\text{O})$ and $c(\text{NH}_4\text{Cl})$ when $c(\text{En})_1=1$ mol/L: (a) Original $\text{Cu}_2(\text{OH})_2\text{CO}_3$; $c(\text{NH}_3\cdot\text{H}_2\text{O})$ and $c(\text{NH}_4\text{Cl})$ of (b)–(f) are 3, 2; 1, 1; 0.5, 4.5; 0, 5; 1, 5 mol/L, respectively

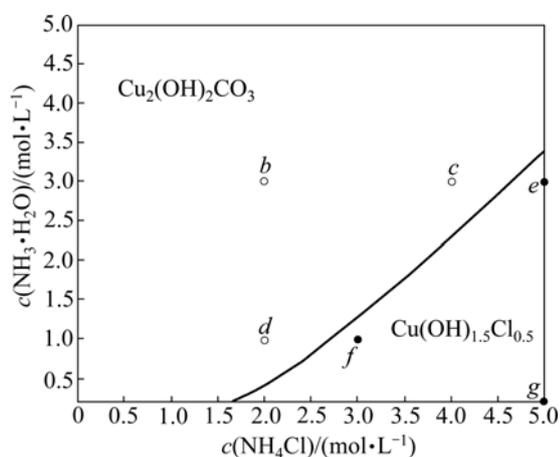


Fig.6 Distribution of point of tested final solid phase when $c(\text{En})_1=0$ mol/L

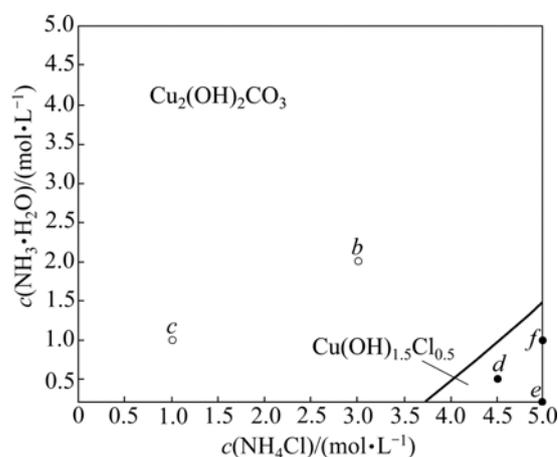


Fig.7 Distribution of point of tested final solid phase when $c(\text{En})_1=1$ mol/L

concentration of Cl^- in the solution as $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ forms, leads to the movement of $c(\text{NH}_3\cdot\text{H}_2\text{O})$ and $c(\text{NH}_4\text{Cl})$ to the stable area of $\text{Cu}_2(\text{OH})_2\text{CO}_3$, and eventually ends the process of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ transforming to $\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$ before $\text{Cu}_2(\text{OH})_2\text{CO}_3$ is vanished.

Both the calculated and experimental values of the concentration of copper dissolved in the solution and the pH of the solution under specific conditions when $c(\text{NH}_3\cdot\text{H}_2\text{O})$, $c(\text{NH}_4\text{Cl})$ and $c(\text{En})_{\text{T}}$ are located at the stable area of the original solid are shown in Table 6. It is apparent that the thermodynamic model is correct and reliable because most of the relative errors of both copper concentration and pH value are less than 10%,

which is satisfactory when the activity of the ions is approximated by their mole concentrations. Since the requirement of keeping the bottles open to the air to make sure that CO_2 is saturated in the solution, the evaporation of ammonia also leads to high relative errors of copper concentration and pH value under some conditions.

The prediction of the concentration of copper when the final solid is a mixture is much more complex. It is not only a function of the concentration of ammonia and ammonium chloride but also related to the amount of the original solid. When different amounts of original solid are transformed to another solid, the consumption or contribution of Cl^- is diverse.

Table 5 Final solid phase composition of original solid phase of $\text{Cu}_2(\text{OH})_2\text{CO}_3$

$c(\text{En})_{\text{T}}/(\text{mol}\cdot\text{L}^{-1})$	Serial No.	$c(\text{NH}_3\cdot\text{H}_2\text{O})/(\text{mol}\cdot\text{L}^{-1})$	$c(\text{NH}_4\text{Cl})/(\text{mol}\cdot\text{L}^{-1})$	Final solid phase
0	<i>a</i>			Original $\text{Cu}_2(\text{OH})_2\text{CO}_3$
	<i>b</i>	3	2	$\text{Cu}_2(\text{OH})_2\text{CO}_3$
	<i>c</i>	3	4	$\text{Cu}_2(\text{OH})_2\text{CO}_3$
	<i>d</i>	1	2	$\text{Cu}_2(\text{OH})_2\text{CO}_3$
	<i>e</i>	3	5	$\text{Cu}_2(\text{OH})_2\text{CO}_3+\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$
	<i>f</i>	1	3	$\text{Cu}_2(\text{OH})_2\text{CO}_3+\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$
	<i>g</i>	0	5	$\text{Cu}_2(\text{OH})_2\text{CO}_3+\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$
1	<i>a</i>			Original $\text{Cu}_2(\text{OH})_2\text{CO}_3$
	<i>b</i>	3	2	$\text{Cu}_2(\text{OH})_2\text{CO}_3$
	<i>c</i>	1	1	$\text{Cu}_2(\text{OH})_2\text{CO}_3$
	<i>d</i>	0.5	4.5	$\text{Cu}_2(\text{OH})_2\text{CO}_3+\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$
	<i>e</i>	0	5	$\text{Cu}_2(\text{OH})_2\text{CO}_3+\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$
	<i>f</i>	1	5	$\text{Cu}_2(\text{OH})_2\text{CO}_3+\text{Cu}(\text{OH})_{1.5}\text{Cl}_{0.5}$

Table 6 Results of verifying tests

$c(\text{NH}_3\cdot\text{H}_2\text{O})/(\text{mol}\cdot\text{L}^{-1})$	$c(\text{NH}_4\text{Cl})/(\text{mol}\cdot\text{L}^{-1})$	$c(\text{En})_{\text{T}}/(\text{mol}\cdot\text{L}^{-1})$	$c(\text{Cu})_{\text{T}}/(\text{mol}\cdot\text{L}^{-1})$		Relative error of $c(\text{Cu})_{\text{T}}/\%$	pH value		Relative error of pH/%
			Calculated	Tested		Calculated	Tested	
0	1	0	2.92	2.58	-11.50			-4.37
1	1	0	20.54	21.65	5.37	9.65	9.14	-5.31
1	2	0	30.28	32.80	8.34	8.93	8.41	-5.82
2	3	0	59.91	67.19	12.15	9.03	8.21	-9.12
3	4	0	89.87	86.85	-3.36	9.08	8.73	-3.86
4	4	0	107.83	100.52	-6.78	9.62	8.83	-8.18
4	5	0	119.97	95.44	-20.44	9.11	8.21	-9.84
5	5	0	137.64	133.34	-3.13	9.60	9.13	-4.87
2	3	1	126.61	118.62	-6.31	10.03	9.67	-3.61
1	1	1	82.83	91.74	10.76	10.25	10.87	6.07
1	3	1	113.29	96.41	-14.90	9.65	9.78	1.35
2	4	1	142.76	128.3	-10.13	9.64	9.11	-5.45
3	2	1	123.79	111.57	-9.87	10.33	11.05	7.02
1	1	2	145.49	135.96	-6.55	10.42	11.29	8.33

5 Conclusions

A thermodynamic model describing the dissolution characteristics of $\text{Cu}_2(\text{OH})_2\text{CO}_3$ was established. Through the verifying tests, it is found that the thermodynamic model is correct and reliable. The model is helpful to the leaching process when choosing lixiviant with the appropriate concentration of ammonia, ammonium chloride and ethylenediamine. Furthermore, the stable area diagrams of each phase are also useful to the precipitation and the synthesizing of the copper salts.

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(Edited by YUAN Sai-qian)