

Phase equilibrium of $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system

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Abstract: In order to provide the theoretical guidance for applying the neutralization method to treatment of heavy metals wastewater with high concentration of sulfate, and to better understand the mechanism of calcium sulfate scale formation, the equilibrium solubility data of $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system at 298.15 K were theoretically calculated via the Pitzer semi-empirical ion-interaction theory, and determined experimentally by the optical method combining with X-ray diffractometry, and the calculated and determined phase diagrams of $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system were plotted and compared. Physical definition of each area was studied, and the physical law of characteristic point and line was explained in detail. Adjusting the pH value of neutralization-hydrolysis solution depended on the SO_4^{2-} concentration in the system. And interaction characteristics between the solubilities of $\text{CaSO}_4(\text{s})$ and $\text{Ca(OH)}_2(\text{s})$ were found out.

Key words: $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system; phase equilibrium; phase diagram; wastewater

1 Introduction

Large amounts of sulfate wastewater containing heavy metals were discharged annually for the common use of sulfate system in industries, such as electroplating, steel pickling, mining, nonferrous smelting, sulphuric acid production and alkali making [1–4]. Heavy metals belong to persistent pollutants in environment because of their high toxicity. It was considered that sulfate in water would result in a series of problems. For example, water resistance would be decreased, pipeline would be eroded directly, and recycle of sulfate reducing bacteria (SRB) and spread of biology would be influenced indirectly. Higher concentration of sulfate ion in water would lead to soil salinization. Therefore, more and more attentions have been paid to control the content of sulfate ion in water.

Nowadays, lime-milk neutralization process is regarded as a simple, cheap, efficient and sustainable technique, by which heavy metals are removed as hydroxide [5–9]. However, effluent leads to a series of problems. Purification and reutilization of industrial wastewater are limited for high concentration of calcium

ion and sulfate ion [10]. Commonly, SO_4^{2-} concentration in effluent reaches up to 2000 mg/L, which result in the formation of calcium sulfate scales and pipeline erosion.

Practically, effluent from lime-milk neutralization and precipitation process with high SO_4^{2-} concentration (1800 mg/L) is used to prepare lime milk and then to treat heavy metal wastewater. It was found that pH value of wastewater treatment system could not be adjusted to the expected value, which brought side-effect to removal of heavy metals and increased lime-milk consumption. Thus, the reason of those phenomena should be explained from the view point of thermodynamics [11]. In addition, the related parameters, such as activity, diffusion coefficient and solvent activity, are of practical interest in many environmental and industrial processes. MA et al [12] pointed out that it was feasible to precipitate CaSO_4 from $\text{Na}_2\text{SO}_4\text{--H}_2\text{O}$ system in the presence of CaO. Therefore, it is necessary to calculate, determine and analyze the phase diagram of $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system for properly adding Ca(OH)_2 and removal of SO_4^{2-} from wastewater.

At present, the most widely used calculation model for aqueous systems over a relatively high range of ionic

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strength is the Pitzer theory, which allows successful fitting of thermodynamic properties [13]. Pitzer approach permits a description of thermodynamic properties of multi-component systems in terms of both the mixed and the individual parameters of the involved components.

In this work, based on the Pitzer semi-empirical ion-interaction theory for multi-components system, the solubilities of $\text{CaSO}_4(\text{s})$ and $\text{Ca}(\text{OH})_2(\text{s})$ in $\text{CaSO}_4\text{--Ca}(\text{OH})_2\text{--H}_2\text{O}$ system are calculated, and then calculated phase diagram is plotted. In order to verify the calculation and offer precise guidance for effective removal of sulfate ion and proper addition of $\text{Ca}(\text{OH})_2$ in heavy metals wastewater with high SO_4^{2-} concentration, optical method is adopted to determine equilibrium solubility, and the determined phase diagram of $\text{CaSO}_4\text{--Ca}(\text{OH})_2\text{--H}_2\text{O}$ system is plotted.

2 Calculation of phase diagrams of $\text{CaSO}_4\text{--Ca}(\text{OH})_2\text{--H}_2\text{O}$ system

2.1 Activity coefficient model

The Pitzer activity coefficient model was applied in the calculation process, and the related equations are presented in the following.

The dissociation equilibrium is

$$K_{\text{sp1}} = \gamma_{\pm}^2 (\text{CaSO}_4) [\text{Ca}^{2+}] [\text{SO}_4^{2-}] \quad (1)$$

$$K_{\text{sp2}} = \gamma_{\pm}^3 (\text{Ca}(\text{OH})_2) [\text{Ca}^{2+}] [\text{OH}^-]^2 \quad (2)$$

where K_{sp1} is the dissociation constant of CaSO_4 ; K_{sp2} is the dissociation constant of $\text{Ca}(\text{OH})_2$; $\gamma_{\pm}^2 (\text{CaSO}_4)$ is the average activity coefficients of CaSO_4 ; $\gamma_{\pm}^3 (\text{Ca}(\text{OH})_2)$ is the average activity coefficients of $\text{Ca}(\text{OH})_2$; $[\text{Ca}^{2+}]$, $[\text{SO}_4^{2-}]$ and $[\text{OH}^-]$ are the equilibrium concentrations of Ca^{2+} , SO_4^{2-} and OH^- , respectively.

The charge conservation is

$$m(\text{Ca}^{2+}) = m(\text{SO}_4^{2-}) + \frac{1}{2} m(\text{OH}^-) \quad (3)$$

where $m(\text{Ca}^{2+})$, $m(\text{SO}_4^{2-})$ and $m(\text{OH}^-)$ are the molality in mol/kg of Ca^{2+} , SO_4^{2-} and OH^- , respectively.

The activity coefficient model for single-component points is

$$\ln \gamma_{\pm \text{MX}} = |z_{\text{M}} z_{\text{X}}| f^{\gamma} + \left(\frac{2\nu_{\text{M}} \cdot \nu_{\text{X}}}{\nu} \right) m \cdot B_{\text{MX}}^{\gamma} + \left(\frac{2(\nu_{\text{M}} \cdot \nu_{\text{X}})^{3/2}}{\nu} \right) m^2 \cdot C_{\text{MX}}^{\gamma} \quad (4)$$

The activity coefficient model for multi-component points is

$$\begin{aligned} \ln \gamma_{\pm \text{MX}} = & |z_{\text{M}} z_{\text{X}}| f^{\gamma} + (2\nu_{\text{M}} / \nu) \sum_{\text{a}} m_{\text{a}} [B_{\text{Ma}} + (\sum m z) C_{\text{Ma}} + \\ & \left(\frac{\nu_{\text{X}}}{\nu_{\text{M}}} \right) \theta_{\text{Xa}}] + (2\nu_{\text{X}} / \nu) \sum_{\text{c}} m_{\text{c}} [B_{\text{cX}} + (\sum m z) C_{\text{cX}} + \\ & \left(\frac{\nu_{\text{M}}}{\nu_{\text{X}}} \right) \theta_{\text{Mc}}] + \sum_{\text{c}} \sum_{\text{a}} m_{\text{c}} m_{\text{a}} [|z_{\text{M}} z_{\text{X}}| B'_{\text{ca}} + \\ & \frac{1}{\nu} (2\nu_{\text{M}} z_{\text{M}} C_{\text{ca}} + \nu_{\text{M}} \psi_{\text{Mca}} + \nu_{\text{X}} \psi_{\text{caX}})] + \\ & \frac{1}{2} \sum_{\text{c}} \sum_{\text{c}'} m_{\text{c}} m_{\text{c}'} \left[\frac{\nu_{\text{X}}}{\nu} \psi_{\text{ccX}} + |z_{\text{M}} z_{\text{X}}| \theta'_{\text{cc}'} \right] + \\ & \frac{1}{2} \sum_{\text{a}} \sum_{\text{a}'} m_{\text{a}} m_{\text{a}'} \left[\frac{\nu_{\text{M}}}{\nu} \psi_{\text{Maa}'} + |z_{\text{M}} z_{\text{X}}| \theta'_{\text{aa}'} \right] \quad (5) \end{aligned}$$

where MX represents electrolyte; c represents cations including M ion; a represents anions including X ion; z_{M} is the charge number of cation M; z_{X} is the charge number of anion X; ν_{M} is the amount of cation M; ν_{X} is the amount of anion X; ν is the total amount of M and X which are ionized from electrolyte MX, $\nu = \nu_{\text{M}} + \nu_{\text{X}}$; m_{c} and m_{a} represent the molality of cations c and anions a, respectively, mol/kg; θ is the Pitzer mixing parameter between two different ions with the same charge; ψ is the mixing parameter among the three ions with different charges.

$$\sum m z = \sum m_{\text{c}} z_{\text{c}} = |\sum m_{\text{a}} z_{\text{a}}|$$

$$f^{\gamma} = -A_{\phi} [I^{1/2} / (1 + 1.2I^{1/2}) + \frac{1}{0.6} \ln(1 + 1.2I^{1/2})]$$

where I is the ionic strength.

For water, $A_{\phi} = 0.392$ at 25°C , $C_{\text{ca}} = C_{\text{ca}}^{\phi} / (2|z_{\text{c}} z_{\text{a}}|^{1/2})$, $\theta' = \frac{\partial \theta}{\partial I}$.

For electrolyte containing at least one univalent ion at 25°C ,

$$\begin{aligned} B_{\text{ca}} = & \beta_{\text{ca}}^{(0)} + \beta_{\text{ca}}^{(1)} \cdot \frac{2[1 - (1 + 2I^{1/2}) \exp(-2I^{1/2})]}{(2I^{1/2})^2} \\ B'_{\text{ca}} = & \left\{ \beta_{\text{ca}}^{(1)} \cdot \frac{-2[1 - (1 + 2I^{1/2} + 4I/2) \exp(-2I^{1/2})]}{(2I^{1/2})^2} \right\} / I \end{aligned}$$

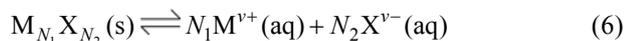
For electrolyte with bivalent-bivalent style at 25°C ,

$$\begin{aligned} B_{\text{ca}} = & \beta_{\text{ca}}^{(0)} + \beta_{\text{ca}}^{(1)} \cdot \frac{2[1 - (1 + 1.4I^{1/2}) \exp(-1.4I^{1/2})]}{(1.4I^{1/2})^2} + \\ & \beta_{\text{ca}}^{(2)} \cdot \frac{2[1 - (1 + 12I^{1/2}) \exp(-12I^{1/2})]}{(12I^{1/2})^2} \\ B'_{\text{ca}} = & \left\{ \beta_{\text{ca}}^{(1)} \cdot \frac{-2[1 - (1 + 1.4I^{1/2} + 1.4^2 I/2) \exp(-1.4I^{1/2})]}{(1.4I^{1/2})^2} + \right. \\ & \left. \beta_{\text{ca}}^{(2)} \cdot \frac{-2[1 - (1 + 12I^{1/2} + 12^2 I/2) \exp(-12I^{1/2})]}{(12I^{1/2})^2} \right\} / I \end{aligned}$$

where $\beta_{\text{ca}}^{(0)}$, $\beta_{\text{ca}}^{(1)}$ and $\beta_{\text{ca}}^{(2)}$ are character parameters of electrolyte.

2.2 Criterion for solid-liquid equilibrium

According to the chemical equilibrium principle, the dissolution equilibrium of any compound can be obtained as compound saturated in solution. The dissolution equilibrium for a given compounds (e.g. $M_{N_1}X_{N_2}$) is expressed as follows:



$$(a_{M^{v+}})^{N_1} \cdot (a_{X^{v-}})^{N_2} = K_{M_{N_1}X_{N_2}} \quad (7)$$

where α_{M^+} and α_{X^-} represent the activities of cation and anion, respectively, mol/L; K is the dissolution equilibrium constant of compound.

The solubility product of CaSO_4 is 9.1×10^{-6} and that of Ca(OH)_2 is 5.5×10^{-6} [12].

2.3 Calculation procedure

According to the Pitzer model of aqueous electrolytes, the mixing parameters were divided into two types: $\theta(i, j)$, the parameter of two ions with the same charge, and $\psi(i, j, k)$, the parameter of two ions with the same charge and an ion with opposite charge. i, j denote two definite ions with the same charge.

Calculation procedure can be summarized as follows: 1) Choice of Pitzer parameters of single electrolyte $\beta_{MX}^{(0)}$, $\beta_{MX}^{(1)}$, $\beta_{MX}^{(2)}$ and C^Φ ; 2) Choice of Pitzer ternary parameters $\{\theta_{\text{OH-SO}_4}$ and $\psi_{\text{Ca-OH-SO}_4}\}$; 3) Calculation of solubility isotherms of three-component solutions. The Pitzer model allows the determination of activity coefficients in saturated and unsaturated electrolyte solutions with an accuracy of 2%–6% [24].

The parameters of single-electrolyte and Pitzer mixing parameters of multi-component systems were determined by many researchers. The values of the Pitzer parameters for $\text{CaSO}_4(\text{aq})$ and $\text{Ca(OH)}_2(\text{aq})$, the Pitzer mixing parameters for $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system and the parameters of single-electrolyte are listed in Table 1 [16].

Table 1 Pitzer parameters of electrolyte and mixing parameters

Compound	$\beta_{\text{ca}}^{(0)}$	$\beta_{\text{ca}}^{(1)}$	$\beta_{\text{ca}}^{(2)}$	$\theta_{\text{OH-SO}_4}$	$\psi_{\text{Ca-OH-SO}_4}$
Ca(OH)_2	-0.174 7	-0.230 3	-	-0.013	0
CaSO_4	0.20	3.776 2	-58.388		

In CaSO_4 saturation area, the product P of ion activity is calculated by:

$$P = m(\text{Ca}^{2+}) \cdot m(\text{SO}_4^{2-}) \cdot \gamma_{\pm}^2(\text{CaSO}_4)$$

For Ca(OH)_2 saturation area, the product P of ion activity is calculated by:

$$P = m(\text{Ca}^{2+}) \cdot m^2(\text{OH}^-) \cdot \gamma_{\pm}^3(\text{Ca(OH)}_2)$$

The values of C^Φ for $\text{CaSO}_4(\text{aq})$ and $\text{Ca(OH)}_2(\text{aq})$

can be neglected because CaSO_4 and Ca(OH)_2 are compounds with a small solubility according to NIU et al [16].

The calculation procedure is complex that it should be completed through program shown in Fig. 1.

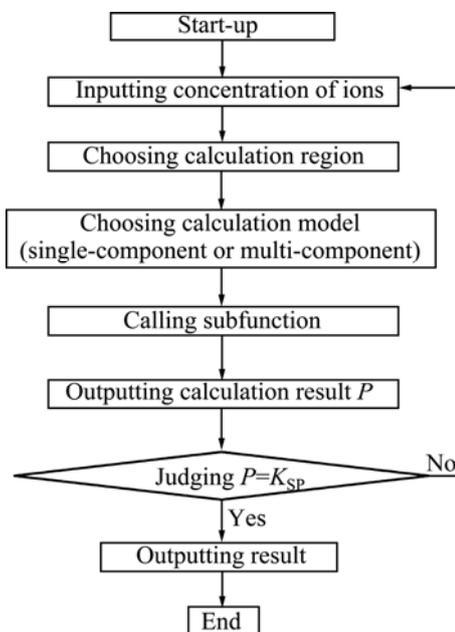


Fig. 1 Calculation procedure of activity coefficient for $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system

2.4 Calculation results

The calculated activity coefficients of compounds for $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system are listed in Table 2.

Table 2 Calculated solubility in $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system

No.	Component of liquid/%		Solid phase
	Ca(OH)_2	CaSO_4	
1	0.1841	0	Ca(OH)_2
2	0.1820	0.0272	Ca(OH)_2
3	0.1790	0.068	Ca(OH)_2
4	0.1762	0.1088	Ca(OH)_2
5	0.1743	0.1385	$\text{Ca(OH)}_2\text{--CaSO}_4\cdot 2\text{H}_2\text{O}$
6	0.148	0.1439	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$
7	0.074	0.1673	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$
8	0.037	0.1834	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$
9	0.0185	0.1944	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$
10	0	0.208	$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$

Because the solubilities of CaSO_4 and Ca(OH)_2 are very small, the values of the calculated solubility are magnified by one hundred times to plot the phase diagram of $\text{CaSO}_4\text{--Ca(OH)}_2\text{--H}_2\text{O}$ system at 298.15 K on the top of the triangle (Fig. 2).

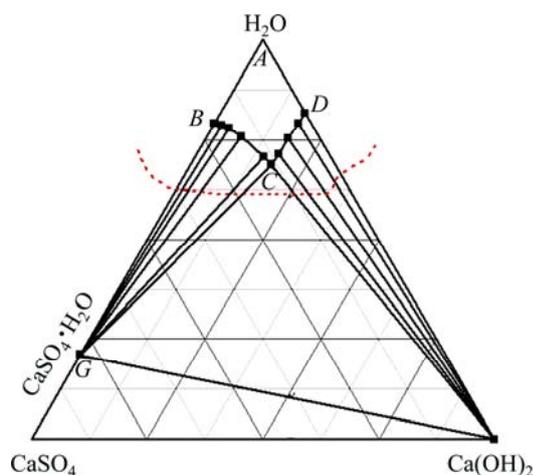


Fig. 2 Calculated phase diagram of $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system in triangle coordinate system

According to the phase rule ($F=C-P+2$) [16], the $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system is a ternary system, so the independent component number C is 3. The degree of freedom F is 4 when the system is in single-phase area, which indicates that there are four independent variables, namely temperature, pressure and relative content of two components. If the pressure keeps constantly at 101.325 kPa and temperature is controlled at 298.15 K, there are just two independent variables which are the relative contents of two components, so the rectangular coordinate can be utilized to express the phase equilibrium of $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system. The original point of coordinate represents pure H_2O , the infinite area of abscissa represents pure CaSO_4 , and the infinite area of ordinate denotes pure Ca(OH)_2 . The calculated phase diagram of $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system is shown in Fig. 3.

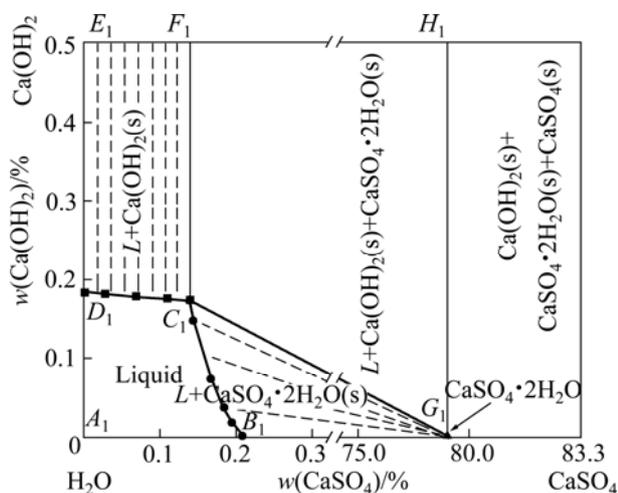


Fig. 3 Calculated phase diagram of $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system in rectangular coordinate system

The calculation shows that only the crystallization of simple salts Ca(OH)_2 and $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ is established in $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system. The solubility of single Ca(OH)_2 is 1.841 g/L and the solubility of single CaSO_4 is 2.080 g/L. The composition of invariant point is 0.1743% Ca(OH)_2 and 0.1385% CaSO_4 .

3 Experimental

3.1 Chemical reagents

The standardized solution of NaOH (0.02 mol/L) was prepared from analytical grade sodium hydroxide, EDTA standard solution was prepared from analytical grade EDTA-2Na and HCl standard solution (0.1 mol/L) was prepared from concentrated hydrochloric acid in all experiments. Besides, phenolphthalein indicator (1%), calcium carboxylic acid indicator (1%) and benzidine hydrochloride solution (8 g/L) were prepared.

3.2 Experimental procedure

3.2.1 Solution preparation

The accurately weighed calcium hydroxide and concentrated sulfuric acid were put into the iodine measuring flask with the volume of 500 mL, then 500 mL ultra pure water was added to configure a series of system points for $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system.

3.2.2 Experiment and sampling

The prepared samples were put into water and stirred by a magnetic stirrer. The temperature of the solution was controlled at 298.15 K. When the dissolution reached equilibrium, the solution was stood for 30 min, then the samples of supernatant solution were taken out for analyzing. The precipitate in the solution was detected after filtration and drying [14].

3.3 Principle of solution preparation

According to the calculated results, the saturated solubility of Ca(OH)_2 is 1.842 g/L and that of CaSO_4 is 2.080 g/L. It is necessary to ensure one of the components excessive for two-phase equilibrium points and two components excessive for co-saturated point [15]. Therefore, the Ca(OH)_2 concentration is greater than 1.842 g/L for crystallization area of Ca(OH)_2 , then the amounts of Ca(OH)_2 and ultrapure water are fixed, while the amount of CaSO_4 is changed to prepare a series of system points. Similarly, the CaSO_4 concentration is higher than 2.080 g/L for crystallization area of CaSO_4 , then the amounts of CaSO_4 and ultrapure water are fixed, while the amount of Ca(OH)_2 is altered to prepare a series of system points. The concentrations of Ca(OH)_2 and CaSO_4 are higher than 1.842 g/L and 2.080 g/L respectively for co-saturated point.

In addition, the active CaSO_4 is generated from

reaction between $\text{Ca}(\text{OH})_2$ and H_2SO_4 in order to shorten the time of dissolution equilibrium.

3.4 Original composition of solution

The original composition of solution is listed in Table 3. The samples No.1–3 are composed of fixed dosage of 2.0 g $\text{Ca}(\text{OH})_2$ and 500 mL ultrapure water, and altered dosage of CaSO_4 of 0, 0.4 and 0.8 g, respectively. The samples No.4–7 are composed of fixed dosage of 3.0 g CaSO_4 and 500 mL ultrapure water, and varied dosage of $\text{Ca}(\text{OH})_2$ of 0.5, 0.3, 0.1 and 0 g, respectively.

Table 3 Original composition of prepared solution

Solution No.	$m(\text{Ca}(\text{OH})_2)/\text{g}$	$m(\text{CaSO}_4)/\text{g}$	$V(\text{H}_2\text{O})/\text{mL}$
1	2.0	0	500
2	2.0	0.4	500
3	2.0	0.8	500
4	0.5	3.0	500
5	0.3	3.0	500
6	0.1	3.0	500
7	0	3.0	500

3.5 Determination of solid-phase composition

The X-ray diffraction (XRD, Rigaku D/max 2550VB+, Japan) was used to detect the solid phase from the solution. The composition of precipitate was confirmed by comparing with the standard patterns [16–18].

3.6 Determination of equilibrium time

The concentrations of calcium ion, sulfate ion and hydroxyl ion were determined at interval of 24 h, and the system was considered to reach equilibrium when the difference of concentration was less than 0.2% for the successive determination [19].

3.7 Determination of ion concentration in equilibrium liquid-phase composition

The sulfate ion, calcium ion and hydroxyl ion were determined by acid-base titration [20,21], sodium EDTA titration [22,23] and HCl titration, respectively.

Each sample was tested in triplicate and the mean value was presented.

4 Results

4.1 Phase composition of precipitates at equilibrium point

The XRD patterns of equilibrium solid-phase for samples No.1–7 are shown in Fig. 4.

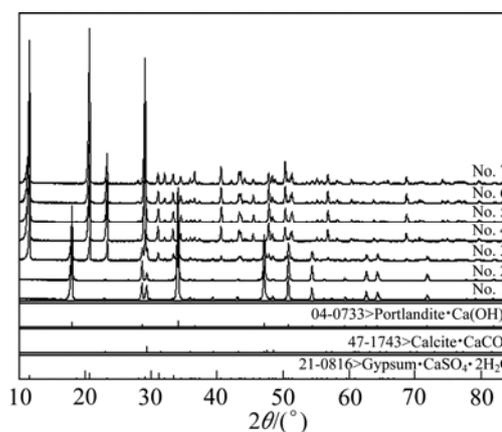


Fig. 4 XRD patterns of equilibrium solid-phase

Comparing with the standard XRD patterns, the main precipitate of samples No.1 and 2 is $\text{Ca}(\text{OH})_2$, that of No. 3 is $\text{Ca}(\text{OH})_2$ and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and that of No. 4–7 is $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. Besides, there is a few CaCO_3 in samples No. 1, 2 and 3, which results from the unavoidable reaction between a little carbon dioxide and $\text{Ca}(\text{OH})_2$. The determined equilibrium solubility of CaSO_4 – $\text{Ca}(\text{OH})_2$ – H_2O system is listed in Table 4.

Table 4 Determined phase equilibrium data of CaSO_4 – $\text{Ca}(\text{OH})_2$ – H_2O system

No.	Composition of liquid/%		Solid-phase
	$\text{Ca}(\text{OH})_2$	CaSO_4	
1	0.170	0	$\text{Ca}(\text{OH})_2$
2	0.156	0.078	$\text{Ca}(\text{OH})_2$
3	0.153	0.149	$\text{Ca}(\text{OH})_2 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
4	0.111	0.173	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
5	0.044	0.177	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
6	0.017	0.200	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
7	0	0.204	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$

4.2 Determined phase diagram of CaSO_4 – $\text{Ca}(\text{OH})_2$ – H_2O system

According to the phase equilibrium data, the phase diagram of CaSO_4 – $\text{Ca}(\text{OH})_2$ – H_2O system in triangle was determined as shown in Fig. 5. On the top of the triangle, the values of the calculated solubility was magnified by one hundred times to plot the phase diagram owing to the minor solubility of CaSO_4 and $\text{Ca}(\text{OH})_2$.

When the rectangular coordinate was used, the phase diagram of CaSO_4 – $\text{Ca}(\text{OH})_2$ – H_2O system (shown in Fig. 6) was obtained from experimental results listed in Table 4.

There is a liquid area $ABCD$ in Fig. 6, which represents the area of unsaturated solution, in which the

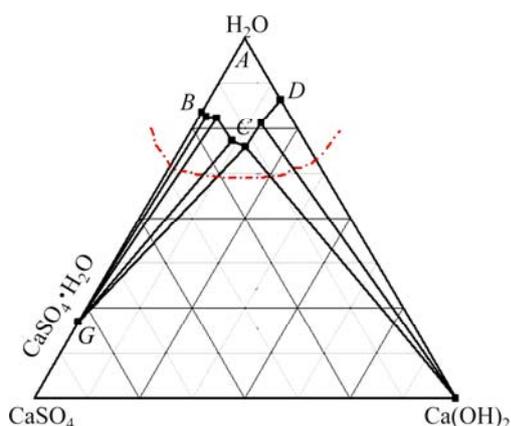


Fig. 5 Determined phase diagram of $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system in triangle coordinate system

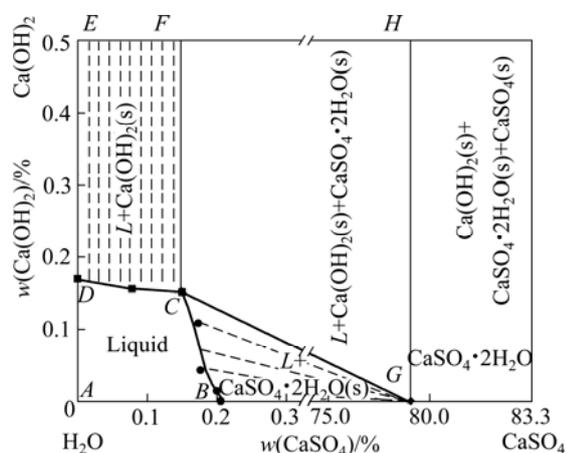


Fig. 6 Determined phase diagram of $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system in rectangular coordinate system

concentrations of both CaSO_4 and Ca(OH)_2 are in instauration, and the scope of this area is restricted by the solubility curves BC and CD . The area $EDCF$ is a two-phase area that is composed of solid Ca(OH)_2 and solution containing CaSO_4 and Ca(OH)_2 , in which solid Ca(OH)_2 is in equilibrium with solution. Line CD represents the relationship between CaSO_4 concentration and Ca(OH)_2 solubility. Area BCG is a two-phase area that is composed of solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and solution containing CaSO_4 and Ca(OH)_2 , in which solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is in equilibrium with solution. Line BC represents the relationship between Ca(OH)_2 concentration and CaSO_4 solubility. Point C is a three-phase equilibrium point, named co-saturated point, where the concentrations of Ca(OH)_2 and CaSO_4 are all saturated. The degree of freedom is zero for co-saturated point, so the composition of each equilibrium phase is constant as evaporation at this point, but the relative amount of each species would change. Area $FCGH$ is a three-phase area composed of co-saturated solution, solid Ca(OH)_2 and solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, where the co-saturated solution is in equilibrium with both solid Ca(OH)_2 and

solid $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. The right area of line HG is the mixed area of three solid phases such as Ca(OH)_2 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and CaSO_4 .

5 Discussion

The determined phase diagrams of Figs. 5 and 6 are in accordance with the calculated phase diagrams of Figs. 2 and 3, which proves that the calculation procedure is correct and the diagrams could be used to interpret and guide reuse of water containing sulfate ion.

The calculation results show that only the crystallization of simple salts Ca(OH)_2 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ is established in ternary $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system. The solubility of single Ca(OH)_2 is 1.841 g/L and that of single CaSO_4 is 2.080 g/L. The composition of invariant point is 0.1743% Ca(OH)_2 and 0.1385% CaSO_4 .

The diagrams in the rectangular coordinate (Figs. 3 and 6) consist of five areas: one single-phase area, three two-phase areas and one three-phase area. The single-phase area is an unsaturated solution area, and three two-phase areas include crystallization area of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, crystallization area of Ca(OH)_2 and coexisting area of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Ca(OH)_2 . Interaction characteristics between the solubility of $\text{CaSO}_4(\text{s})$ and $\text{Ca(OH)}_2(\text{s})$ are also obtained, which can be used to guide for treatment and reuse of water containing sulfate ion and calcium ion.

The area $FCGH$ is a three-phase equilibrium area (Fig. 6). Because the degree of freedom for $\text{CaSO}_4\text{-Ca(OH)}_2\text{-H}_2\text{O}$ system is zero, the equilibrium composition of liquid is constant and decided by co-saturated point C . So pH value of the neutralization-hydrolysis solution can not be adjusted when SO_4^{2-} concentration of neutralization-hydrolysis solution is in area $FCGH$, and pH value is constant and decided by the composition of co-saturated solution for point C . The area BCG is a two-phase equilibrium area. Because the degree of freedom is one, the equilibrium composition of liquid is decided by curve BC . Adjustment of pH value of neutralization-hydrolysis solution is decided by line BC when SO_4^{2-} concentration is in the area BCG . The area $ABCD$ is a single-phase equilibrium area. The degree of freedom is two, so pH value of neutralization-hydrolysis solution can be adjusted arbitrarily when SO_4^{2-} concentration is in the area $ABCD$, and the maximum pH value is decided by curve CD . The area $EDCF$ is a two-phase equilibrium area. The degree of freedom is one, and the equilibrium composition of liquid is decided by curve CD . Adjustment of pH value of neutralization-hydrolysis solution is decided by line CD when SO_4^{2-} concentration of neutralization-hydrolysis solution is in the area $EDCF$.

6 Conclusions

1) Adjusting the pH value of neutralization-hydrolysis solution depends on SO_4^{2-} concentration of neutralization-hydrolysis solution. The pH value cannot be adjusted as SO_4^{2-} concentration is in the three-phase equilibrium area, and pH value is constant and decided by the composition of co-saturated solution. Adjustment of pH value is decided by the solubility curve of CaSO_4 as SO_4^{2-} concentration is in the two-phase equilibrium area of liquor and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. pH value can be adjusted arbitrarily as SO_4^{2-} concentration is in the single-phase equilibrium area, and the maximum pH value is decided by the solubility curve of $\text{Ca}(\text{OH})_2$. Adjustment of pH value is decided by the solubility curve of $\text{Ca}(\text{OH})_2$ as SO_4^{2-} concentration is in the two-phase equilibrium area of liquor and $\text{Ca}(\text{OH})_2$.

2) The interaction characteristics between the solubilities of $\text{CaSO}_4(\text{s})$ and $\text{Ca}(\text{OH})_2(\text{s})$ was embodied in the points, lines and areas of phase diagram, which can provide some theoretical guidance for application of neutralization method in treating heavy metal wastewater containing high concentration of sulfate ion and purification of industrial reused water.

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CaSO₄–Ca(OH)₂–H₂O 体系相平衡

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摘要: 为了给含高浓度硫酸根离子的重金属废水中和法处理提供理论指导, 并更好地理解硫酸钙结垢的形成机制, 采用 Pitzer 电解质溶液理论计算 298.15 K 时 CaSO₄–Ca(OH)₂–H₂O 三元体系的溶解度, 并采用光学法结合 XRD 测试技术测定该体系的等温平衡溶解度, 采用计算和实验方法分别绘制相图。研究了 5 个区域的物理定义及特征点、线所表达的物理规律, 并分析了各区域 SO₄²⁻ 浓度对中和水解过程 pH 调节的影响。中和水解过程 pH 值的调节取决于体系中 SO₄²⁻ 离子的浓度。Ca(OH)₂ 与 CaSO₄·2H₂O 在水中溶解时, 相互影响的规律体现在相图中的点、线及面上。

关键词: CaSO₄–Ca(OH)₂–H₂O 体系; 相平衡; 相图; 废水

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