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Gypsum crystallization and potassium chloride regeneration by reaction of calcium chloride solution with potassium sulfate solution or solid

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Abstract: Gypsum crystallization along with the simultaneous regeneration of KCl was investigated by the reaction of CaCl₂ solution with K₂SO₄. Well developed sheet structure gypsum crystals were produced when K₂SO₄ solution was added into the CaCl₂ solution by slow titration or in multiple stages over 2–8 h followed by 2 h equilibration. In order to regenerate KCl solution as concentrated as possible, K₂SO₄ solid was added into the given CaCl₂ solution instead of K₂SO₄ solution, obtaining gypsum crystals with almost the same quality by multistage addition with $[SO_4^{2^-}]/[Ca^{2^+}]$ molar ratio no larger than 0.8. However, impurity of K₂SO₄·CaSO₄·H₂O was detected by XRD and was further confirmed by SEM-EDS in the produced crystals when the $[SO_4^{2^-}]/[Ca^{2^+}]$ ratio increased to 1.1. It is proved that appearance of the double sulfate is attributed to the relatively high concentration of K₂SO₄ even at the expense of low calcium removal rate.

Key words: crystallization; gypsum; KCl regeneration; calcium removal

1 Introduction

Potassium chloride is one of the most important potassium fertilizers, and also is the major raw material of non-chloride potassium fertilizers. In the past four years, it is remarkable that price of KCl have been increased by about 1 000 yuan per ton, while the price of K_2SO_4 only increased by about 200–250 yuan per ton. Moreover, the effective potassium content of KCl is higher than that of the same amount of K_2SO_4 .

On the other hand, CaCl₂ is a common impurity in the industrial practice of KCl production. A typical example is: in the process of recovering KCl from the electrostatic precipitator sintering dust of iron and steel making by water leaching[1–2], KCl, NaCl and CaCl₂ are detected as the three major constituents in the water leaching solution. Undoubtedly adverse effect of CaCl₂ on quality of KCl product would be caused if the mixture solution was directly evaporated and crystallized for KCl recovery. So, it is necessary to remove Ca²⁺ first. In view of the situation analysis mentioned above, an alternative precipitating agent K_2SO_4 is thus selected according to the following reaction:

$$CaCl_{2}(aq)+K_{2}SO_{4}(aq \text{ or } s)+2H_{2}O \longrightarrow$$

$$CaSO_{4}\cdot 2H_{2}O(s)+2KCl(aq)$$
(1)

Taking K_2SO_4 as the precipitator, not only Ca^{2+} concentration could be decreased, but potassium could be finally left in the solution and be regenerated in the form of KCl, which is suitable for those systems which aim at obtaining pure KCl and are obsessed with impurity of CaCl₂.

AL-OTHMAN and DEMOPOULOS[3] did some work on gypsum crystallization and HCl regeneration by reaction of CaCl₂ solution with H_2SO_4 in a relatively concentrated CaCl₂ solution of 3–3.5 mol/L with 2.6–8 mol/L H_2SO_4 as precipitating agent[3], which shows higher requirement to the equipments compared with a neutral system.

In industrial practice, crystallization process will be followed by solid-liquid separation in order to obtain the final product. The energy consumption in such operation is a decisive factor that depends on the properties of the

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crystals produced[4]. The crystal quality can be improved by supersaturation control[5–7]. In this work, supersaturation is controlled by the addition method of K_2SO_4 solution or solid.

The objective of this work is to systematically investigate the different reaction conditions such as rate of K_2SO_4 addition, $CaCl_2$ and K_2SO_4 concentration, temperature and stirring speed on the quality of produced crystals. Meanwhile, it is also very important to regenerate KCl as concentrated as possible and check the Ca^{2+} concentration in the end of the reaction. In order to purify the KCl solution, Ca^{2+} concentration is better to be decreased to the lowest. However, it is found impracticable to decrease Ca^{2+} concentration and at the same time increase KCl concentration by adding excessive K_2SO_4 solid into the given $CaCl_2$ solution.

2 Experimental

All the experiments were performed at constant temperature range of 20–60 $^{\circ}$ C using 1 L Pyrex, baffled reactor equipped with an agitator and a temperature controller.

In the first part of the work, K₂SO₄ solution with a limited dosage was added into the given CaCl₂ solution under different conditions: variable addition rate, variable concentration in the range of 0.2-0.4 mol/L, different total molar ratio of $[SO_4^{2^-}]$ to $[Ca^{2^+}]$ either 0.6 or 0.8, whereas calcium chloride solution (200 mL) was in the concentration range of 0.90-0.99 mol/L. These conditions were chosen in such a way to keep always an amount of unreacted calcium chloride in the final solution to suppress the solubility of CaSO₄ in the regenerated solution[8]. When different K₂SO₄ solution concentrations were used, the solution was added in different volumes to ensure always that the same amount of solids was produced in all experiments. The addition time of the K₂SO₄ solution was varied between two cases that all the solution was added at once and up to 4 h of addition either by titration or in small doses (stages). After the addition of the K₂SO₄ solution, the mixture obtained was continued to be agitated at constant temperature for the purpose of crystal ripening. This equilibration period was varied from 0 to 8 h. The effect of temperature and stirring speed on crystal quality was as well examined in the range of 20–60 $^{\circ}$ C and 0–300 r/min, respectively. All the produced crystals were observed by SEM (Scanning electron microscopy) in an appliance of JSM-35F; and concentrations of K^+ and Ca^{2+} in the solution were measured by flame photometer FP640 and titration with EDTA respectively. Calcium removal is the molar fraction of Ca²⁺ removed through the production of gypsum.

In the second part, to obtain an ideal KCl

concentration in the regenerated solution, K₂SO₄ solid instead of solution was added into the given CaCl₂ solution under the optimized condition in the first part of the work. Variation of Ca²⁺ concentration in the solution under different addition stages was monitored by sampling. In addition, in an attempt to decrease Ca²⁺ concentration in the solution as low as possible, $[SO_4^{2^-}]/[Ca^{2^+}]$ ratio was increased on purpose, of which KCl concentration regenerated was compared with the theoretical value calculated based on the stoichiometry of the chemical reaction presented in Eq.(1). Then, XRD (X-ray diffractometry) and SEM-EDS (Scanning electron microscopy with X-ray energy dispersive spectrometry) were resorted to explain the deviation between the practical KCl concentration in the regenerated solution with the theoretical value using an appliance model M21 from MAC Co. Ltd, Japan for XRD and CAMBRIDGE S-360, Tracer Northern for SEM-EDS.

3 Results and discussion

3.1 Effect of concentration of K₂SO₄ solution

The concentration of the precipitating agent (in this case, K_2SO_4) and the addition method have a great impact on supersaturation, hence, on the quality of produced crystals[9], which is better seen by referring to Eq.(2):

$$S = \frac{a_{\text{Ca}} \cdot a_{\text{SO}_4} \cdot a_{\text{H}_2\text{O}}^2}{K_{\text{sp}}} \approx \frac{c(\text{Ca}) \cdot c(\text{SO}_4)}{K_{\text{sp}}}$$
(2)

where *S* is the saturation ratio[5], *a* and *c* are activity and concentration respectively, and K_{sp} is the solubility product of gypsum.

One of the objectives of this work is the regeneration of KCl out of the CaCl₂ solution. For a given concentration of CaCl₂ solution, it is obvious that K_2SO_4 should be used as concentrated as possible, even in the solid phase, which will be discussed in the later Here, K₂SO₄ solution with different sections. concentrations was investigated as titrant to precipitate the calcium ions. The morphologies of obtained gypsum crystal at different initial concentrations of K2SO4 solution are shown in Fig.1. As expected, particle size of the gypsum obtained with 0.2 mol/L K₂SO₄ as titrant is to some extent larger than that with 0.6 mol/L K₂SO₄, which can also be explained by Eq.(2). Higher titrant concentration decides higher supersaturation degree, thus a large number of crystal nucleus were produced instantaneously, eventually leading to small crystal particle. The measured settling rates of the crystals obtained with initial titrant concentrations of 0.2, 0.4 and 0.6 mol/L are 30, 20 and 7.5 cm/h, respectively (see Table 1), which is probably due to the decrease of crystal



Fig.1 Effect of K₂SO₄ concentration on gypsum crystal morphology: (a) 0.2 mol/L (b) 0.6 mol/L (Conditions: 200 mL 0.95 mol/L CaCl₂, titration for 2 h followed by 2 h equilibration, $[SO_4^{2-}]/[Ca^{2+}]$ ratio 0.6, 20 °C)

 $\label{eq:solution} \mbox{Table 1} \ \mbox{Effect of concentration of K_2SO_4$ solution on settling} \\ \mbox{rate and calcium removal} \\$

$\begin{array}{c} Concentration \ of \ K_2 SO_4 \\ solution/(mol \cdot L^{-1}) \end{array}$	Settling rate/ $(cm \cdot h^{-1})$	Ca ²⁺ removal/%
0.2	30.0	54.1
0.4	20.0	55.5
0.6	7.5	56.3

particle size with elevation of the titrant concentration.

3.2 Effect of addition method

Three methods of K_2SO_4 addition were investigated: all the precipitating agent added at once, K_2SO_4 solution added by titration and added in stages. In all the cases, the XRD analysis of the crystals obtained confirmed the presence of only gypsum (DH phase).

The effects of addition method of K_2SO_4 solution on the induction time, settling rate and calcium removal are listed in Table 2. And SEM morphologies of the produced gypsum with different addition methods are shown in Fig.2.

Since induction period is considerably affected by

Table 2 Effect of addition method of K_2SO_4 solution on induction time, settling rate and calcium removal (Conditions: 381.0 mL of 0.4 mol/L K_2SO_4 added to 200 mL 0.95 mol/L CaCl₂ at $[SO_4^{2-1}]/[Ca^{2+1}]$ of 0.8 at 20 °C)

Addition method	Induction time/min	Settling rate/ (cm·h ⁻¹)	Calcium removal/%	
Added at once	0.8	-	66.6	
Titration 1 h	8.0	8	75.2	
Titration 2 h	12.0	15	75.6	
Titration 4 h	21.0	30	75.8	



Fig.2 SEM morphologies of produced gypsum with K_2SO_4 solution added at once (a) and titration for 2 h (b) (Conditions: 381.0 mL of 0.4 mol/L K_2SO_4 added to 200 mL 0.95 mol/L CaCl₂ at $[SO_4^{2-}]/[Ca^{2+}]$ of 0.8 at 20 °C)

the level of supersaturation[10], the induction time examined in this test showed the expected results. When the precipitating solution was added by titration, the settling rate of the crystals increased with longer addition time, and the calcium removal increased as well. For example, the setting rate was increased from 8 cm/h when the K_2SO_4 solution was added by 1 h titration to 30 cm/h with 4 h of titration, and the calcium removal increased from 66.6% when all the K_2SO_4 solution was added at once to 75.8% with 4 h titration. The improved results with titration can be understood upon evaluation of their crystal size and morphological characteristics in

Fig.2.

It is clear that, when K_2SO_4 solution was added at once, the clustered gypsum crystals, with a "broom" appearance, were obtained, as shown in Fig.2(a). However, the crystals obtained with gradual addition of the solution, i.e. by titration for 2 h as seen in Fig.2(b) or by 4 h of titration (not shown) were well developed and dispersed. Since there was no much difference in gypsum crystal and calcium removal between 2 and 4 h titration, it was decided to conduct most of the subsequent titration tests with 2 h addition period of K_2SO_4 solution.

On the other hand, equilibration time has a noticeable effect on the crystal morphological characteristic, as shown in Fig.3. It can be easily seen that equilibration benefits crystal ripening[10].



Fig.3 Effect of equilibration on gypsum crystal morphology: (a) Without equilibration; (b) 2 h of equilibration (Conditions: 285.8 mL of 0.4 mol/L K₂SO₄ added to 200 mL 0.95 mol/L CaCl₂ at $[SO_4^{2^-}]/[Ca^{2^+}]$ of 0.6 at 20 °C)

3.3 Effect of temperature

The effect of temperature on the morphology of produced gypsum is illustrated in Fig.4. As shown in Fig.4, the particle size of the crystal increases with temperature increasing, which is due to the increase in growth rate. So, it is not difficult to understand the increase of solid settling rate with temperature increasing. The result obtained is the same as that of some researches done in gypsum crystallization by reaction of calcium chloride solution with sulfuric acid[3].

The temperature range investigated is just 20-60 °C, so, further examination is needed beyond this temperature range in the future work. Researchers have done a lot of works on the phase conversion of calcium sulfate dihydrate to hemihydrates or anhydrate in various



Fig.4 Effect of temperature on gypsum crystal morphology: (a) 20 °C; (b) 40 °C; (c) 60 °C (Conditions: 382 mL of 0.4 mol/L K₂SO₄ added to 200 mL 0.95 mol/L CaCl₂ for 2 h followed by 2 h equilibration at $[SO_4^{2^-}]/[Ca^{2^+}]$ of 0.8)

systems as temperature elevated. MARSHALL and SLUSHER[11] investigated thermodynamics of calcium sulfate dihydrate in aqueous sodium chloride solutions in temperature range of 0-110 °C, finding that no phase conversion of calcium sulfate in this temperature range.

3.4 Effect of stirring speed

In the crystallization process, stirring is another important factor affecting quality of the crystal obtained. A fast stirring speed may break crystals into fragments, narrow the metastable region and increase secondary nucleation rate, causing crystal particles with small size. And too slow stirring is not advantageous for slurry suspension. On the other hand, approximate stirring intensity favors the diffusion of molecules, eliminating partial over-concentration and benefitting the formation of even supersaturation degree. Effect of stirring speed on the morphology of the produced gypsum in this test was investigated and the results are shown in Fig.5. It can be clearly seen that the needle like crystal clusters are obtained when no stirring is taken. However, when stirring speed is 300 r/min, the crystals seem to be broken. So, 200 r/min is considered as a proper stirring speed.

3.5 Step-wise addition method

It is demonstrated that good quality gypsum crystal is produced by titration method under proper condition; however, it is not so suitable for industrial application as step-wise addition method[5]. With dual purpose of verifying that the step-wise method gives equivalent results to titration and determining the optimum number of steps (or stages) required to approximate the titration procedure, a new set of tests was conducted. In each experiment, 2 h of equilibration was applied after the limited reactant was consumed. The results in terms of crystal quality, settling rate and calcium removal are shown in Fig.6 and Table 3, respectively.

It can be clearly seen that the produced gypsum has a larger particle size and a smoother surface with increasing addition stages. Furthermore, the settling rate increases apparently from 10 cm/h at 1 stage to 48 cm/h at 6 stages, which is equivalent to the settling rate value of titration addition method, as shown in Table 3. In addition, almost the same calcium removal is obtained in staged addition with that of titration addition method,



Fig.5 Effect of stirring speed on morphology of produced gypsum: (a) 0 r/min; (b) 100 r/min; (c) 200 r/min; (d) 300 r/min (Conditions: 382 mL of 0.4 mol/L K₂SO₄ added to 200 mL 0.95 mol/L CaCl₂ for 2 h followed by 2 h equilibration at 40 °C with $[SO_4^{2^-}]/[Ca^{2^+}]$ of 0.8)





Fig.6 Gypsum morphology at different addition stages: (a) 1 stage; (b) 2 stages; (c) 4 stages; (d) 6 stages (Conditions: 381 mL of 0.4 mol/L K₂SO₄ added to 200 mL 0.95 mol/L CaCl₂ over period of 2 h by staged addition at 40 °C with $[SO_4^{2-}]/[Ca^{2+}]$ of 0.8 and 2 h equilibration)

Table 3 Results of titration vs staged addition of K₂SO₄ solution

Addition method	Settling rate/(cm \cdot h ⁻¹)	Ca ²⁺ removal/%
4 h titration	48	75.8
1 stage	10	74.4
2 stages	20	74.2
4 stages	30	75.1
6 stages	48	75.6

Conditions: 381 mL of 0.4 mol/L K2SO4 added to 200 mL 0.95 mol/L CaCl2 over period of 2 h by staged addition at 40 °C with [SO₄²⁻]/[Ca²⁺] of 0.8 and 2 h equilibration.

confirming that it is feasible to take the step-wise addition method.

As discussed above, concentration of KCl regenerated from the reaction system is another very important term needed to pay great attention. On the other hand, concentration of the regenerated KCl is dependent on the concentration of K₂SO₄ added. As we know, concentration of saturated K₂SO₄ solution at room temperature is less than 0.7 mol/L, which decides that volume of the reaction system will be enlarged to a large extent if K₂SO₄ solution is taken as the precipitating agent of the calcium ions. So, it was decided to use K₂SO₄ in the form of solid. The step-wise addition method tests were also done with K2SO4 solid to precipitate the calcium ions, indicating that quality of crystals obtained was as good as that of crystals obtained with K₂SO₄ solution (figures not shown). In view of a dissolution process of K₂SO₄ solid before reacting with $CaCl_2$, concentration of Ca^{2+} in the system is monitored with the passage of time at 1, 4 and 6 addition stages to investigate the equilibration time. The results are shown in Fig.7.

It is evident from Fig.7 that Ca²⁺ concentration decreases sharply when K₂SO₄ was added at once into the CaCl₂ solution, and it decreases periodically and slowly when the same amount of K₂SO₄ was added in 4 and 6 stages. The more the stages are divided into, the closer the concentration-time curve to the equilibration curve is, which can also be explained by Eq.(2), and thus it is not difficult to understand the gradual increase of



Fig.7 Concentration of Ca^{2+} vs time (Conditions: 33.3 g K₂SO₄ added to 200 mL 0.96 mol/L CaCl₂ in 1, 4 and 6 stages within 2 h followed by another 2 h equilibration with $[SO_4^{2-}]/[Ca^{2+}]$ of 1.0 at 40 °C)

particle size of the produced crystal with increasing addition stages.

3.6 KCl regeneration

As mentioned earlier, one of the objectives of this work is to regenerate KCl from CaCl₂ solutions by reaction with K₂SO₄. Fig.8 compares the theoretical KCl concentration with the actual one obtained from different $[SO_4^{2^-}]/[Ca^{2^+}]$ ratios used to treat 200 mL 0.99 mol/L CaCl₂ at 40 °C. The theoretical concentration was calculated based on the stoichiometry of the chemical reaction presented in Eq.(1), assuming that all K₂SO₄ solid reacted and neglecting the volume variation brought by the addition of K₂SO₄ solid and the production of the precipitum.

As expected, Ca²⁺ concentration firstly decreased



Fig.8 Actual and theoretical KCl concentration in regenerated solutions obtained at different $[SO_4^{2^-}]/[Ca^{2^+}]$ ratios (Conditions: K₂SO₄ solid added to 200 mL 0.99 mol/L CaCl₂ solution at 40 °C)

and then kept constant with increase of $[SO_4^{2^-}]/[Ca^{2^+}]$ ratio, as shown in Table 4, partly because the solubility of gypsum increases with ionic intensity increasing in the solution. However, the actual KCl concentration did not increase with the increase of [SO42-]/[Ca2+] ratio from 0.8 to 1.4, even deviated from the theoretical value farther and farther, as shown in Fig.8, which is unexpected. In addition, the higher the initial CaCl₂ concentration, the smaller the $[SO_4^{2^-}]/[Ca^{2^+}]$ ratio which resulted in no derivation. To find out where the potassium went, XRD and SEM-EDS were resorted to analyze the obtained crystal. The XRD analysis was done to the crystals obtained by reaction of the given CaCl₂ solution with K₂SO₄ solution or solid at different $[SO_4^{2^-}]/[Ca^{2^+}]$ ratios. The results are shown in Fig.9. As illustrated in Fig.9, only gypsum phase was observed no matter K₂SO₄ solution or solid was added when $[SO_4^{2^-}]/[Ca^{2^+}]$ was kept at 0.8; while a new phase syngenite $(K_2SO_4 \cdot CaSO_4 \cdot H_2O)[12]$ appeared when the $[SO_4^{2^-}]/[Ca^{2^+}]$ was 1.1. Now, it is easy to understand that KCl cannot be regenerated completely in the solution with $[SO_4^{2^-}]/[Ca^{2^+}]$ increasing. For further verification of the new phase appearance, the produced crystal sample corresponding to Fig.9(c) was also subjected to SEM-EDS analysis. The results are shown in Fig.10. It can be clearly seen that there are some small pieces of particles consisting of calcium, potassium, sulfur, oxygen and hydrogen (element hydrogen cannot be detected using the present analyzer) attached on the surface of rodlike crystals of gypsum.

Table4 Ca^{2+} concentrationvariationwithincreasing $[SO_4^{2^-}]/[Ca^{2^+}]$ ratios (initial Ca^{2+} concentration of 0.99 mol/L)

Initial [SO ₄ ²⁻]/[Ca ²⁺]	Final Ca ²⁺ concentration
0.56	0.454
0.65	0.372
0.80	0.117
0.90	0.071
1.00	0.088
1.10	0.082
1.20	0.086
1.40	0.086

Double sulfates of potassium and calcium including K_2SO_4 ·CaSO₄·H₂O, K_2SO_4 ·2CaSO₄·3H₂O and K_2SO_4 ·5CaSO₄·H₂O have been studied by many investigators as early as 1850s[13–15]. And the equilibrium conditions at different temperatures have been determined. ANDERSON and NESTELL[16] pointed out that required concentration of potassium sulfate for the equilibrium represented by the following equations varies with temperature:



Fig.9 XRD analysis results of crystals obtained by reaction of 200 mL 0.99 mol/L CaCl₂ solution with 0.4 mol/L K₂SO₄ solution with $[SO_4^{2^-}]/[Ca^{2^+}]$ of 0.8 (a), K₂SO₄ solid with $[SO_4^{2^-}]/[Ca^{2^+}]$ of 0.8 (b), and K₂SO₄ solid with $[SO_4^{2^-}]/[Ca^{2^+}]$ of 1.1 (c)

$$5(CaSO_4 \cdot 2H_2O) + K_2SO_4 \rightarrow K_2SO_4 \cdot 5CaSO_4 \cdot H_2O + 9H_2O$$
(3)

$$K_{2}SO_{4} \cdot 5CaSO_{4} \cdot H_{2}O + 4K_{2}SO_{4} + 4H_{2}O \rightarrow 5(K_{2}SO_{4} \cdot CaSO_{4} \cdot H_{2}O)$$

$$(4)$$

As a result, if K_2SO_4 was selected as precipitating agent to remove Ca^{2+} in the solution, it is essential to appropriately control the addition amount of K_2SO_4 , and



Fig.10 SEM-EDS analysis results of cystal obtained by reaction of 200 mL 0.99 mol/L CaCl₂ solution with K_2SO_4 solid with $[SO_4^{2-}]/[Ca^{2+}]$ of 1.1

make sure that the Ca^{2+} is in excess in the solution, especially for the solution which itself contains a certain concentration of K^+ .

4 Conclusions

1) Crystallization chemistry reaction of CaCl₂ (0.47–0.99 mol/L)-K₂SO₄ (0.2–0.6 mol/L) can be controlled in such a way that the production of well-grown and clean gypsum (CaSO₄·2H₂O) crystals is obtained with the simultaneous regeneration of KCl in the temperature range of 20–60 $^{\circ}$ C.

2) Well-developed sheet structure gypsum crystals are achieved through supersaturation control by addition of K_2SO_4 solution or solid in titration or multiple stages. Gypsum crystals grow with increasing addition stages and temperature in the range of 20–60 °C. Stirring speed of 200 r/min is optimized as the proper speed in this

reaction system.

3) K₂SO₄ solid instead of K₂SO₄ solution can also precipitate Ca²⁺ and produce good quality gypsum crystals by multiple stage addition with $[SO_4^{2^-}]/[Ca^{2^+}]$ less than 0.8. But K₂SO₄·CaSO₄·H₂O is detected when $[SO_4^{2^-}]/[Ca^{2^+}]$ is increased to 1.1 with the help of XRD and SEM-EDS. Appearance of the double sulfate is attributed to the relatively high concentration of K₂SO₄, so it is essential to properly control the $[SO_4^{2^-}]/[Ca^{2^+}]$ ratio and make sure $[Ca^{2^+}]$ in excess to suppress the solubility of CaSO₄ even at the expense of low calcium removal percentage.

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