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Crystallization Routes and Metastability of α-Calcium Sulfate Hemihydrate in Potassium Chloride Solutions under Atmospheric Pressure

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The phase transitions of α-calcium sulfate hemihydrate (α-HH) in KCl solutions were studied at (80 to 105) °C under atmospheric pressure in an attempt to estimate the metastability of α-HH and to sketch out the routes for α-HH's hydration, dehydration, or recrystallization. The crystal water content and morphology of the product during the reaction period were comprehensively examined. It was found that the metastability of α-HH heavily relied on KCl concentration and temperature. The phase transition of α-HH is successfully outlined as a function of KCl concentration and temperature. Calcium sulfate dihydrate (DH) is stable in region I and metastable in region III. Anhydrite (AH) is stable in regions III and IV and coexists with goergeyite. HH is metastable in only region II. The results show that α-HH tends to hydrate or dehydrate in KCl solution, but there is still a narrow metastable region for α-HH crystallization in which KCl concentration and temperature are strictly limited.

Introduction

Calcium sulfate mainly exists in the forms of calcium sulfate dihydrate (DH), hemihydrate (HH), and anhydrite (AH). HH has two forms, namely, *β*-HH and α-HH. The former is usually used in the construction industry, whereas the latter has been applied in comprehensive areas such as precision instrument molds, ceramics, industrial arts, and architecture because of its superior workability and high strength. α-HH is produced from DH by processes of solid autoclaving or slurry autoclaving in industry.[1] Another process of preparation of α-HH is the salt solution method, which appears to be more attractive for its conditions of atmospheric pressure and mild temperature.[2,3] Unfortunately, it has not been applied in industry for its crudeness.

The three $CaSO_4$ modifications have solubilities that vary under various salt solutions, and transitions from one phase to the other have been observed. The $CaSO_4-H_2O$ system[4] and $CaSO_4-H_3PO_4-H_2O$ system[5] have previously been focused on. Little attention has been paid to other electrolyte aqueous solution systems (such as $H_2SO_4-H_2O$ and chloride electrolytes).

For the $CaSO_4-H_2O$ system, van't Hoff and coworkers[6] reported that the transition temperature between DH and AH was 63.5 °C, whereas the transition point of DH into HH was determined to be 107.2 °C. Afterward, Hardie[7] reported the transition temperature of DH−AH to be 58 °C. His results were supported by Raju and Atkinson's research work.[8]

The phase-transition rules of three $CaSO_4$ phases in the $H_3PO_3-H_2O$ system were expressed via equilibrium diagrams, which have been applied to the phosphoric acid industry.[9] Recently, Ling[10,11] gained solubility data for calcium sulfates in the $H_2SO_4-H_2O$ system by a dissolution equilibrium method and obtained phase equilibrium diagrams. Later on, Li developed a chemical model for the solubilities of calcium sulfate phases in the $HCl-CaCl_2-H_2O$ system and established phase equilibrium diagrams in which the temperature region for forming α-HH under atmospheric pressure was presented. On the basis of the diagrams, DH was converted to metastable α-HH via metastable/stable calcium sulfate AH. As for the $KCl-CaSO_4-H_2O$ system, Li[15] reported that pure α-HH could be prepared in KCl solution with or without additives. In contrast, Marinkovic and Kostic-Pulek[16] showed that the product obtained in 1.0 M KCl solution was *β*-HH, and α-HH mixed with potassium pentacalcium sulfate monohydrate (goergeyite, Go) was the product in more concentrated KCl solution ((1.5 to 4) M). No explanation of the difference between their results was offered.

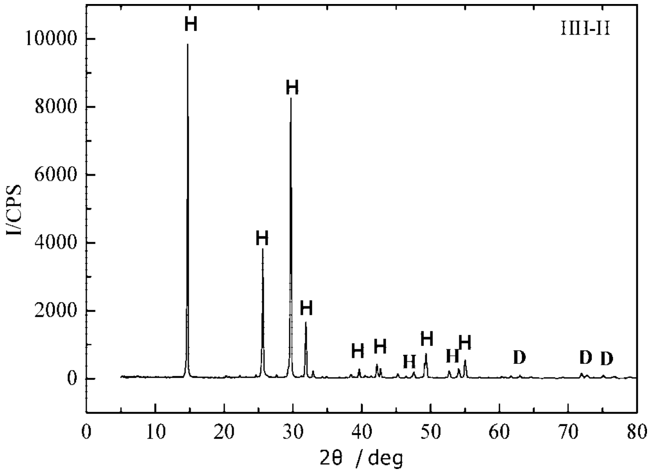

Figure 1. XRD pattern of raw α-calcium sulfate hemihydrate (α-HH): H, hemihydrate; D, calcium sulfate dihydrate (DH).

Though investigators have drawn curves that separate the areas of $CaSO_4$ phases on a plot of electrolyte concentration versus temperature by solubility measurements or dissolution equilibrium, the phase transitions of three $CaSO_4$ phases are still obscure, and the metastability of α-HH is uncertain in KCl aqueous solution. Moreover, the discrepancy of phase transition on the basis of the solubility data should be taken into account when the diagram is applied to industry. In this article, considering the scarcity of information on $CaSO_4$ phase transi-

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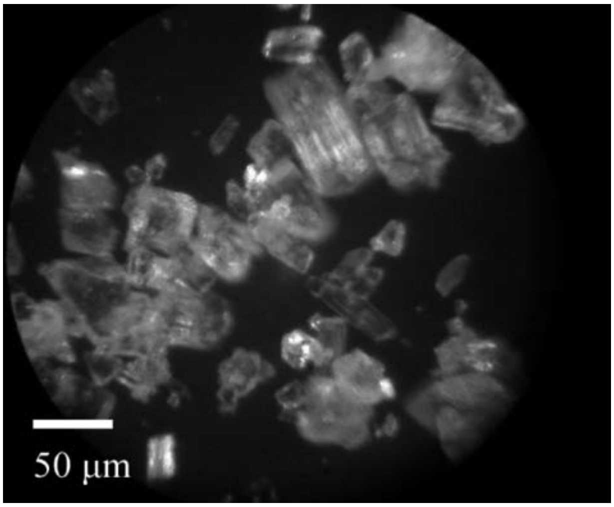


Figure 2. Morphology of raw α-calcium sulfate hemihydrate (α-HH).

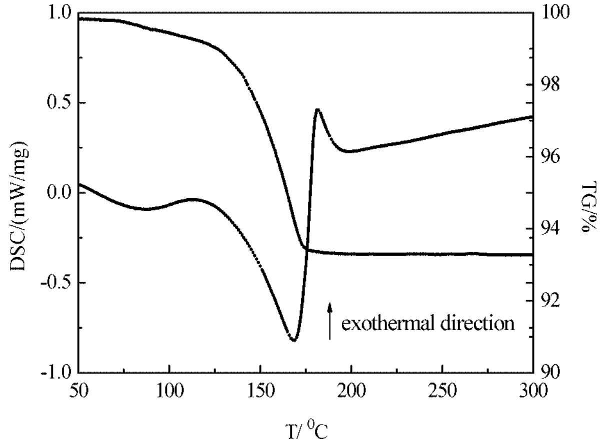


Figure 3. TG/DSC curves of raw α-calcium sulfate hemihydrate (α-HH).

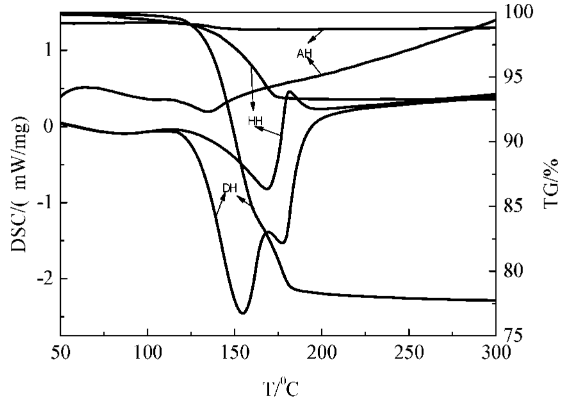
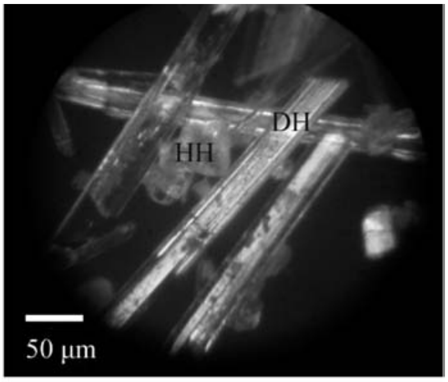


Figure 4. Typical TG/DSC curves for calcium sulfate dihydrate (DH), α-calcium sulfate hemihydrate (α-HH), and calcium sulfate anhydrite (AH).

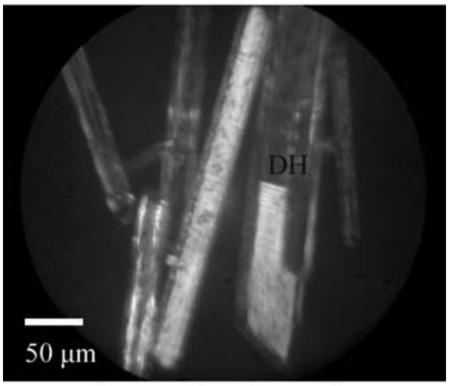
tion and its stability in KCl solution, we mixed α-HH in KCl solution to gain its phase-transition processes. The three $CaSO_4$ phases are plotted as a function of electrolyte concentration and temperature under atmospheric pressure, and more attention is paid to the metastability of α-HH.

Experimental Section

Chemicals. KCl aqueous solution was prepared using reagent grade with deionized water in all experiments. The KCl was produced by the Sinopharm Chemical Reagent Co. Ltd. (P. R. China).



a. reaction time: 1h



b. reaction time: 6h

Figure 5. Morphology variation of crystals during the transformation from α-calcium sulfate hemihydrate (α-HH) to calcium sulfate dihydrate (DH) in 2.0 wt % KCl solution at 90 °C.

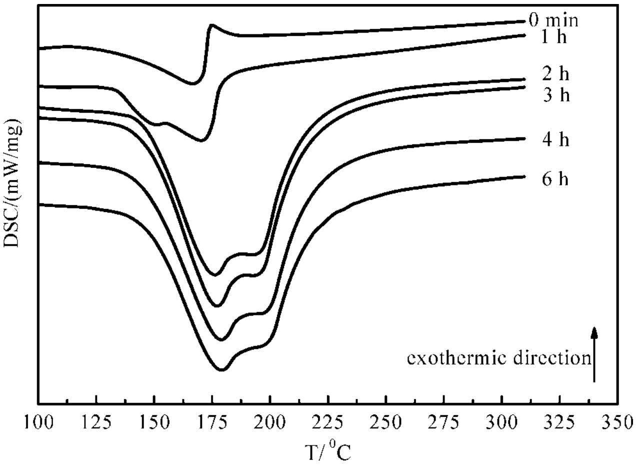


Figure 6. DSC curves for α-calcium sulfate hemihydrate (α-HH) hydration to calcium sulfate dihydrate (DH) in 2.0 wt % KCl solution at 90 °C.

The raw material was prepared via a solid autoclaving method in the Jinxin Construction Material Co. Ltd. (Shandong, P. R. China). Its X-ray diffraction (XRD) pattern is shown in Figure 1. It indicates that HH is almost the only mineral except for a trace amount of DH in the raw material. Figure 2 shows a typical morphology of α-HH with short columnar or prism shape and a volume mean particle size of 30 μm. Furthermore, TG/DSC curves (Figure 3) confirm the raw material to be α-HH because the DSC pattern shows an endothermic peak at 165 °C, followed by an exothermic peak at 175 °C, and the crystal water content is about 6.5 %. According to XRD and TG/DSC analysis, the

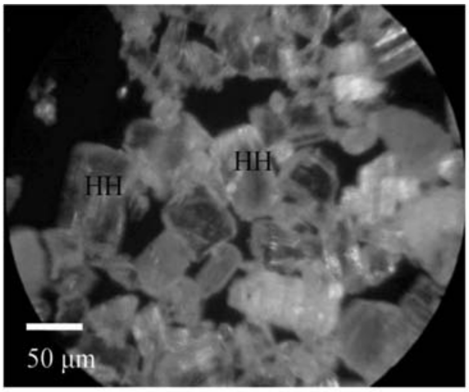
Table 1. Variation of Crystal Water Content in the Process of α-Calcium Sulfate Hemihydrate (α-HH) Hydrating to Calcium Sulfate Dihydrate (DH)

transformation conditions		crystal water content/%						
temp/°C	KCl concentration/wt %	initial time	after 30 min	after 1 h	after 2 h	after 3 h	after 4 h	after 6 h
80	0.0	6.43	6.69	7.97	12.74	18.86	19.89	20.06
	5.0	6.26	19.23	20.10	20.51	20.46	20.34	20.40
	8.0	6.20	19.41	19.56	19.73	19.71	19.73	19.66
85	0.0	6.56	6.67	6.74	8.02	9.20	10.52	14.38
	3.0	6.26		19.40	19.90	19.69	19.83	19.64
90	0.0	6.52	6.62	6.65	6.69	7.05	7.79	10.46
	2.0	5.70	6.10	11.19	17.57	20.19	20.14	20.38
95	0.0	5.98	6.02	6.04	6.15	6.32	6.38	6.56
	0.5	5.51	5.54	5.28	5.50	5.73	6.47	7.00
	1.0	5.65	5.51	5.59	5.68	6.24	6.36	6.44
100	0.0	6.12		5.79	5.98		5.86	5.82
	0.5	6.01		6.07	5.98		5.81	6.08

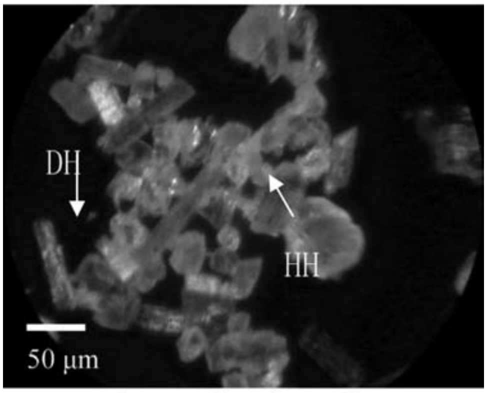
mass percentage of α-HH in the raw material is up to 95 %. Here the typical DSC patterns of DH, HH, and AH are given in Figure 4.

Procedures. The experiments were carried out in a 1.5 L five-necked double-jacketed glass reactor. The glass reactor was equipped with a reflux condenser for vapor reflux and a Teflon stirrer for obtaining a homogeneous suspension. The reactor was heated by circulating hot oil through the double walls. The temperature of the suspension was monitored by a thermometer inserted into the reactor, and the temperature was controlled at an expected value within a deviation of ± 0.3 °C.

First, an aqueous solution of a certain KCl concentration was added to the reactor and preheated to the expected temperature. Then, α-HH preheated to 60 °C in an oven was quickly put in the reactor at a fixed solid−solution ratio. After that, the mixture was kept at constant temperature until the transition was finished. During the batch operation, samples were withdrawn at different time intervals and immediately filtered with a 0.45 μm cellulosic membrane and were then quickly washed with boiling deionized water three times. The solid phase was separated by vacuum filtration, rinsed with acetone twice, and dried at 60 °C in an oven for 4 h.



a. reaction time: 6h



b. reaction time: 8h

Figure 7. Morphology variation of crystals during α-calcium sulfate hemihydrate (α-HH) recrystallization in 1.0 wt % KCl solution at 95 °C.

The solid phase was subjected to a metallographic microscope (XJP-6A) to investigate the crystal morphology and to examine the phase transition. The solid samples were examined with XRD performed on a Rigaku D/Max-2550pc X-ray diffractometer using Cu Kα radiation at a scanning rate of 8°·min^{-1} in the 2θ range from 5° to 85°. The XRD analysis results on the given products were interpreted by the use of KCPDS (ASTM) cards. Thermal analysis was performed on a NETZSCH STA 409PC differential scanning calorimeter for calcium sulfate phase identification and crystal water content determination. For TG/DSC measurements, 20 mg dry sample was sealed in an Al_2O_3 crucible with lid and scanned at a rate of 10 °C·min^{-1} under a N_2 gas atmosphere.

Results and Discussion

Phase Transitions of α-Calcium Sulfate Hemihydrate in KCl Aqueous Solution. α-Calcium Sulfate Hemihydrate Hydrating to Calcium Sulfate Dihydrate. The hydration of α-HH in KCl aqueous solutions from (80 to 100) °C was carefully examined. It was found that α-HH tended to hydrate to DH when it was mixed in KCl solutions of relatively low concentration. Here the hydration of α-HH in 2.0 % KCl

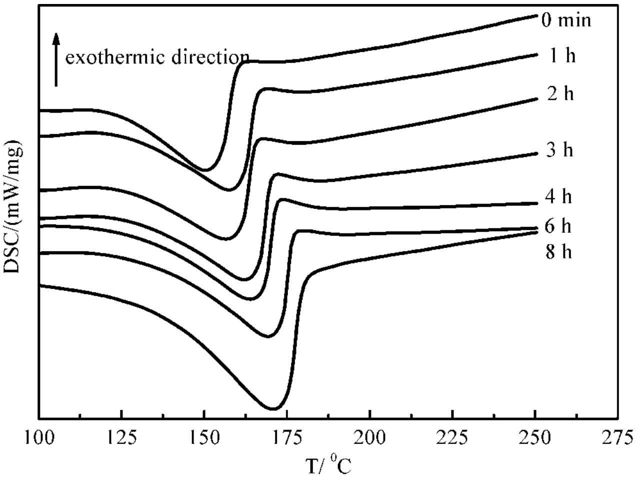


Figure 8. DSC curves for α-calcium sulfate hemihydrate (α-HH) in 1.0 wt % KCl solution at 95 °C.

Table 2. Variation of Crystal Water Content in the Process of α-Calcium Sulfate Hemihydrate (α-HH) Recrystallization

transformation conditions		crystal water content/%							
temp/°C	KCl concentration/wt %	initial time	after 30 min	after 1 h	after 2 h	after 3 h	after 4 h	after 6 h	after 8 h
85	5.0	5.90	17.05	18.62	19.62	19.32	17.67	9.01	8.10
88	3.0	5.80		19.40	19.90	19.69	19.72	19.83	19.64
90	3.0	5.78		5.98	5.82	5.98	6.05	6.12	6.12
95	0.5	5.51	5.54	5.28	5.50	5.73	6.47	7.00	7.56
	1.0	5.65	5.51	5.59	5.68	6.24	6.36	6.44	6.94
	2.0	5.65	5.26	5.44	5.33	5.79	5.76	6.53	6.61
100	0.0	6.12		5.79	5.98		6.00	6.10	
	0.5	6.01		6.07	5.98		5.81	6.08	
	1.0	5.54		5.97	5.46	5.57	5.71	5.59	
102	0.2	5.65	5.60	5.65	5.68	6.08	6.06	6.05	6.10
	0.6	5.68	5.63	5.94	5.68	5.96	6.02	6.00	6.04
	1.0	5.68	6.00	5.75	5.56	5.42	5.00	4.89	4.80

solution at 90 °C was taken for an example. From the morphology observation, α-HH gradually dissolved after being mixed with KCl solution, and DH crystals began to precipitate when the concentration of Ca^{2+} in the solution achieved a dissolution equilibrium level. About 2 h later, α-HH (short columnar shape) mostly hydrated to DH (long columnar shape) (shown in Figure 5a). Furthermore, DH crystals grew in size after the transformation, but their morphology always appeared to be long columnar (shown in Figure 5b), which could be explained by selective adsorption of K^+ on certain faces of the DH crystal.[17]

DSC analysis was conducted to investigate the hydration of α-HH in 2.0 % KCl solution at 90 °C. The DSC curves of the solid phase are shown in Figure 6. The exothermic peak disappeared, and the initial endothermic peak split into two parts 1 h after α-HH was mixed with the KCl solution, which denotes that some of the α-HH crystals had hydrated to DH. From (2 to 6) h, DSC curves present uniform profiles, which demonstrates the complete hydration of α-HH. The TG data in Table 1 also indicates α-HH's hydration to DH. The crystal water content for the 2 h product is 17.57 %, and that for the 3 h, 4 h, and 6 h products are all above 20.0 %. Thus, the hydration process illustrated in Figure 6 is very consistent with the morphology variation illustrated in Figure 5. Obviously, α-HH is unstable and DH is stable in the solution containing 2.0 % KCl at 90 °C under atmospheric pressure.

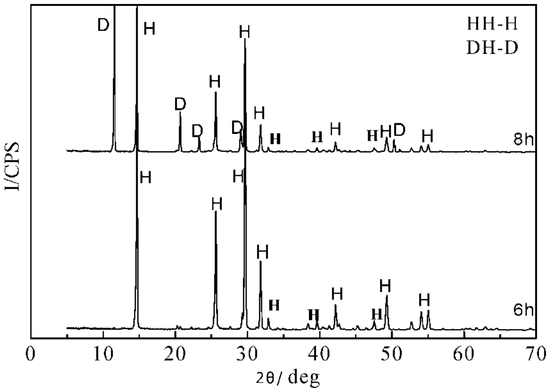


Figure 9. XRD patterns of the products during the process in 1.0 wt % KCl solution at 95 °C: H, α-calcium sulfate hemihydrate (α-HH); D, calcium sulfate dihydrate (DH).

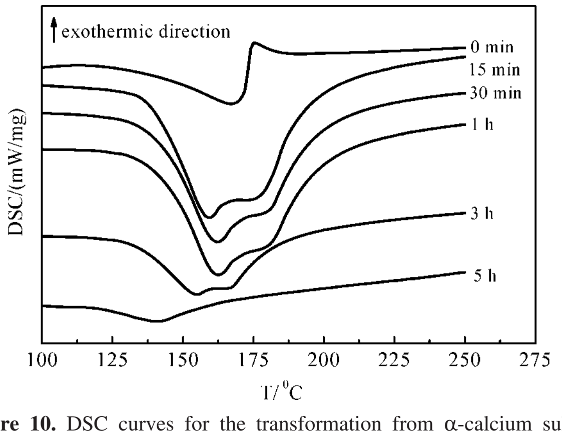


Figure 10. DSC curves for the transformation from α-calcium sulfate hemihydrate (α-HH) to calcium sulfate anhydrite (AH) via calcium sulfate dihydrate (DH) in 7.0 wt % KCl solution at 85 °C.

To determine DH's stable region, α-HH's hydration process was comprehensively investigated in (0 to 8.0) % KCl solutions over the range of (80 to 100) °C. The important data relative to α-HH hydration is listed in Table 1. Here α-HH's transition is regarded as the function of temperature and KCl concentration. At a temperature of 95 °C or higher, α-HH could hydrate only in solution at relatively low KCl concentration. The critical KCl concentration was about 1.0 % for α-HH hydration to DH at 95 °C. At 80 °C or lower temperature, α-HH quickly hydrated to DH. For instance, α-HH completely converted to DH in half an hour in 5.0 % KCl solution at 80 °C. The experimental data shows that the hydrating rate is distinctly accelerated as the reaction temperature decreases. As for the impact of KCl concentration on α-HH's hydration process, it can be speculated that K^+ ions act as a hydrating booster in solution at certain KCl concentrations[18] because the hydration in KCl solution at (80 to 100) °C is clearly accelerated compared with the hydration rate in deionized water, especially between (80 and 90) °C.

It can be concluded that the hydration of α-HH to DH depends on the combined effect of KCl concentration and temperature.

α-Calcium Sulfate Hemihydrate Recrystallization. In the range of investigated temperature ((80 to 105) °C), it was found that α-HH could be kept metastable under certain conditions in KCl aqueous solutions. For example, α-HH's recrystallization was observed in 1.0 wt % KCl solution at 95 °C. Along with the reaction time, α-HH crystals gradually grew in dimension with more symmetrical morphology and smoother crystal surfaces (Figure 7a). It was not until 8 h later that some DH crystals could be identified (Figure 7b). Moreover, the material phase examinations confirmed the products to be α-HH all the time within 6 h. According to the DSC curves (Figure 8), the products within 6 h are α-HH, and 8 h later, α-HH tends to hydrate. This can be validated by the difference between the DSC curve for the 8 h product and that for the others, because there is a great shrinkage of α-HH's typical exothermic peak at 175 °C on the 8 h DSC curve. Meanwhile, the TG data for this condition in Table 2 corresponds highly with the DSC

Table 3. Variation of Crystal Water Content in the Process of α-Calcium Sulfate Hemihydrate (α-HH) Dehydrating to Calcium Sulfate Anhydrite (AH) via Calcium Sulfate Dihydrate (DH)

transformation conditions		crystal water content/%							
temp/°C	KCl concentration/wt %	initial time	after 30 min	after 1 h	after 2 h	after 3 h	after 4 h	after 6 h	after 8 h
80	9.0	5.80	18.14	19.20	20.02	20.14	19.04	18.43	15.36
85	5.0	5.90	17.05	18.62	19.62	19.32	17.67	9.01	8.10
	5.5	5.47	14.94	19.07	16.89	15.46	13.98	11.06	8.32
	6.0	5.42	15.81	16.26	12.24	11.2	6.92	2.55	1.63
	6.5	5.59	13.59	14.09	10.43	7.86	6.82	2.43	1.54
	7.0	5.74	12.33	11.08	7.33	4.78	2.65	0.24	0.20
88	4.0	5.78		19.56	19.90	19.47	19.02	17.09	15.76
90	4.0	5.36		14.99	15.85	13.23	11.47	9.63	7.06
	5.0	5.13	7.36	13.95	9.02		1.96	0.91	0.08
	5.5	5.80	7.68	10.31	6.44	5.62	4.47	2.55	

curves. The crystal water content for the 8 h product is 6.94 % above the theoretical crystal water content of 6.21 % for HH. The XRD patterns (Figure 9) also illustrate that the products withdrawn within 6 h are nearly pure α-HH, and DH would be distinctively detected after 8 h. Thus, α-HH is metastable in solution of 1.0 % KCl at 95 °C for several hours. However, it is inclined to hydrate into DH when the reaction time is long enough. Therefore, α-HH is just a metastable phase in KCl solution under such conditions.

α-HH's recrystallization was investigated in solutions containing (0.5 to 2.0) wt % KCl at (80 to 105) °C under atmospheric pressure. The crystal water content data of the products withdrawn at different time intervals are shown in Table 2. Then, the region of temperature and KCl concentration for α-HH recrystallization can be obtained. It is found that the region is very narrow, restricted by KCl concentration and temperature. At 102 °C or higher temperature, α-HH begins to dehydrate in 1.0 % KCl solution, whereas at 85 °C or lower temperature, it tends to hydrate even in 5.0 % KCl solution. Thus, α-HH's metastability not only depends on reaction temperature but also strongly relates to KCl concentration. Even if the reaction temperature is in the temperature range for α-HH existence, α-HH is going to hydrate or dehydrate when the concentration of KCl solution has little discrepancy from that where α-HH is metastable. Thus, if the final product is desired to be α-HH in KCl solution, then the reaction temperature and concentration of KCl solution must be cautiously controlled.

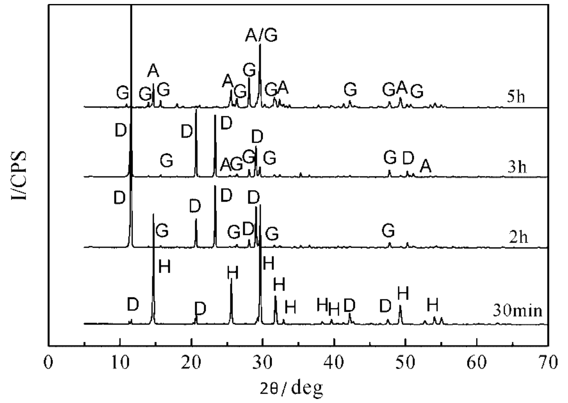


Figure 11. XRD patterns of the products during the process in 7.0 wt % KCl solution at 85 °C: H, α-calcium sulfate hemihydrate (α-HH); D, calcium sulfate dihydrate (DH); A, calcium sulfate anhydrite (AH); G, goergeyite.

α-Calcium Sulfate Hemihydrate Dehydrating to Anhydrite. α-HH's dehydration in relatively high concentration KCl solution from (80 to 105) °C was investigated. When α-HH was mixed in solutions of relatively high KCl concentration, for example, 7.0 % KCl solution at 85 °C, it would finally dehydrate into AH. According to the DSC curves (Figure 10), the products withdrawn within 1 h are mostly DH because DH's two typical endothermic peaks at 153 and 174.5 °C are present on the curves. The curve for the 5 h product indicates that AH has formed for the typical endothermic peaks of DH disappear. This phenomenon can be confirmed by the TG data in Table 3. The crystal water content for products withdrawn within 8 h first increases to 12.33 % and then drops to 0.20 %. The route can also be validated by the XRD patterns (Figure 11) for the products withdrawn during α-HH's transformation in 7.0 % KCl solution at 85 °C. A few DH crystals are present 30 min after the mixing of the α-HH and KCl solution. Goergeyite ($K_2Ca_5(SO_4)_6 \cdot H_2O$, Go) begins to form 2 h later. After 3 h, DH dehydrates to AH. Thus, the solid phase examinations

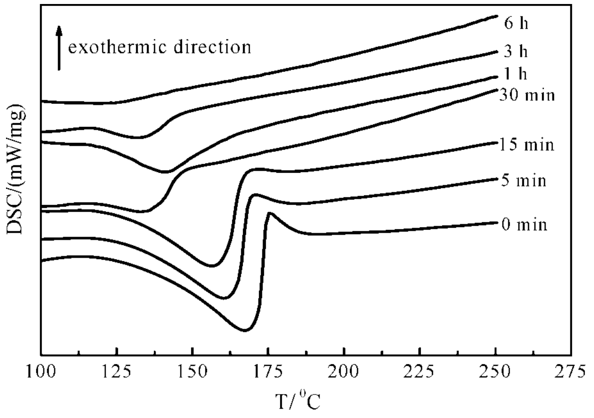


Figure 12. DSC curves for the transformation of α-calcium sulfate hemihydrate (α-HH) to calcium sulfate anhydrite (AH) in 8.0 wt % KCl solution at 90 °C.

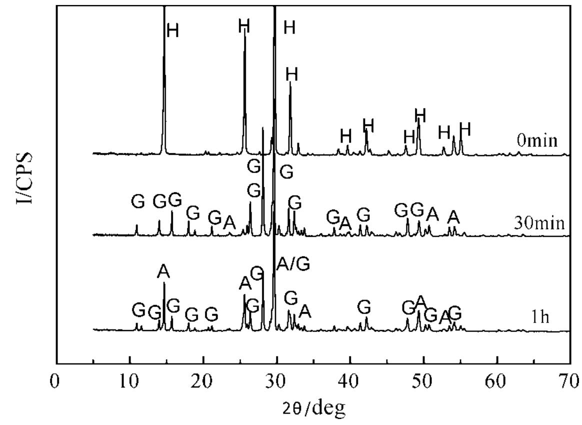


Figure 13. XRD patterns of the products during the process in 8.0 wt % KCl solution at 90 °C: H, α-calcium sulfate hemihydrate (α-HH); A, calcium sulfate anhydrite (AH); G, goergeyite.

Table 4. Variation of Crystal Water Content in the Process of α-Calcium Sulfate Hemihydrate (α-HH) Directly Dehydrating to Calcium Sulfate Anhydrite (AH)

transformation conditions		crystal water content/%						
temp/°C	KCl concentration/wt %	initial time	after 30 min	after 1 h	after 2 h	after 3 h	after 4 h	after 6 h
80	10.0	6.69	5.53	2.88	0.35	0.25	0.34	0.34
	15.0	5.83	1.52	0.17	0.15	0.13		
85	8.0	5.57	5.00	1.85	0.18	0.12	0.14	0.09
	10.0	5.72	1.98	1.06	0.09	0.10	0.08	
	15.0	5.72	0.49	0.11	0.04	0.07		
90	6.0	5.48	6.39	4.49	0.03	0.25	0.29	0.02
	8.0	5.83	1.77	0.75	0.55	0.07	0.11	0.01
95	4.0	5.22	5.21	4.71	3.25	2.15	2.00	0.82
	5.0	5.63	5.02	2.27	0.41	0.17	0.01	0.20
	8.0	4.80	2.56	0.44	0.50	0.23		
100	3.0	5.89	5.92	5.82	5.93	5.72	5.10	3.41
	5.0	5.82	4.35	2.52	0.81	0.59	0.19	
	8.0	5.83	0.88	0.69	0.18	0.10		
102	1.0	5.68	6.00	5.75	5.56	5.42	5.00	4.89

(illustrated by DSC curves and XRD patterns) are highly consistent with the morphology observation. The above analysis points to a possible phase transition of α-HH in KCl solution at relatively high concentration under atmospheric pressure, which can be described as α-HH → DH → AH.

However, when α-HH was mixed in even higher concentration KCl solutions (such as 8.0 % KCl solution at 90 °C), it would directly dehydrate into AH. DSC curves (Figure 12) show that α-HH's typical exothermic peak at 175 °C gradually shrinks 15 min after the mixing of α-HH and KCl solution, and the peak disappears 30 min later. From (1 to 6) h, the DSC curves demonstrated the formation of AH. This route can be confirmed by XRD (Figure 13) examination. It shows that α-HH mostly dehydrates to AH that coexists with Go. The high consistency between the results of phase examinations and that of the crystal morphology observation proves the phase transition of α-HH in concentrated KCl solutions to be α-HH → AH.

α-HH's hydration process in (1.0 to 15.0) % KCl solution at (80 to 102) °C was systemically studied by the variation of the crystal water content of the solid phase within 6 h. Table 3 shows the crystal water content data for α-HH → DH → AH routes, and Table 4 shows the crystal water content data for α-HH → AH routes.

As indicated by the data, no matter which route α-HH's phase transition undergoes, the dehydration is enhanced by increasing the reaction temperature or KCl concentration. The only difference is that the α-HH → DH → AH route goes through an additional hydration step that results in a lower whole dehydration rate than that of the α-HH → AH route. The critical concentration of KCl solutions for α-HH dehydration decreases when the temperature increases. For example, the critical concentration is only 1.0 % at 102 °C, whereas at 80 °C it is 10.0 %.

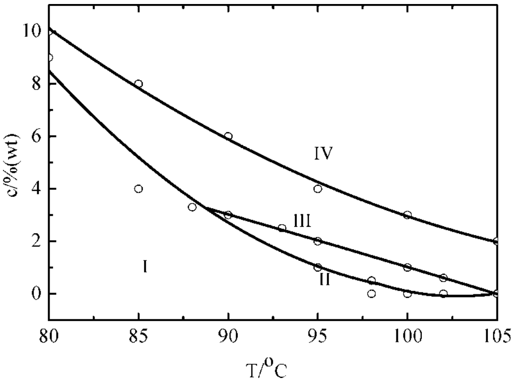


Figure 14. $CaSO_4$ phase transition in KCl solution under atmospheric pressure: region I, DH stable, AH and HH unstable; region II, HH metastable; region III: AH stable, DH metastable, HH unstable; region IV, AH stable, HH and DH unstable.

There are two possible phase-transition routes from α-HH to AH, that is, α-HH → DH → AH and α-HH → AH. The temperature for α-HH's transition is expected to vary with KCl concentration. In a range of relatively low temperature such as below 85 °C, the dehydration of α-HH to AH opts for the route of α-HH → DH → AH, whereas at a higher temperature such as 95 °C, the dehydration of α-HH to AH opts for the other route of α-HH → AH directly. Thus, in the process of α-HH dehydrating to AH, AH is the stable phase (mixed with Go), and DH is metastable in the α-HH → DH → AH route and unstable the in α-HH → AH route.

Gypsum Phase's Transformation and the Metastability Window of α-Calcium Sulfate Hemihydrate in KCl Solution. On the basis of the analysis of α-HH's hydration, dehydration, and recrystallization, the diagram of the three $CaSO_4$ phases stable/metastable regions can be sketched out as a function of KCl concentration and temperature. (See Figure 14.)

When α-HH is mixed in KCl aqueous solution under the conditions shown in region I, the final phase is DH, whereas in region II, α-HH recrystallizes with larger dimensions, better symmetry, and smoother crystal surfaces. In regions III and IV, α-HH finally converts to AH mixed with Go, and the dehydration rate is accelerated by increasing the reaction temperature or KCl concentration. There are two possible phase-transition routes from α-HH to AH, that is, α-HH → DH → AH and α-HH → AH. In region III, α-HH first hydrates to DH and then dehydrates to AH, whereas in region IV, α-HH directly dehydrates to AH. Thus, AH is the stable phase in regions III and IV, whereas DH is metastable in region III and unstable in region IV.

α-HH has the tendency to hydrate to DH at lower temperature or in lower concentration KCl solution or to dehydrate to AH at higher temperature or in higher concentration KCl solution. But there is still a narrow metastable window for α-HH, which depends heavily on the KCl concentration and temperature. This region is outlined as (0 to 3.0) wt % concentration for KCl solution and (89 to 105) °C for reaction temperature. If the final product is desired to be α-HH, the concentration of KCl solution and temperature must be strictly controlled. Meanwhile, the reaction time should be controlled within a certain time, for example, (5 to 6) h.

Conclusions

The phase transition of α-HH in KCl solution under conditions of atmospheric pressure and (80 to 105) °C undergoes four routes, that is, α-HH hydrating to DH, α-HH recrystallization, α-HH dehydrating to AH via DH, and α-HH directly dehydrating to AH. The four routes strongly depend on reaction temperature and the KCl concentration of solution.

The diagram of the three $CaSO_4$ phases stable/metastable regions in KCl solution at (80 to 105) °C under atmospheric pressure is successfully outlined as a function of KCl concentration and temperature, namely, regions I, II, III, and IV. DH is stable in region I and metastable in region III. AH is the stable phase in regions III and IV and coexists with Go. Only in a narrow region II is α-HH metastable.

A narrow operating window for α-HH's recrystallization has been determined. This window is limited by KCl concentration ((0 to 3.0) wt %) and reaction temperature ((89 to 105) °C). In general, the reaction time should be controlled within a certain time, for example, (5 to 6) h.

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