

Solubility in the Quaternary $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ System at 50°C

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Abstract

Background: The four-component system $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ is a subsystem of more complex six-component system Na, Ca $\text{SO}_4\text{,CO}_3\text{,HCO}_3\text{,F-H}_2\text{O}$ whose state of phase equilibria determines the conditions for utilization of liquid wastes of aluminum production.

Aim: To investigate the solubility in the quaternary $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ system and construction of its solubility diagram at 50°C .

Methods: In the present work, the results of studying the quaternary $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ system at 50°C using the solubility method, with the purpose of determining the concentration parameters at the position of its geometrical figures (fields, curves, points) and also establishing the ratio of crystallization fields of individual equilibrium solid phases are considered.

Results: Due to the low solubility of salts under these conditions, which is accompanied by a shift of the position of the figurative points to the water angle, the concentration of water is in the ratio 1: 5.

Keywords: Solubility, Equilibrium, Liquid phase, Chemical analysis, Crystal-optical analysis, Diagram, Geometric images

Introduction

In the present work, the results of studying the quaternary $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ system at 50°C using the solubility method, with the purpose of determining the concentration parameters at the position of its geometrical figures (fields, curves, points) and also establishing the ratio of crystallization fields of individual equilibrium solid phases are considered. Earlier [1-5], phase equilibria in the investigated system were determined and its phase equilibria diagram at 50°C was constructed by means of translation method.

Experimental

The three; $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ - gypsum (Gyp); CaCO_3 - calcite (Cal) and CaF_2 - fluorite (Flo) solid phases are in equilibrium at 50°C of the investigated system.

The following reagents were used for the experiments: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (chemically pure); CaCO_3 (pure); CaF_2 (pure). The experiments were carried out according to solution saturation method [6].

The composition of saturated solutions of corresponding ternary invariant points in the three; CaCO_3 - CaF_2 - H_2O ; CaCO_3 - CaSO_4 - H_2O and CaF_2 - CaSO_4 - H_2O systems at 50°C were prepared in accordance with the literature data [7,8]. Then, starting from the scheme of translation of invariant points of ternary composition to the quaternary composition [5], the saturated solutions with the corresponding equilibrium solid phases, were mixed and thermostated at 50°C until the equilibrium was reached.

Thermostating was carried out in an ultrathermostat U-8. Stirring of the mixture was carried out with a magnetic stirrer PD-09 for 60 hours. The temperature was maintained with an accuracy of $\pm 0.1^\circ\text{C}$ by means of a contact thermometer. Crystallization of solid phases was observed with a POLAM - P 311 microscope. After reaching equilibrium in the system, the equilibrium solids were photographed with the digital camera SONY-DSC-S500. The state of equilibrium was determined by the invariance of phase composition of precipitates. The separation of the liquid and solid phases was carried out by means of a vacuum pump through a de-sulphated (blue tape) filter paper on a Buchner funnel. After filtration the precipitate was washed with 96% ethyl alcohol and dried at 120°C .

Results and Discussion

Chemical analysis of the products was carried out according to known methods [9-11] and the results are presented in **TABLE 1**.

1.

Point number	Composition of the liquid phase, mass%				Phase composition of precipitates
	CaSO_4	CaCO_3	CaF_2	H_2O	
e_1	0.2100	-	-	99.790	Gypsum
e_2	-	0.0054	-	99.9946	Calcite
e_3	-	-	0.3400	99.6600	Fluorite
E_1^3	0.1070	0.0042	-	99.8888	Gypsum + Calcite
E_2^3	0.1585	-	0.3850	99.4565	Fluorite + Gypsum
E_3^3	-	0.0029	0.4310	99.5661	Calcite + Fluorite
E_1^4	0.3760	0.0061	0.2030	99.4149	Calcite + Gypsum + Fluorite

TABLE 1. Solubility at the invariant points of CaSO_4 - CaCO_3 - CaF_2 - H_2O system at 50°C .

The results of crystal-optical analysis [12] of equilibrium solid phases (micrographs) are shown in **Fig. 1**.

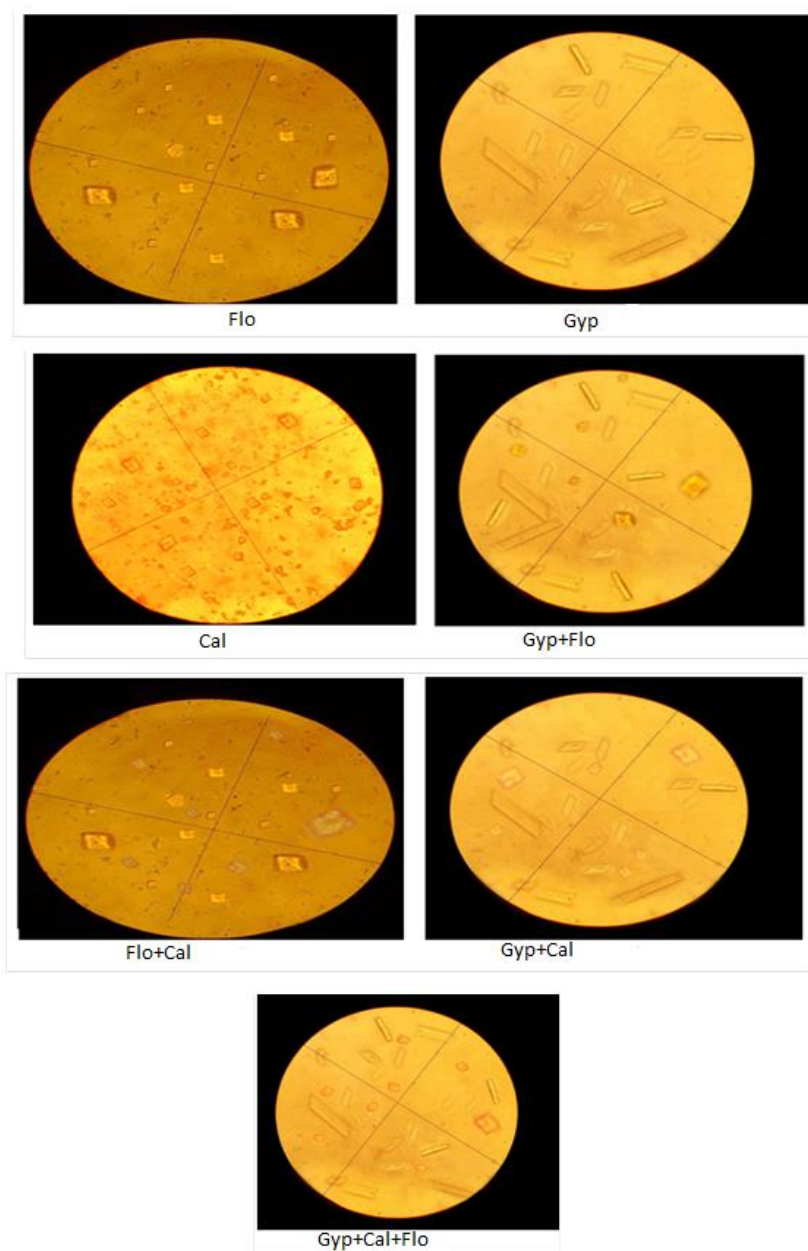


Fig. 1. Microphotographs of equilibrium solid phases in the system $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ at 50°C .

The decrease in the solubility of calcium sulfate in the system $\text{CaSO}_4\text{-CaF}_2\text{-H}_2\text{O}$ (point E), in comparison with its solubility in water (point e1), can obviously be explained by salting out effect of calcium fluoride in the given conditions.

On the basis of the obtained data a solubility diagram shown in Figure 2 for the $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ system at 50°C was constructed. The positions of the invariant points of ternary (E) and quaternary (E) compositions in the diagram, where n denotes the serial number of points, were established by the mass-centric method [13]. Due to the low solubility of salts under these conditions, which is accompanied by a shift of the position of the figurative points to the water angle, the concentration of water is taken in the ratio 1: 5.

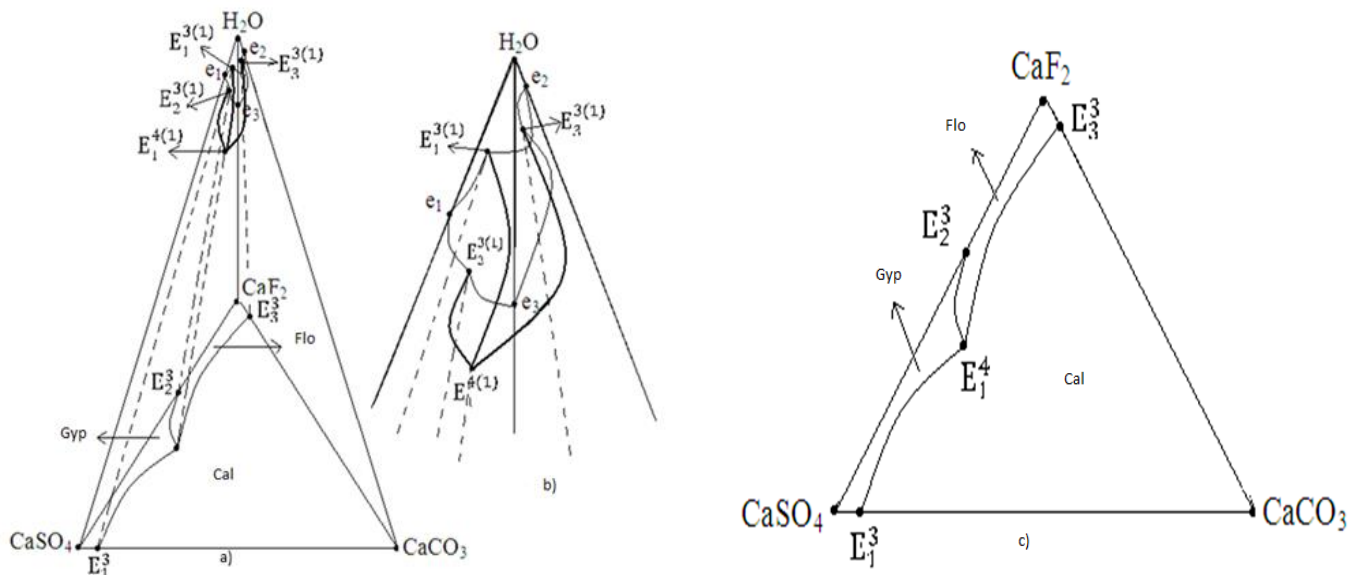


Fig. 2. Solubility diagram of the $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ system at 50°C : a) total; b) water part c) salt part.

Fig. 2 shows the "total" (a) and "salt part" (b) of the solubility diagram of the $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ system at 50°C , where the relative position and relative sizes of the crystallization fields of the corresponding equilibrium phases are reflected.

It follows Fig. 2; at 50°C of the investigated four-component system, the crystallization field of fluorite (CaF_2) and calcite (CaCO_3) occupy significant parts of the solubility diagram, which characterizes the low solubility of these salts under the given conditions. Descriptions of content of geometrical figures in Fig. 2 are given in TABLE 2.

Symbol of geometrical figures	Explanation of the symbol
e_1	The solubility of calcium sulfate in water
e_2	The solubility of calcium carbonate in water
e_3	Solubility of calcium fluoride in water
E_1^3	The common crystallization point of Gypsum + Calcite phases in the system of $\text{CaSO}_4\text{-CaCO}_3\text{-H}_2\text{O}$
E_2^3	The common crystallization point of Gypsum + Fluorite phases in the $\text{CaSO}_4\text{-CaF}_2\text{-H}_2\text{O}$ system

E_3^3	The common crystallization point of Calcite + Fluorite phases in the $\text{CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ system
E_1^4	The common crystallization point of Gypsum + Calcite + Fluorite phases in the $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$ system
$e_1E_1^3E_1^4E_2^3e_1$	The crystallization field of Gypsum in the system $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$
$e_3E_2^3E_1^4E_3^3e_3$	The Fluorite crystallization field in the system $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$
$e_2E_1^3E_1^4E_3^3e_2$	The crystallization field Calcite in the system $\text{CaSO}_4\text{-CaCO}_3\text{-CaF}_2\text{-H}_2\text{O}$

TABLE 2. Descriptions of geometric figures.

Conclusion

The decrease in the solubility of calcium sulfate in the system $\text{CaSO}_4\text{-CaF}_2\text{-H}_2\text{O}$ (point E), in comparison with its solubility in water (point e1), can be explained by salting out effect of calcium fluoride in the given conditions. Due to the low solubility of salts under these conditions, which is accompanied by a shift of the position of the figurative points to the water angle, the concentration of water is in the ratio 1: 5.

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