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Solubility in the Na,Ca||SO_4,HCO_3–H_2O system at 25 °C

Water solubility at 25 °C was studied in the four-component water-salt system comprised of sodium and calcium sulfates and hydrocarbonates in order to determine the concentration parameters of solution and crystallization of the constituent salts and to experimentally verify the phase equilibria in the geometric images of the system predicted previously by the translation method. The prediction of possible phase equilibria in geometric images of the system, followed by plotting its phase diagram, appreciably decreases the time and material costs of experimentation and improves the reliability of results. Our results can serve both as reference information and as a scientific base for optimizing the parameters of natural and artificial processes, in particular, the recycling of salt from liquid waste of aluminum production facilities.

Keywords: sodium; calcium; sulfate; hydrocarbonate; solubility diagram

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Introduction

The four-component Na, Ca||SO_4, HCO_3–H_2O system is a constituent of the more complex six-component Na,Ca||SO_4,CO_3,HCO_3,F–H_2O system; the phase equilibria in the latter determines the conditions for recycling of aluminum liquid waste. The wastewater after cryolite recovery in aluminum plants contains fluorides, carbonates, hydrocarbonates and sulfates of sodium and calcium [1, 2].

In this paper we have examined the concentration parameters of equilibrium solid phases for the particular crystallization fields in the Na,Ca||SO_4,HCO_3–H_2O system studied by the solubility method at 25 °C. Phase equilibria in the form of phase diagram established by the translation method were studied in our previous work [3].

The use of the translations method for predicting and constructing of phase diagrams for various systems is based on the principle of compatibility of the structure of constituent n-component systems with elements of the structure of a common (n+1) component system in one diagram [4]. According to the translation method, while the components number in the system is increasing from n to n+1, the geometric images of constituent n-component systems (i.e. nonvariant points, monovariants curves, divariant fields) are increasing their dimension by one, i.e. they have transformed and translated into the general area of (n+1) component composition.

At a level of (n+1) — component composition, transformed by the translation procedure geometrical images of the *n*-component constituent systems involved in the formation of the phase complex of the overall system, in accordance with their topological properties and requirements of the Gibbs phase rule [5]. Based on the obtained data, it is possible to construct an isolated phase diagram of the studied system.

The application of the translation method for predicting and constructing phase diagrams for multicomponent water-salt systems is described in detail elsewhere [6–7].

The use of the translation method for prediction and construction of phase diagrams of multicomponent systems significantly reduces the time and material expenses of experimental study of various systems [9–11] constituting the six-component Na,Ca||SO_4,CO_3,HCO_3,F–H_2O system. The equilibrium solid phases of the system under study at 25 °C are calcium hydrocarbonate, nahcolite, mirabilite, and gypsum [12, 13].

Experimental

Following reagents were used in our work: $Na_2SO_4 \cdot 10H_2O$; $NaHCO_3$; $Ca(HCO_3)_2$; $CaSO_4 \cdot 2H_2O$. The experiments were carried out according to the “until saturation” method in accordance with the following. Based on the data reported in works [3–15], we preliminary prepared the mixtures of precipitates with saturated solutions corresponded to the nonvariant points of the ternary systems, namely: Na_2SO_4–$NaHCO_3$–H_2O; $CaSO_4$–$Ca(HCO_3)_2$–H_2O; Na_2SO_4–$CaSO_4$–H_2O and $NaHCO_3$–$Ca(HCO_3)_2$–H_2O at 25 °C, which are constituting the four-component system under study. Then, according to the translation scheme, the nonvariant points of the level of three-component system were transformed to the level of four-component system [3] by the mixing of appropriate amounts of the prepared saturated solutions with the corresponding equilibrium solid phases at 25 °C in an ultrathermostat U-8 with stirring using magnetic stirrers PD-09 for 50–100 h. The temperature was maintained with an accuracy of ±0.1 °C using a contact thermometer. The crystallization of the solid phases was detected using a POLAM-R 311 microscope. After reaching an equilibrium state in the system, the equilibrium solid phases were photographed with a SONY — PSC 500 digital camera. The achievement of equilibrium was judged by the unchanged phase composition of precipitation. Separation of liquid and solid phases was carried out with the help of a vacuum pump through a desalted (blue ribbon) filter paper on a Büchner funnel.

The precipitate after filtration was wasted with 96% ethyl alcohol and dried at 120 °C. Chemical analysis of products was carried out using well-known methods described elsewhere [15–17].

Results and discussion

The micrographs of the crystalline equilibrium solid phases are presented in Fig. 1, and the results of chemical analysis of saturated solutions are presented in Table 1. The phases are denoted as follows: CaH — calcium hydrocarbonate, $Ca(HCO_3)_2$; Gp — gypsum, $CaSO_4 \cdot 2H_2O$; Mb — mirabilite, $Na_2SO_4 \cdot 10H_2O$; Nh — nahcolite, $NaHCO_3$; Gb — glauberite, $Na_2SO_4 \cdot CaSO_4$.

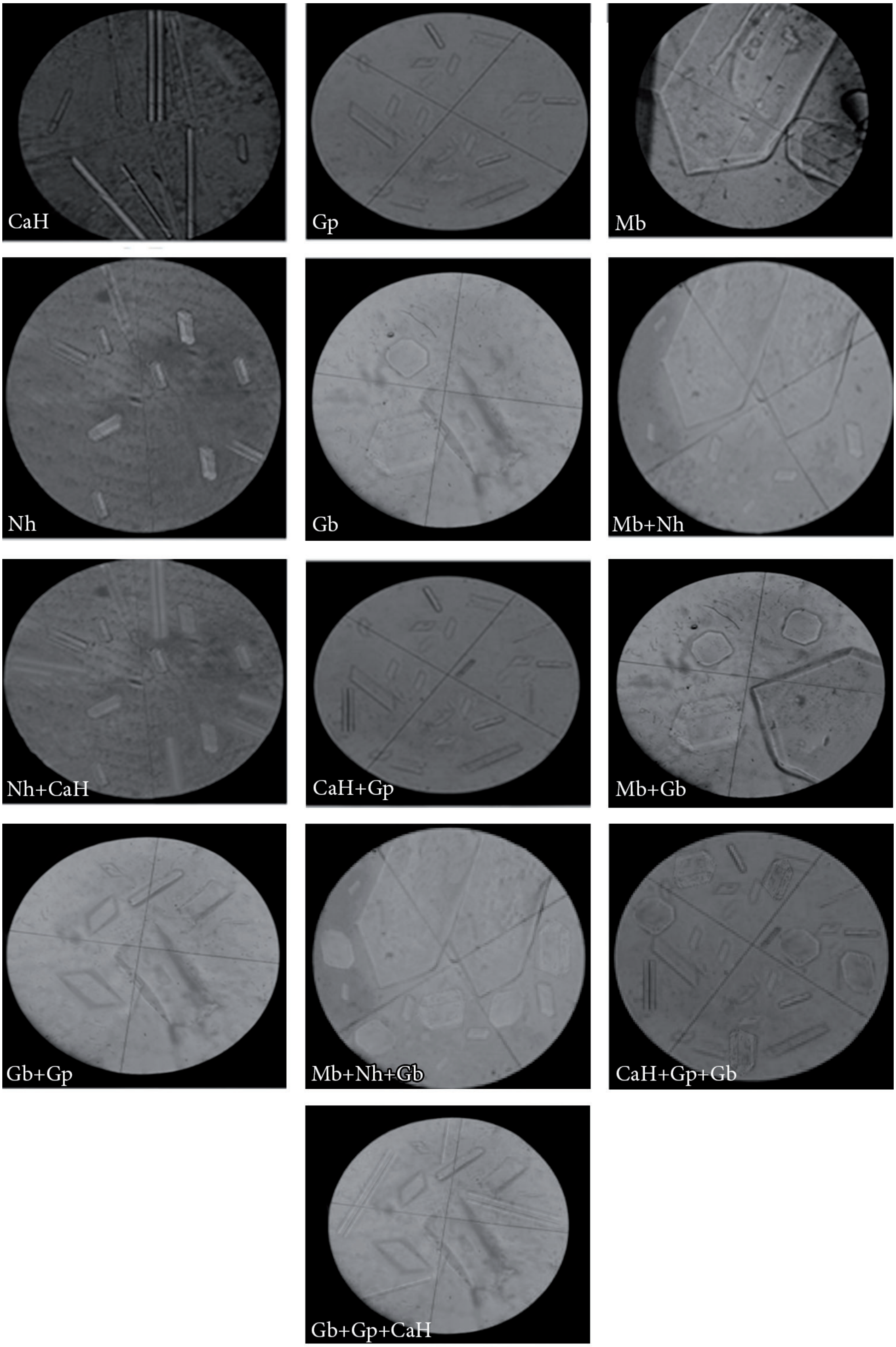

Fig. 1. Micrographs of equilibrium solid phases of the Na,Ca||SO_4,HCO_3-H_2O system at 25 °C

Table 1

The solubility values of various salts correspondent to the invariant points in the $Na,Ca||SO_4,HCO_3–H_2O$ system at 25 °C

Point no.	Liquid phase, wt. %					Phase composition of precipitates
	$NaHCO_3$	Na_2SO_4	$Ca(HCO_3)_2$	$CaSO_4$	H_2O	
e_1	9.31	–	–	–	90.69	Nh
e_2	–	21.9	–	–	78.10	Mb
e_3	–	–	0.0160	–	99.984	CaH
e_4	–	–	–	0.219	99.78	Gp
E_1^3	4.16	20.68	–	–	75.16	Nh+Mb
E_2^3	4.89	–	0.0109	–	95.09	Nh+CaH
E_3^3	–	–	0.0168	0.186	99.797	CaH+Gp
E_4^3	–	21.75	–	0.197	78.05	Mb+Gp
E_5^3	–	25.78	–	0.188	74.03	Gb+Gp
E_1^4	5.20	28.38	–	0.270	66.15	Nh+Mb+Gb
E_2^4	–	25.14	0.0136	0.184	74.66	Gb+Gp+CaH
E_3^4	7.12	24.40	0.0163	–	68.46	Nh+CaH+Gb

Based on the obtained results, the solubility diagram for the $Na,Ca||SO_4,HCO_3–H_2O$ system at 25 °C was constructed (Fig. 2).

The location of invariant points at each level of the diagram within three-component (E_n^3) and four-component (E_n^4) systems under study was established by the mass-centric method [19, 20]. The mass-centric method which is used for presentation of multicomponent systems allows changing the scale of one of the constituent parts without disturbance of the general diagram laws, and it also allows using the polygon area more rationally, i.e. to increase the length of small individual geometric images. This is especially important when the solubility of salts in water is small and the use of the same scale leads to the situation when the figurative point of the mixture is shifted towards the water angle while constructing of water-salt system diagrams.

Fig. 2 shows the total (*a*) and salt (*b*) parts of the solubility diagram for the $Na,Ca||SO_4$, $HCO_3–H_2O$ system at 25 °C, where the relative position and the relative sizes of the crystallization fields for the corresponding equilibrium solid phases are reflected. As follows from Fig. 2, the crystallization fields of $Ca(HCO_3)_2$ and $CaSO_4·2H_2O$ occupy a significant part of the solubility diagram for the studied four-component system, which characterizes the low solubility of these salt in water solution of given content at 25 °C. A description of content for the geometric images (fields, curves, points) in Fig. 2 is given in Table 2.

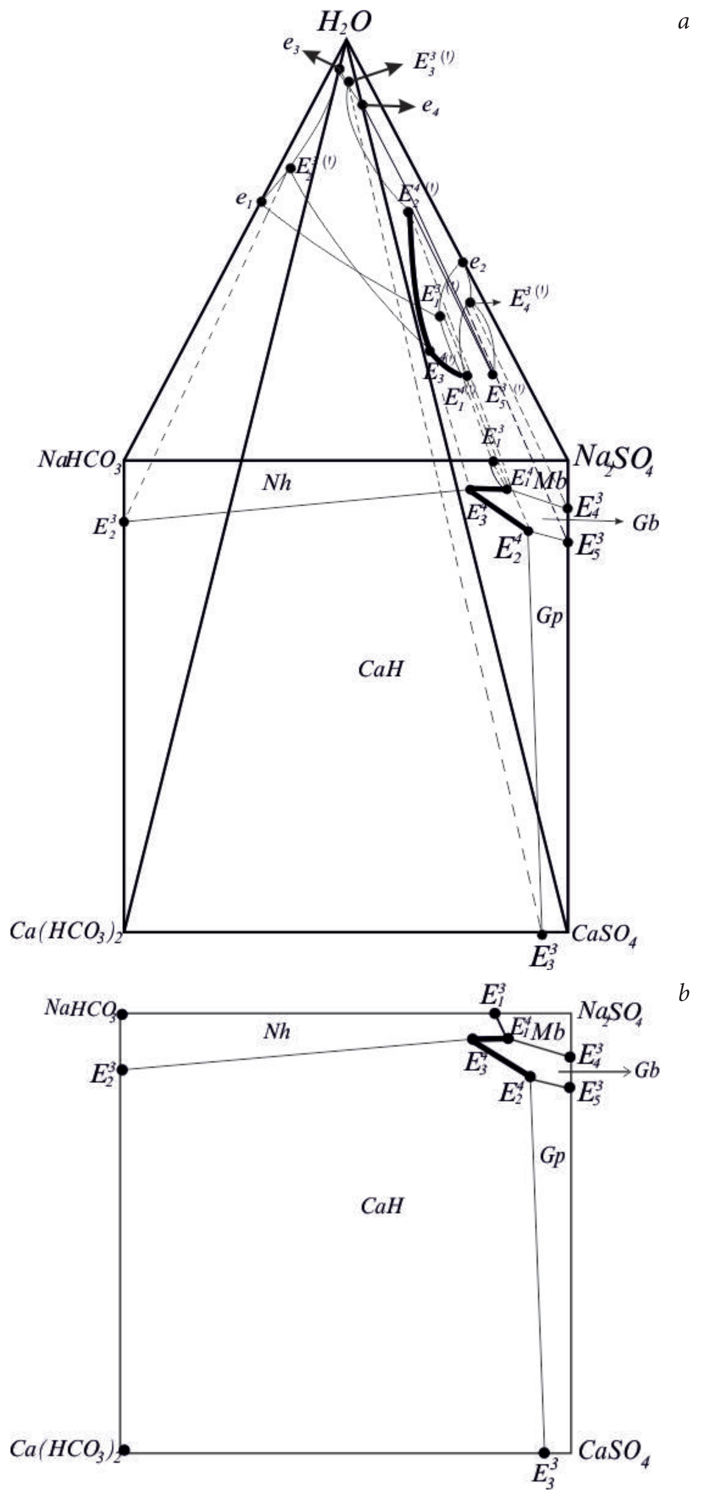

Fig. 2. (*a*) General and (*b*) salt-area solubility diagrams for the $Na,Ca||SO_4,HCO_4–H_2O$ system at 25 °C

Table 2

Description of the content for the geometric images in Fig. 2

Designation	Content
e_1	Solubility of sodium hydrocarbonate in water
e_2	Solubility of sodium sulfate in water
e_3	Solubility of calcium hydrocarbonate in water
e_4	Solubility of calcium sulfate in water
E_1^3	Joint crystallization point Mb+Nh in the system $NaHCO_3–Na_2SO_4–H_2O$
E_2^3	Joint crystallization point Nh+CaH in the system $NaHCO_3–Ca(HCO_3)_2–H_2O$
E_3^3	Joint crystallization point CaH+Gp in the system $Ca(HCO_3)_2–CaSO_4–H_2O$
E_4^3	Joint crystallization point Mb+Gb in the system $Na_2SO_4–CaSO_4–H_2O$
E_5^3	Joint crystallization point Gp+Gb in the system $Na_2SO_4–CaSO_4–H_2O$
E_1^4	Joint crystallization point Nh+Mb+Gb in the system $Na,Ca\|\|SO_4,HCO_3–H_2O$
E_2^4	Joint crystallization point CaH+Gb+Gp in the system $Na,Ca\|\|SO_4,HCO_3–H_2O$
E_3^4	Joint crystallization point Nh+Gb+CaH in the system $Na,Ca\|\|SO_4,HCO_3–H_2O$
E_1^3———E_1^4	Curve of the joint crystallization of Nh+Mb in system $NaHCO_3–Na_2SO_4–H_2O$
E_2^3———E_3^4	Curve of the joint crystallization of Nh+CaH in system $NaHCO_3–Ca(HCO_3)_2–H_2O$
E_2^3———E_2^4	Curve of the joint crystallization of CaH+Gb in system $Ca(HCO_3)_2–CaSO_4–H_2O$
E_4^3———E_1^4	Curve of the joint crystallization of Mb+Gb in system $Na_2SO_4–CaSO_4–H_2O$
E_5^3———E_2^4	Curve of the joint crystallization of Gb+Gp in system $NaHCO_3–Na_2SO_4–H_2O$
E_1^4———E_3^4	Curve of the joint crystallization of Nh+Gb in system $Na,Ca\|\|SO_4,HCO_3–H_2O$
E_2^4———E_3^4	Curve of the joint crystallization of CaH+Gb in system $Na,Ca\|\|SO_4,HCO_3–H_2O$
$NaHCO_3E_1^3E_1^4E_3^4E_2^3NaHCO_3$	Crystallization field Nh
$Ca(HCO_3)_2E_2^3E_3^4E_2^4E_3^3$ $Ca(HCO_3)_2$	Crystallization field CaH
$Na_2SO_4E_1^3E_1^4E_4^3Na_2SO_4$	Crystallization field Mb
$CaSO_4E_3^3E_2^4E_5^3CaSO_4$	Crystallization field Gp
$E_4^3E_1^4E_3^4E_2^4E_5^3E_4^3$	Crystallization field Gb
(I)	Notation of the figurative point of the mixture in the water-salt area of the diagram

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