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L. Soliev, M. T. Jumaev
Tajik State Pedagogical University named after S. Ayni, Dushanbe, 734025, Republic of Tajikistan
e-mail: soliev.lutfullo@yandex.com; jumaev_m@bk.ru

Phase equilibria in the $Na,Ca//SO_4,CO_3,HCO_3–H_2O$ system at 0 °C

Phase equilibria in the $Na,Ca//SO_4,CO_3,HCO_3$-H_2O system have been studied at 0 °C. The studied system at 0 °C involves 4 invariant points, 13 monovariant curves and 15 divariant fields. The obtained results served as a basis for the construction of phase diagram (phase complex) of the studied system at 0 °C.

Keywords: system; phase equilibria; diagram; geometric images

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Results and discussion

The laws of phase equilibria in the $Na,Ca//SO_4,CO_3,HCO_3$-H_2O system are not only of scientific interest, but also necessary for elaboration of optimal conditions for halurgicol processing of natural mineral raw materials and industrial wastes containing sulfates, carbonates, hydrocarbonates of sodium and calcium. However, these equilibria have not been studied yet, and necessary information is absent in the available literature [1].

We have studied phase equilibria in the $Na,Ca,//SO_4,CO_3,HCO_3$-H_2O system at 0 °C by the translation method which follows from the principle of compatibility of the structural elements for the *n* and *n*+1 component systems in one diagram [2]. According to the translation method, the subsequent (*n*+1) component is added to the *n*-component system, and the latter is translated to the *n*+1 component state by the transformation of geometric images of the *n*-component system. Transformed geometric images have formed corresponding phase diagram components on the *n*+1 level, according to their topological properties (fields, curved, points), taking into account the Gibbs phase rule for the *n*+1 component system. More detailed description of the translation method that can be used for predicting and constructing of equilibrium phase diagrams for the multicomponent water — salt systems are considered in the works [3–5]. Previously, this method was used to study the five-component system [6].

Five-component $Na,Ca,//SO_4$, CO_3, $HCO_3–H_2O$ system includes the following four 4-component systems: $Na_2SO_4–Na_2CO_3–NaHCO_3–H_2O$; $CaSO_4–CaCO_3$-$Ca(HCO_3)_2–H_2O$; $Na,Ca,//SO_4$, $CO_3–H_2O$; $Na,Ca,//SO_4$, $HCO_3–H_2O$; $Na,Ca,//CO_3$, $HCO_3–H_2O$. Phase composition of invariant points in the aforementioned 4-component systems have been determined by both the solubility method [1] and the translation method [7–10] described earlier.

Coexisting equilibrium solid phases, representing the invariant points in the 4-component systems, are listed in Table 1.

In Table 1 and further, E denotes an invariant point where the superscript denotes its multiplicity (component of the system), and the subscript denotes its sequence number. The following notation for the equilibrium solid phases have been used: Mb — mirabilite, $Na_2SO_4 \cdot 10H_2O$; CaG — calcium hydrocarbonate, $Ca(HCO_3)_2$; Gp — gypsum $CaSO_4 \cdot {}_2H_2O$; Nk — nakhcolite, $NaHCO_3$; Gl — gaylussite $Na_2CO_3 \cdot CaCO_3 \cdot 5H_2O$; Cc — calcite $CaCO_3$, C · 10 — tenfold hydrogenated sodium carbonate $Na_2CO_3 \cdot 10H_2O$.

Fig. 1, which is drawn based on the data from Table 1, illustrates the equilibrium phase diagram (phase complex) for the Na,Ca,//SO_4,CO_3,HCO_3-H_2O system at 0 °C at the four-component compositional level, where the salt part of the system forms four-sided prism sweep. After its unification (combining identical crystallization fields of the opposite four-component systems), we obtained a schematic diagram [11] for the phase equilibrium in the Na,Ca//SO_4,CO_3,HCO_3-H_2O system at 0 °C at the four-component compositional level, which is shown in Fig. 2.

The constructed diagram contains various geometric images (invariant points, multi-variant curves, divariant fields) for the studied system and correspondent equilibrium solid phases at the four-component compositional level. The phase composition of the precipitation of quadruple invariant points is given in Table 1. The phase composition of the precipitates inside the divariant fields is shown in Fig. 2. The phase composition of the sediments, corresponding to the multi-variant curves that connect four-phase invariant points, can be represented as follows:

E_1^4———E_2^4 = Mb+Nk;
E_1^4———E_5^4 = Mb+C·10;
E_1^4———E_8^4 = C·10+Nk;
E_2^4———E_3^4 = Nk+Gp;
E_2^4———E_7^4 = Gp+Mb;
E_3^4———E_4^4 = CaG+Gp;
E_3^4———E_{10}^4 = Nk+CaG;
E_4^4———E_6^4 = Gp+Cc;
E_4^4———E_9^4 = Cc+CaG;
E_5^4———E_7^4 = Mb+Gl;
E_5^4———E_8^4 = Gl+C·10;
E_6^4———E_7^4 = Gp+Gl;
E_6^4———E_9^4 = Gl+Cc;
E_8^4———E_{10}^4 = Nk+Gl;
E_9^4———E_{10}^4 = Gl+CaG.

Table 1

Phase composition of precipitates for the invariant points in the 4-component systems, which are compile the complex 5-component Na,Ca,//SO_4,CO_3,HCO_3-H_2O system at 0 °C

Invariant points	Solid phases in equilibrium	Invariant points	Solid phases in equilibrium
Na_2SO_4–Na_2CO_3–$NaHCO_3$–H_2O system		Na,Ca‖SO_4,CO_3–H_2O system	
E_1^4	Mb+Nk+C·10	E_5^4	Gl+Mb+C·10
Na,Ca‖SO_4,HCO_3-H_2O system		E_6^4	Gp+Gl+Cc
E_2^4	Gp+Mb+Nk	E_7^4	Gl+Gp+Mb
E_3^4	Gp+Nk+CaG	Na,Ca‖CO_3,HCO_3–H_2O system	
$CaSO_4$–$CaCO_3$–$Ca(HCO_3)_2$–H_2O system		E_8^4	Gl+Nk+C·10
E_4^4	Gp+Cc+CaG	E_9^4	Gl+Cc+CaG
		E_{10}^4	Nk+Gl+CaG

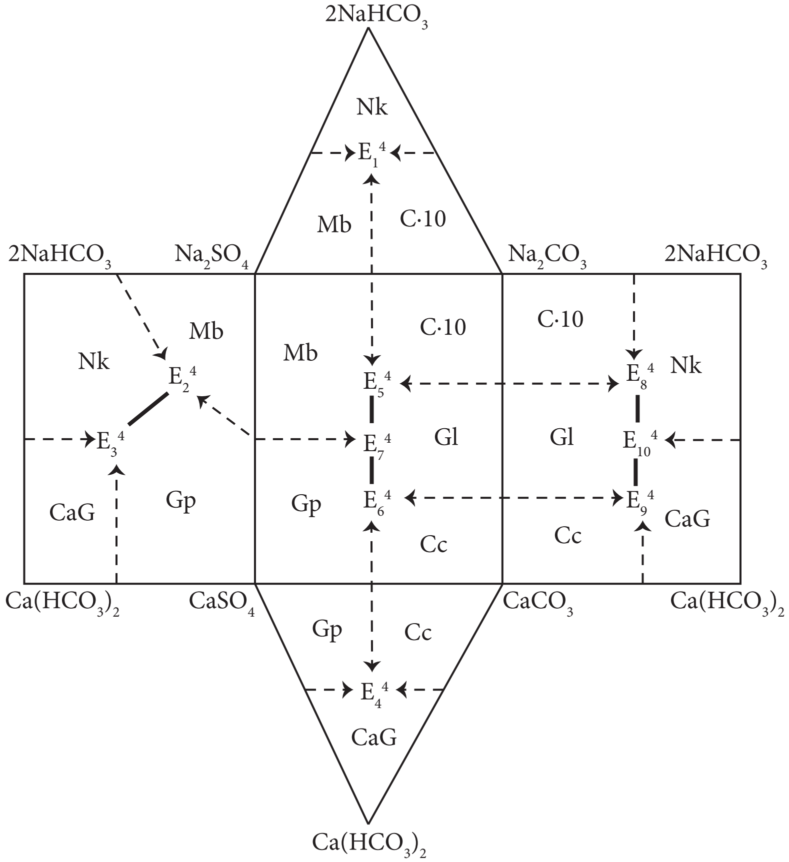


Fig. 1. Prism sweep of the salt part of equilibrium phase diagram for the Na,Ca//SO_4,CO_3,HCO_3-H_2O system at 0 °C at the four-component composition level

A translation procedure [3–5] of invariant points from the four-component compositional level to a five-component level leads to the formation of the following five invariant points with the following coexisted in equilibrium solid phases:

$E_1^4 + E_5^4 + E_8^4 \dashrightarrow E_1^5$ = Nk + Mb + + C·10 + Gl;

$E_2^4 + E_7^4 \dashrightarrow E_2^5$ = Nk + Mb + Gp + + Gl;

$E_3^4 + E_{10}^4 \dashrightarrow E_3^5$ = Nk + CaG + Gp + + Gl;

$E_4^4 + E_6^4 + E_9^4 \dashrightarrow E_4^5$ = Gp + Cc + + CaG + Gl.

The equilibrium phase diagram for the Na,Ca//SO_4,CO_3,HCO_3-H_2O system at 0 °C constructed by the translation method is shown in Fig. 3.

The thin solid lines in Fig. 3 indicate the multivariant curves belonging to the four-component compositional level. The correspondent solid phases that coexisted in equilibrium have been shown above. The dashed lines with arrows indicate monovariant curves belonging to the five-component compositional level. The equilibrium solid phases, which corresponded to these monovariant curves, are identical to the equilibrium solid phases of the translated invariant points in the corresponding quadruple systems. The arrows on these curves indicate the directions

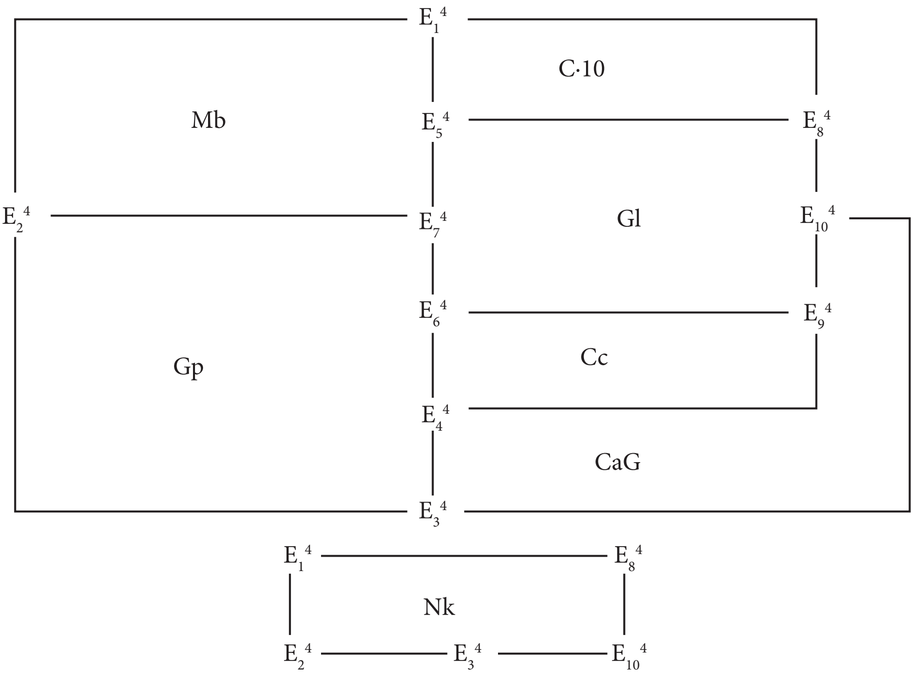


Fig. 2. Schematic diagram for the phase equilibrium in the Na,Ca//SO_4,CO_3,HCO_3-H_2O system at 0 °C at the four-component compositional level, constructed by the translation method

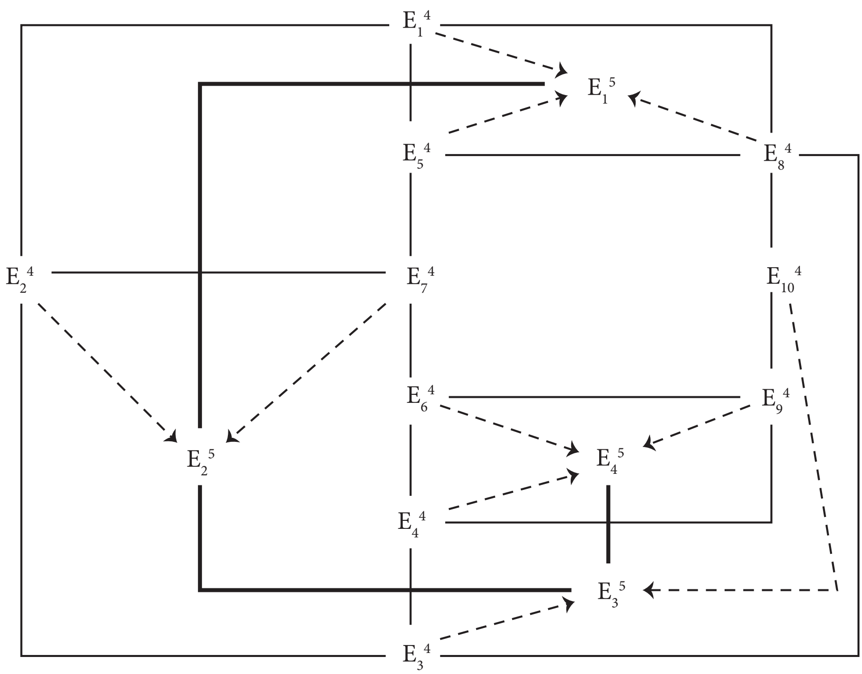
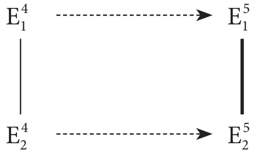
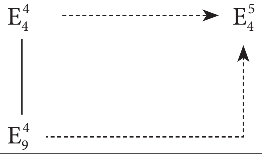
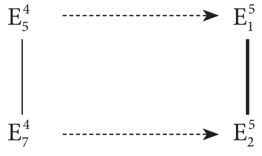
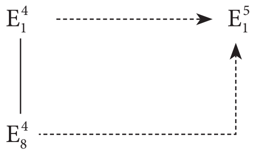
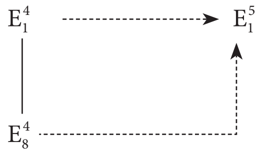
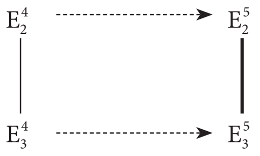
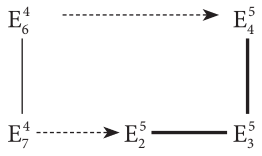
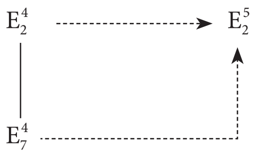
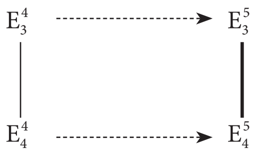
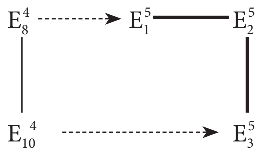
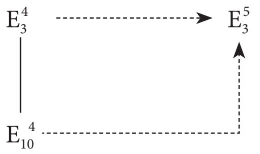
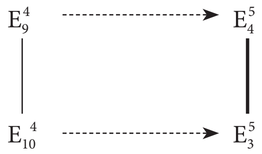
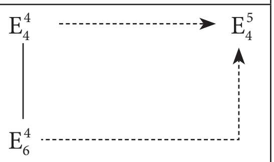


Fig. 3. Schematic phase diagram for the Na,Ca//SO_4,CO_3,HCO_3-H_2O system at 0 °C at the five-component compositional level constructed by the translation method

Table 2

Equilibrium solid phases and contours of the divariant fields in the $Na,Ca//SO_4,CO_3,HCO_3-H_2O$ system at 0 °C

Equilibrium solid phases in the fields	Field contours in the diagram (Fig. 3)	Equilibrium solid phases in the fields	Field contours in the diagram (Fig. 3)
Mb+Nk		Cc+CaG	
Mb+C·10		Mb+Gl	
C·10+Nk		Gl+C·10	
Nk+Gp		Gl+Gp	
Mb+Gp		Gl+Cc	
CaG+Gp		Gl+Nk	
CaG+Nk		Gl+CaG	
Cc+Gp			

of translation. The bold lines also denote monovariant curves belonging to the five-component compositional level. These lines connect five-phase invariant points; equilibrium solid phases correspondent to these lines are:

E_1^5———E_2^5 = Nk + Mb + Gl;
E_2^5———E_3^5 = Gp + Nk + Gl;
E_3^5———E_4^5 = CaG + Gl + Gp.

Table 2 shows the equilibrium solid phases and contours of the divariant fields in the Na,Ca//SO_4,CO_3,HCO_3–H_2O system at 0 °C.

All 15 divariant fields that characterized phase equilibria in the studied system at 0 °C were formed as a result of the translation procedure transforming monovariant curves to the five-component composition level.

Conclusions

Finally, we can conclude that studied Na,Ca//SO_4,CO_3,HCO_3-H_2O system at 0 °C has been described at the four-component compositional level (A) and the five-component compositional level (B) by particular amounts of specific geometric images.

Compositional level	A	B
Nonvariant points	10	4
Monovariant curves	15	13
Divariant fields	7	15

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