Phase complex of the system
\( \text{Na, Ca||SO}_4\text{, CO}_3\text{, HCO}_3 \text{– H}_2\text{O} \) at 100 °C

The article discusses the results of determining the possible phase equilibria in geometric images of a five-component reciprocal water-salt system of sulfates, carbonates, sodium bicarbonates and calcium at 100 °C with subsequent construction of its phase complex diagram. The laws that determine the structure of the phase complex diagram of this system are needed to be obtained for the production of scientific data used both as a reference material and also to create the optimal conditions for the recycling of liquid waste industrial production of aluminum-containing sulfate carbonate and bicarbonate salts of sodium and calcium. It was established that the system under study at 100 °C is characterized by the presence of 31 divariant double saturation fields, 25 monovariant trisaturation curves and 14 invariant points.

**Keywords:** translation method; phase complex diagram; geometric images

Received: 17.04.2020. Accepted: 22.06.2020. Published: 30.06.2020.
© Soliev L., Jumaev M. T., 2020

**Introduction**

The phase diagrams for the complex systems are not only of scientific interest, but also necessary for creating optimal conditions for the galurgic processing of natural mineral raw materials and industrial wastes containing sulfates, carbonates, sodium and calcium bicarbonates [1]. The Na,Ca||SO\(_4\),CO\(_3\),HCO\(_3\)–H\(_2\)O system has not been studied yet at 100 °C. Earlier we studied phase equilibria in this system by the translation method at temperatures of 0 and 50 °C [2, 3].

**Methods**

We have deduced phase equilibria in the Na,Ca||SO\(_4\),CO\(_3\),HCO\(_3\)–H\(_2\)O system at 100 °C using translation methods [4, 5] which follows from the principle of compatibility of structural elements of \( n \) and \( n + 1 \) component systems in one diagram [6, 7]. According to the translation method, the addition of one more component to the \( n \)-component system and its transition to the \( n + 1 \) component state is accompanied by transformation of the geometric image of the \( n \)-component system. The transformed geometric images are translated to the \( n + 1 \) level according to their topological property in accordance with the Gibbs phase rule, forming corresponding geometric images (fields, curves, points) in the \( n + 1 \) component system. The application of translation methods for predicting and constructing phase diagram

...
for multicomponent water-salt systems was considered in more details in our previous work [4]. Earlier this method was successfully used for other multicomponent systems [8, 9].

The five-component system \( \text{Na,Ca||SO}_4,\text{CO}_3,\text{HCO}_3-\text{H}_2\text{O} \) can be represented as a combination of the following four component systems: \( \text{Na}_2\text{SO}_4-\text{Na}_2\text{CO}_3-\text{NaHCO}_3-\text{H}_2\text{O}, \text{CaSO}_4-\text{CaCO}_3-\text{Ca(HCO}_3)_2-\text{H}_2\text{O}, \text{Na,Na||SO}_4,\text{CO}_3,\text{H}_2\text{O}, \text{Na,Na||SO}_4,\text{HCO}_3-\text{H}_2\text{O}, \text{Na,Na||CO}_3,\text{HCO}_3-\text{H}_2\text{O} \). The phase equilibria of invariant points in these four-component systems were studied earlier by the method of the multiple solubility [1, 10] and by the translational method [11–15]. Coexisted equilibrium solid phases inside the invariant four-component systems are listed in Table 1. Phase composition of these non-variant points was used to predict the phase equilibria and for construction of phase complex of the studied system by the translation method.

In Table 1 and further \( E \) denotes the invariant point, where the upper index indicates its multiplicity (the number of system's component), and the lower index indicates its serial number. The following notations for solid phases that were formed in the system were used:

- \( \text{Te} \) — tenaedite, \( \text{Na}_2\text{SO}_4; \)
- \( \text{CaG} \) — calcium hydrocarbonat, \( \text{Ca(HCO}_3)_2; \)
- \( \text{Gp} \) — gypsum, \( \text{CaSO}_4·\text{H}_2\text{O}; \)
- \( \text{Nk} \) — nakhcolite, \( \text{NaHCO}_3; \)
- \( \text{Pr} \) — gayluscite, \( \text{Na}_2\text{CO}_3·\text{CaCO}_3·2\text{H}_2\text{O}; \)
- \( \text{Cc} \) — calcite \( \text{CaCO}_3; \)
- \( \text{Na·1} \) — \( \text{Na}_2\text{CO}_3; \)
- \( \text{Ber} \) — berkeite, \( 2\text{Na}_2\text{SO}_4·\text{Na}_2\text{CO}_3; \)

### Table 1

| Invariant points | Solid phase equilibrium | Invariant points | Solid phase equilibrium |
|------------------|-------------------------|------------------|-------------------------|
| \( \text{Na}_2\text{SO}_4-\text{Na}_2\text{CO}_3-\text{NaHCO}_3-\text{H}_2\text{O} \) system | \( \text{Na,Na||SO}_4,\text{CO}_3,\text{H}_2\text{O} \) system |
| \( E_1^4 \) | \( \text{Te}+\text{Nk}+3\text{Na·C} \) | \( E_{10}^4 \) | \( \text{Te}+\text{Br}+\text{Gb} \) |
| \( E_2^4 \) | \( \text{Br}+\text{Na·1}+\text{Tr} \) | \( E_{11}^4 \) | \( 5\text{Ca·Na·3}+\text{Gp}+\text{Cc} \) |
| \( E_3^4 \) | \( \text{Te}+\text{Br}+\text{Tr} \) | \( E_{12}^4 \) | \( \text{Br}+\text{Na·1}+\text{Pr} \) |
| \( E_4^4 \) | \( \text{Te}+\text{Tr}+3\text{Na·C} \) | \( E_{13}^4 \) | \( \text{Gb}+5\text{Ca·Na·3}+\text{Br} \) |
| \( \text{System CaSO}_4-\text{CaCO}_3-\text{Ca(HCO}_3)_2-\text{H}_2\text{O} \) | | \( E_{14}^4 \) | \( \text{Pr}+\text{Cc}+5\text{Ca·Na·3} \) |
| \( E_5^4 \) | \( \text{Gp}+\text{Cc}+\text{CaG} \) | \( E_{15}^4 \) | \( \text{Br}+\text{Pr}+5\text{Ca·Na·3} \) |
| \( \text{Na,Na||SO}_4,\text{HCO}_3-\text{H}_2\text{O} \) system | | | |
| \( E_6^4 \) | \( \text{Nk}+\text{Te}+\text{Gb} \) | \( E_{16}^4 \) | \( \text{Na·1}+\text{Tr}+\text{Pr} \) |
| \( E_7^4 \) | \( \text{Gp}+5\text{Ca·Na·3}+\text{CaG} \) | \( E_{17}^4 \) | \( \text{Pr}+\text{Cc}+\text{CaG} \) |
| \( E_8^4 \) | \( \text{Nk}+\text{CaG}+\text{Gb} \) | \( E_{18}^4 \) | \( \text{Nk}+3\text{Na·C}+\text{CaG} \) |
| \( E_9^4 \) | \( \text{Gb}+\text{CaG}+5\text{Ca·Na·3} \) | \( E_{19}^4 \) | \( \text{Tr}+3\text{Na·C}+\text{Pr} \) |
| \( E_{20}^4 \) | | | |
Results and discussion

Based on the data listed in Table 1, the phase diagram (phase complex) for the Na, Ca || SO₄, CO₃, HCO₃ – H₂O system was constructed at 100 °C at the level of four component composition of the salt part, which is shown in the figure as projection of tetrahedral faces.

A unification of the salt part of the phase diagram (combining of identical crystallization fields of various constituent four-component systems), we obtain a schematic diagram for the phase equilibria in the Na, Ca || SO₄, CO₃, HCO₃ – H₂O system at 100°C at level of the four-component composition.
system at 100 °C at the level of four-components, which is shown in the Fig. 2.

The constructed diagram contains geometric images (invariant points, multi-variant curves, divariant fields) correspondent to the various states of the system under study as a function of its composition at the level of four component composition. The phase compositions of the quadruple invariants are listed in Table 1. The phase compositions of the precipitation for the divariant fields are shown in the figure. The phase composition for the monovariant curves connecting quadruple invariant are presented as follows:

\[
\begin{align*}
E_1^4 &\rightarrow E_4^4 = \text{Te} + 3\text{Na·C}; \\
E_1^4 &\rightarrow E_6^4 = \text{Nk} + \text{Te}; \\
E_1^4 &\rightarrow E_{18}^4 = \text{Nk} + 3\text{Na·C}; \\
E_2^4 &\rightarrow E_4^4 = \text{Ber} + \text{Tr}; \\
E_2^4 &\rightarrow E_{12}^4 = \text{Ber} + \text{Na·1}; \\
E_2^4 &\rightarrow E_{16}^4 = \text{Tr} + \text{Na·1}; \\
E_3^4 &\rightarrow E_4^4 = \text{Te} + \text{Tr}; \\
E_3^4 &\rightarrow E_{10}^4 = \text{Te} + \text{Ber}; \\
E_4^4 &\rightarrow E_{19}^4 = \text{Tr} + 3\text{Na·C}; \\
E_5^4 &\rightarrow E_7^4 = \text{CaG} + \text{Gp}; \\
E_5^4 &\rightarrow E_{11}^4 = \text{Gp} + \text{Cc}; \\
E_5^4 &\rightarrow E_{17}^4 = \text{Cc} + \text{CaG}; \\
E_6^4 &\rightarrow E_8^4 = \text{Nk} + \text{Gb}; \\
E_6^4 &\rightarrow E_{10}^4 = \text{Te} + \text{Gb}; \\
E_7^4 &\rightarrow E_9^4 = \text{CaG} + 5\text{Ca·Na·3}; \\
\end{align*}
\]

Fig. 2. The schematic diagram of phase equilibrium in the Na, Ca||SO₄, CO₃, HCO₃-H₂O system at 100 °C at the level of four-component composition, constructed by the translation method.
Through and one-way translation procedure [4] of invariant points from the level of four component composition to the level of five-component composition leads to the formation of the following invariant points:

\[
\begin{align*}
E_1^4 + E_6^4 + E_8^4 + E_9^4 + E_{10}^4 + E_{11}^4 + E_{12}^4 + E_{13}^4 + E_{14}^4 + E_{15}^4 + E_{16}^4 + E_{17}^4 + E_{18}^4 + E_{19}^4 + E_{20}^4 &= Gp + 5CaNa3; \\
E_1^5 + E_6^5 + E_7^5 + E_8^5 + E_9^5 + E_{10}^5 + E_{11}^5 + E_{12}^5 + E_{13}^5 + E_{14}^5 + E_{15}^5 + E_{16}^5 + E_{17}^5 + E_{18}^5 + E_{19}^5 + E_{20}^5 &= Gb + Ber + Pr.
\end{align*}
\]

The analysis of phase equilibria in the Na, Ca||SO₄,CO₃,HCO₃-H₂O system at 25 °C based on the obtained data at the level of five-component composition shows that the crystallization fields formed during the translation of monovariant curves of level four-component composition with their characteristic equilibrium solid phases, namely Tr+Pr, Pr+CaG, 3NaC+Pr, Ber+Pr, Gb+Ber and CaG+Gb, do not closed for their closure by the “intermediate” translation [4] method:

\[
\begin{align*}
E_1^5 &= Nk + 3NaC + Gb + Pr; \\
E_2^5 &= Gb + Ber + Tr + CaG; \\
E_3^5 &= Tr + Pr + Ber + Te; \\
E_4^5 &= Pr + CaG + 5CaNa3 + Gb.
\end{align*}
\]

The displaced chart of phase balance in the Na, Ca||SO₄,CO₃,HCO₃-H₂O system at 100 °C the level of four-component system has been constructed taking into account all types of translations (Fig. 3).

Bold lines indicate monovariant level curves of the five-component composition. These lines connected five various invariant points; they are characterized by the following phase composition of the precipitates:

\[
\begin{align*}
E_1^5 + E_6^5 - E_8^5 &= Nk + 3NaC + Gb; \\
E_4^5 + E_{10}^5 + E_{11}^5 &= Ber + Na.1 + Tr + Pr; \\
E_3^5 &= Te + Ber + Tr + Gb; \\
E_4^5 + E_{19}^5 - E_5^5 &= Te + Pr + 3NaC + Pr; \\
E_5^5 + E_{14}^5 + E_{17}^5 &= Gb + CaG + 5CaNa3; \\
E_7^5 &= Gb + CaG + 5CaNa3 + Ber; \\
E_14^5 + E_{17}^5 &= Pr + Cc + 5CaNa3 + CaG; \\
E_{15}^5 &= Ber + Pr + 5CaNa3 + CaG; \\
E_{20}^5 &= Pr + 3NaC + CaG + Gb.
\end{align*}
\]

Table 2 demonstrates the solid phase equilibrium and contour of the divariant sodium-based system Na, Ca||SO₄,CO₃, HCO₃-H₂O at 100 °C. Among 31 divariant fields that characterized the studied system at 100 °C, 30 fields are formed as a result of translation.
of monovariant curves at the level of four-component composition to the level of five-component composition and one more field with equilibrium solid phases Gb+3Na-C was obtained as a result of the contouring of five invariant points and monovariant curves.

The thin solid lines in Figure 3 indicate the monovariant curves at the level of four-component composition. The equilibrium solid phases that are correspondent to these curves were presented above.

Dash lines with arrows (in Table 2) indicate monovariant curves at the level of five-component composition. They are formed as a result of translation therefore the equilibrium phases corresponded to these monovariant curves are identical to the equilibrium solid phases of the invariant points of the corresponding quaternary systems.

Fig. 3. Combined diagram of phase equilibria (phase complex) for the Na, Ca||SO₄, CO₃, HCO₃–H₂O system at 100 ºC at the level of four-component composition constructed by the translation method.
### Table 2

Equilibrium solid phases and contours of the divariante fields in the Na, Ca || SO₄, CO₃, HCO₃-H₂O system

| Equilibrium solid phases of fields | Field contours in the diagram (Fig. 3) | Equilibrium solid phases of fields | Field contours in the diagram (Fig. 3) |
|-----------------------------------|----------------------------------------|-----------------------------------|----------------------------------------|
| 3Na-C+Nk                          | E₁⁴ → E₁⁵                               | CaG+5Ca·Na-3                      | E₅⁴ → E₂⁵ E₁²⁵                         |
| Nk+Te                             | E₁⁴ → E₁⁵                               | CaG+Gb                           | E₄⁴ → E₆⁵ E₁₄⁵                         |
| Te+3Na-C                          | E₁⁴ → E₁⁵                               | CaG+Nk                           | E₈⁴ → E₆⁵                             |
| Na-1+Tr                           | E₁⁴ → E₁⁵                               | 5Ca·Na-3+Gb                      | E₅⁴ → E₆⁵                             |
| Na+Ber                            | E₁⁴ → E₁⁵                               | Gb+Ber                           | E₁₀⁴ → E₃⁵ E₁₂⁵                       |
| CaG+Gp                            | E₁⁴ → E₁⁵                               | Gp+5Ca·Na-3                      | E₉⁴ → E₈⁵                             |
| Te+Ber                            | E₁⁴ → E₁⁵                               | Na-1+Pr                          | E₁₂⁴ → E₂⁵                           |
| Te+Tr                             | E₁⁴ → E₁⁵                               | Ber+5Ca·Na-3                     | E₁₃⁴ → E₇⁵                             |

Diagram (Fig. 3)
| Equilibrium solid phases of fields | Field contours in the diagram (Fig. 3) | Equilibrium solid phases of fields | Field contours in the diagram (Fig. 3) |
|-----------------------------------|---------------------------------------|-----------------------------------|---------------------------------------|
| **Tr+3Na·C**                      | $E_4^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ | **Ber+Pr**                        | $E_{12}^4 \longrightarrow \ldots \longrightarrow \ E_{13}^5 \longrightarrow \ E_{14}^5 \longrightarrow \ E_{15}^5 \longrightarrow \ E_{16}^5$ |
| **Cc+CaG**                        | $E_3^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ | **Cc+5Ca·Na·3**                   | $E_{14}^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ |
| **Gp+Cc**                         | $E_4^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ | **Pr+Cc**                         | $E_{14}^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ |
| **CaG+Gp**                        | $E_4^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ | **Tr+Pr**                         | $E_{16}^4 \longrightarrow \ldots \longrightarrow \ E_5^5 \longrightarrow \ E_{13}^5 \longrightarrow \ E_4^5$ |
| **Te+Gb**                         | $E_{10}^4 \longrightarrow \ E_1^5 \longrightarrow \ E_{11}^5 \longrightarrow \ E_4^5$ | **Pr+CaG**                        | $E_{17}^4 \longrightarrow \ldots \longrightarrow \ E_5^5 \longrightarrow \ E_9^5$ |
| **Nk+Gb**                         | $E_4^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ | **3Na·C+CaG**                     | $E_{18}^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ |
| **5Ca·Na·3**                      | $E_{11}^4 \longrightarrow \ldots \longrightarrow \ E_5^5$ | **3Na·C+Pr**                      | $E_{19}^4 \longrightarrow \ldots \longrightarrow \ E_5^5 \longrightarrow \ E_{11}^5 \longrightarrow \ E_4^5$ |
|                                   |                                       | **Gb+3Na·C**                      | $E_{20}^5 \longrightarrow \ldots \longrightarrow \ E_{10}^5 \longrightarrow \ E_{14}^5 \longrightarrow \ E_{15}^5 \longrightarrow \ E_6^5$ |
Conclusions

The translation method applied for the Na,Ca||SO₄,CO₃,HCO₃-H₂O system at 100 °C while transforming the phase equilibria from the level of four-component (A) to the level of five-component (B) reveals following changes in the numbers of geometric patterns:

| Component level       | A   | B   |
|-----------------------|-----|-----|
| Invariant point       | 20  | 14  |
| Monovariant curves    | 30  | 33  |
| Divariant fields      | 13  | 31  |

The decrease in the number of invariant points from 20 at the level of four-component composition to 14 at the level of five-component composition is due to the mutual combination (from mathematical approach) of quadruple invariant points, or mutual intersection of monovariant curves (within the graphical approach) formed during the transformation and subsequent translation of these quadruple invariant points to the level of five-component composition and the formation of quintuple invariant points. The increase in the number of monovariant curves from 30 at the level of four-component composition up to 33 at the level of five-component composition is due to the fact that 20 of them are formed as a result of translation and quadruple invariant points, and another 13 connected five invariant points. The raise of components’ number by unity from four to five leads to the increase of divariant fields’ number from 13 at the level of four-component composition to 31 at the level of five-component composition. It was shown that 30 of them were formed in a course of translation procedure of monovariant curves of the level of four-component composition and one more was obtained as a result of the surface contouring in the system with five invariant points and monovariant curves connecting these points.

References

1. Spravochnik eksperimental’nykh dannykh po rastvorimosti mnogokomponentnykh vodno-solevykh system [Reference book on experimental data for solubility in multicomponent water-salt systems]. Vol. II., Books. 1–2. Saint-Petersburg: Khimizdat, 2004. 1247 p. Russian.
2. Soliev L, Jumaev MT. Phase equilibria in the Na,Ca//SO₄,CO₃,HCO₃–H₂O system at 0 °C. Chimica Techno Acta. 2019;6(1):24. DOI: 10.15826/chimtech.2019.6.1.03
3. Soliev L, Jumaev MT. Phase equilibrium of Na,Ca||SO₄,CO₃,HCO₃–H₂O systems at 50 °C. Applied Solid State Chemistry. 2018;4(5):192–8. DOI: 10.18572/2619-0141-2018-4-5-192-198
4. Soliev L. [Prediction of structure of multicomponent water-salt systems phase equilibria diagram by means of translation method]. VINITI № 8990-B87, 1987. 28 p. Russian.
5. Goroshenko YaG, Soliev L. [New trends in methodology of physicochemical analysis of complex and multicomponent systems (for 125th anniversary of N.S. Kurnakov)]. Zh. Neorg. Khim. 1987;32(7):1676. Russian.
6. Goroshchenko YaG. Masstsentricheskiy metod izobrazheniya mnogokomponentnykh system [The Center of Mass Method for Multi-component Systems Imaging]. Kiev: Naukova Dumka, 1982. 264 p. Russian.
7. Tursunbadalov Sh, Soliev L. Phase Equilibria in the quinery Na,K||SO₄,CO₃,HCO₃–H₂O system at 75 °C. J Solution Chem. 2015;44(8):1626–39. DOI: 10.1007/s10953-015-0368-3
8. Tursunbadalov Sh, Soliev L. Phas Equilibria in multicomponent water-salt system. J Chem Eng Data. 2016;61(7):2209–20. DOI: 10.1021/acs.jced.5b00875
9. Soliev L, Jumaev MT, Turaev RO, Makhmadov KhR. [Solubility in the system Na₂SO₄–Na₂CO₃–NaHCO₃–H₂O at 50 °C]. Chemical Journal of Kazakhstan. 2017;4(60):29. Russian.
10. Soliev L, Jumaev MT, Nuri V, Valantino N. Phase Equilibria System Na,Ca||SO₄,HCO₃–H₂O at 25 °C. Bulletin of the Tajik National University (Series of natural sciences). 2012;1(3):85:221.
11. Soliev L, Jumaev MT, Iqbol G, Nizomov IM. Phase Equilibria in the Na,Ca||CO₃,HCO₃-H₂O system at 25 °C. Reports of the Academy of Sciences of the Republic of Tajikistan. 2012; 55(3):220. Russian.
12. Usmonov MB. Fazovye ravnovesiya i rastvorimost’ v sisteme Na,Ca||SO₄,CO₃,F-H₂O pri 0 i 25°C [Phase equilibria and solubility in the Na,Ca||SO₄,CO₃,F-H₂O system at 0 and 25°C] [dissertation]. Tajik State Pedagogical University; 2015. 126 p. Russian.
13. Valantena N. Fazovye ravnovesiya i rastvorimost’ v sisteme Na,Ca||SO₄,HCO₃,F-H₂O pri 0 i 25°C [Phase equilibria and solubility in the Na,Ca||SO₄,HCO₃,F-H₂O system at 0 and 25°C] [dissertation]. Tajik State Pedagogical University; 2016. 121 p. Russian.
14. Gulomiqbol G. [Phase equilibria and solubility in the Na,Ca||CO₃,HCO₃,F-H₂O system at 0 and 25°C] [dissertation]. Tajik State Pedagogical University; 2018. Russian.
15. Soliev L. [Schematic phase equilibria diagrams for multicomponent systems]. Russ J Inorg Chem. 1988;33(5):1305. Russian.