Phase Relations in the Na, K/Cl, SO₄, CO₃−H₂O Quinary System at 35 °C

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ABSTRACT: The phase equilibria in the quinary Na, K/Cl, SO₄, CO₃−H₂O system at 35 °C were determined, and a total phase equilibria diagram of the system was constructed by means of the translation method. Six points saturated with four solid phases, 19 curves saturated with three solid phases, and 21 fields saturated with two solid phases were determined in the system. Structures of dry-salt diagrams for the parts saturated with each of the nine solid phases were extracted from the total phase equilibria diagram of the system. The obtained results for the parts saturated with halite and sylvite agree well with the available literature data and verify the rest of the data obtained in this work.

INTRODUCTION

Multicomponent systems are unquestionably potential sources of chemicals required in the chemical industry. Rational exploitation of these sources and extraction of valuable ingredients from them require phase equilibria knowledge on the systems. Unfortunately, present means of elucidation of the phase equilibria in these systems are not adequately capable. The need to search and develop new methods of investigation of multicomponent water–salt systems is a must. The need is also obvious in the presentation of the obtained results from phase equilibria investigations. What researchers in the field of phase equilibria investigations are familiar with is the parts saturated with a single solid phase which are obtained as a result of laborious experimental studies. Unfortunately, it is not possible to find a set of parts of any quinary system in the literature that can be used in the construction of total diagram of the relevant system. Moreover, only experimental results are not adequate to reveal the relations of the nearby crystallization areas in the diagrams of complex systems.1 Hence, there is always a need for sound theoretical elucidations which support, guide, and analyze the experimental investigations.

The Searles Salt Lake brines chiefly contain minerals composed of Na, K, CO₃, SO₄, Cl, B₄O₇, and H₂O.2 There are several studies performed related with the Searles Salt Lake brines.3−5 The quinary Na K/Cl, CO₃, SO₄−H₂O system was investigated by Teeple whose results were compiled in a monograph.3 The study included all five quaternary sub-systems at 20, 35, 50, 75, and 100 °C isotherms. The author presented a total of eight phase diagrams of the system between 20 and 100 °C. One diagram for the part of the system saturated with halite at each of 20 and 100 °C. He gave two diagrams for the parts of the system saturated with halite and sylvite at each of 3, 50, and 75 °C isotherms. These diagrams which were used in the utilization of Searles Salt Lake brines have been sources of information since 1929. Although the monograph describes the phase equilibria in the system to a certain degree, the author states, “the diagrams naturally give a very incomplete picture of the five-component system.” However, there is also the statement “they cover only a small part of it at a very few temperatures, but we have no more to offer now” in his monograph. Most importantly, he emphasized the lack of means of presentation of the obtained results from the investigation of phase equilibria in quinary systems. The Searles Lake evaporite deposit consists of a complex suite of minerals and mineral assemblages which cover wide ranges of bulk compositions. Because of the large number of components involved, presentation of phase relations by conventional temperature-composition diagrams, alone, is impossible.5 Overall review of literature shows the requirement of investigation of the phase equilibria in the quinary Na K/Cl, CO₃, SO₄−H₂O system more broadly in
This work is devoted to the presentation of results of the overall system. 12 The method links the component subsystems with the geometrical compatibility principle of geometrical figures of polythermal phase equilibria diagrams, the diagrams for quaternary phase equilibria data and the data for the halite—data for the quaternary composition of the system. The set of among which phase equilibria for only two phases were system at 35 °C isotherms which can lead to obtain comprehensive phase equilibria results when the system is investigated by the same author who gave his results in the same monograph.3 The nine solid phases, as listed in Table 1, shows that all quaternary subsystems of the system were also investigated by the same monograph. 3 The nine solid phases, as listed in Table 1, refers to points, curves, and figures of the overall system. For example, invariant point, monovariant curve, and divariant fields, and so on. The formation of geometrical figures of the (n + 1)-component subsystems is envisaged by this method when the system enters the overall (n + 1)-component systems. Thus, transformed forms of geometrical figures of subsystems participate in the formation of geometrical figures of overall system. For example, invariant points transform into monovariant curves, monovariant curves into divariant fields, and so on. The formation of geometrical figures of the (n + 1)-component composition occurs in accordance with their topological properties and the Gibbs phase rule. As the method was applied for isothermal—isobaric processes in the present work, the general equation for the Gibbs phase rule $F = C – P + 2 + z$ is reduced to $F = C – P$. Every invariant point, monovariant curve, and divariant field is saturated with four, three, and two different solid phases, respectively, along with relevant liquid phases in quinary systems.

The data on four-component subsystems are used in the determination of phase equilibria in overall five-component systems by means of the translation method. These data are mainly in equilibrium solid phases at the geometrical figures of the subsystems. By the term geometrical figure, the method refers to points, curves, fields, and volumes in the diagrams. The quinary Na, K//Cl, SO₄, CO₃—H₂O system is composed of five Na, K//Cl, SO₄—H₂O; Na, K//Cl, CO₃—H₂O; Na, K//Cl, CO₃—H₂O; Na, K//Cl, CO₃—H₂O; Na, K//Cl, CO₃—H₂O subsystems. The literature review shows that all quaternary subsystems of the system were also investigated by the same author who gave his results in the same monograph. 3 The nine solid phases, as listed in Table 1, are in equilibrium in the quinary Na, K//Cl, SO₄, CO₃—H₂O system at 35 °C.

### Quaternary Phase Equilibria

Table 2 compiles the equilibrium solid phases at the invariant points of the quaternary subsystems. There are 14 quaternary invariant points in the system saturated with three solid phases along with relevant liquid phases. In Table 2, further $E_{ij}$ notations refer to points, curves, fields, and figures of the overall system. For example, invariant point, monovariant curve, and divariant fields, and so on. The formation of geometrical figures of the (n + 1)-component composition occurs in accordance with their topological properties and the Gibbs phase rule. As the method was applied for isothermal—isobaric processes in the present work, the general equation for the Gibbs phase rule $F = C – P + 2 + z$ is reduced to $F = C – P$. Every invariant point, monovariant curve, and divariant field is saturated with four, three, and two different solid phases, respectively, along with relevant liquid phases in quinary systems.

### METHODOLOGY

The translation method is derived from the compatibility principle of physicochemical analysis and functions in accordance with the Gibbs phase rule. The increase in the dimension of geometrical figures of n-component subsystems is envisaged by this method when the system enters the overall (n + 1)-component systems. Thus, transformed forms of geometrical figures of subsystems participate in the formation of geometrical figures of overall system. For example, invariant points transform into monovariant curves, monovariant curves into divariant fields, and so on. The formation of geometrical figures of the (n + 1)-component composition occurs in accordance with their topological properties and the Gibbs phase rule. As the method was applied for isothermal—isobaric processes in the present work, the general equation for the Gibbs phase rule $F = C – P + 2 + z$ is reduced to $F = C – P$. Every invariant point, monovariant curve, and divariant field is saturated with four, three, and two different solid phases, respectively, along with relevant liquid phases in quinary systems.

There are experimental results for the quaternary and quinary compositions which can lead to obtain comprehensive phase equilibria data on the Na, K//Cl, SO₄, CO₃—H₂O system at 35 °C. There are nine solid phases in the system among which phase equilibria for only two phases were described by the Teeple. At the same time, he presented full data for the quaternary composition of the system. The set of quaternary phase equilibria data and the data for the halite- and sylvite-saturated parts on the quinary composition facilitate further investigation of the system. For the generation of polythermal phase equilibria diagrams, the diagrams for different isotherms are required. Hence, the method can be applied for other isotherms of the systems and results from different isotherms can be used for the generation of polythermal phase equilibria diagrams.

### Table 1. Equilibrium Solid Phases in the Quinary Na, K//Cl, SO₄, CO₃—H₂O System at 35 °C

| mineral name | symbol | mineral name | symbol |
|--------------|--------|--------------|--------|
| NaCl         | halite | K₂SO₄        | arcanite |
| KCl          | sylvite| 2Na₂SO₄Na₂CO₃| berkeite |
| 3Na₂CO₃·H₂O  | glaserite| Na₂CO₃-K₂CO₃| nk     |
| Na₂CO₃·H₂O  | n1     | Na₂SO₄       | ns     |
| K₂CO₃·1.5H₂O | k1.5   |              |        |

### Table 2. Equilibrium Solid Phases at the Quaternary Invariant Points in the Na, K//Cl, SO₄, CO₃—H₂O System at 35 °C

| invariant point | equilibrium solid phases | invariant point | equilibrium solid phases | invariant point | equilibrium solid phases |
|-----------------|--------------------------|-----------------|--------------------------|-----------------|--------------------------|
| quaternary Na, K//Cl, and SO₄—H₂O system | sylvite + arcanite + glaserite | E₁            | halite + n1 + sylvite + glaserite | E₄          | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| E₂            | n1 + sylvite + glaserite | | n1 + k1.5 + sylvite + glaserite | E₃          | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| E₃            | halite + ns + glaserite | | n1 + k1.5 + sylvite + glaserite | E₁²         | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| invariant point | equilibrium solid phases | invariant point | equilibrium solid phases | invariant point | equilibrium solid phases |
| quaternary NaCl·Na₂SO₄·Na₂CO₃·H₂O system | NaCl + Na₂SO₄ + Na₂CO₃ + H₂O | E₁        | k1.5 + arcanite + glaserite | E₁₃        | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| E₁           | n1 + K₁.5 + arcanite + glaserite | | n1 + arct + glaserite | E₁₄        | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| E₂           | halite + ns + K₁.5 + arcanite + glaserite | | n1 + arct + glaserite | E₁₅        | Na₂SO₄ + K₁.5 + arcanite + glaserite |

## Table 1. Equilibrium Solid Phases at the Quaternary Invariant Points in the Na, K//Cl, SO₄, CO₃—H₂O System at 35 °C

| mineral name | symbol | mineral name | symbol |
|--------------|--------|--------------|--------|
| NaCl         | halite | K₂SO₄        | arcanite |
| KCl          | sylvite| 2Na₂SO₄Na₂CO₃| berkeite |
| 3Na₂CO₃·H₂O  | glaserite| Na₂CO₃-K₂CO₃| nk     |
| Na₂CO₃·H₂O  | n1     | Na₂SO₄       | ns     |
| K₂CO₃·1.5H₂O | k1.5   |              |        |

## Table 2. Equilibrium Solid Phases at the Quaternary Invariant Points in the Na, K//Cl, SO₄, CO₃—H₂O System at 35 °C

| invariant point | equilibrium solid phases | invariant point | equilibrium solid phases | invariant point | equilibrium solid phases |
|-----------------|--------------------------|-----------------|--------------------------|-----------------|--------------------------|
| quaternary Na, K//Cl, and SO₄—H₂O system | sylvite + arcanite + glaserite | E₁            | halite + n1 + sylvite + glaserite | E₄          | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| E₂            | n1 + sylvite + glaserite | | n1 + k1.5 + sylvite + glaserite | E₃          | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| E₃            | halite + ns + glaserite | | n1 + k1.5 + sylvite + glaserite | E₁²         | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| invariant point | equilibrium solid phases | invariant point | equilibrium solid phases | invariant point | equilibrium solid phases |
| quaternary NaCl·Na₂SO₄·Na₂CO₃·H₂O system | NaCl + Na₂SO₄ + Na₂CO₃ + H₂O | E₁        | k1.5 + arcanite + glaserite | E₁₃        | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| E₁           | n1 + K₁.5 + arcanite + glaserite | | n1 + arct + glaserite | E₁₄        | Na₂SO₄ + K₁.5 + arcanite + glaserite |
| E₂           | halite + ns + K₁.5 + arcanite + glaserite | | n1 + arct + glaserite | E₁₅        | Na₂SO₄ + K₁.5 + arcanite + glaserite |
represent the invariant points. The superscript \( x \) and subscript \( y \) symbolize the complexity in the system which depends on the number of components and a serial number of the relevant point, respectively.

The set of quaternary phase equilibria diagrams which were constructed based on the data in Table 2 is shown on an unfolded prism in Figure 1. Both the dashed arrows and thick solid curves represent the quaternary monovariant curves in Figure 1. The former and latter represent the curves formed from an extension of relevant ternary points and the curves that form between the quaternary points, respectively. By the same analogy, the curves of the overall quinary system are also classified and represented in the same way throughout this work. The dashed arrows represent the ones formed from quaternary points, while thick curves represent the quinary curves extending between points when the quinary system is considered.

Combining crystallization fields in different parts of the unfolded prism, as shown in Figure 1, produces the transition diagram, as shown in Figure 2. The occurrence of the combined fields of phases varies as two and three systems depending on the location of the phases. For instance, \( \text{Na}_2\text{CO}_3\cdot\text{K}_2\text{CO}_3 \) is found in two quaternary systems, and \( \text{K}_2\text{CO}_3\cdot1.5\text{H}_2\text{O} \) is observed in three quaternary systems. Sylvite also occurs in three different quaternary subsystems.

Transition-phase equilibria diagram, as shown in Figure 2, reflects the surface of a triangular prism which represents the quaternary composition of the system. The separate part of this diagram represents the sylvite crystallization field and completes the surface of the prism. Although the sylvite field was chosen for convenience in construction of this diagram, any other field may also be chosen.

![Figure 1](image1.png)  
*Figure 1. Set of quaternary phase equilibria diagrams in the quinary Na, K//Cl, \( \text{SO}_4\cdot\text{CO}_3\cdot\text{H}_2\text{O} \) system at 35 °C.*

![Figure 2](image2.png)  
*Figure 2. Transition phase equilibria diagram of the quinary Na, K//Cl, \( \text{CO}_3\cdot\text{SO}_4\cdot\text{H}_2\text{O} \) system at 35 °C from the quaternary to quinary composition.*

Traditionally, the interior of the prism is used to represent the composition of the quinary systems, while the exterior reflects the quaternary geometrical figures of the system. Hence, every geometrical figure inside the prism belongs to the quinary composition. Unfortunately, space restriction does not allow a clear presentation of the interior. What the translation method offers in this respect is the superimposition of the quinary geometrical figures on the transition diagrams, which substantially alleviates the presentation of the quinary composition of systems. Hence, the diagram in Figure 2 will be used as a matrix and base for the superimposition of quinary geometrical figures.
Transition diagram, as shown in Figure 2, is the compact version of the unfolded prism, as shown in Figure 1. It is composed of 14 quaternary points and 21 quaternary monovariant curves which link them. The monovariant curves and invariant points which outline the sylvin field are the same curves and points that are available in the main part of the diagram. Outlines of the nine solid phases in the system can be seen in the diagram in Figure 2.

**Quinary Phase Equilibria and Total Diagram of the System.** Determination of invariant points on the overall system ensures the extension of geometrical figures from subsystems. The initial step of this determination is the determination of invariant points which facilitates further predicting of the curves and fields of the overall composition.

There are two quinary points in the system, which are generated because of the transformation of three quaternary points into the quinary curves. The invariant E1 and E2 points in a and b form at the intersection of the latter curves that originated from three points of the different quaternary subsystems.

\[ E^5_1 + E^5_8 + E^5_{10} \rightarrow E^5_5 = ns + gla + hal + bk \]  
\[ E^5_4 + E^5_4 + E^5_4 \rightarrow E^5_3 = k1.5 + arc + nk + syl \]

Each of the four points in eqs c–f form at the intersection of two different curves that generated from the transformation of quaternary points.

\[ E^5_9 + E^5_11 \rightarrow E^5_5 = bk + n1 + hal + gla \]  
\[ E^5_5 + E^5_{12} \rightarrow E^5_5 = gal + arc + n1 + syl \]  
\[ E^5_2 + E^5_{13} \rightarrow E^5_5 = nk + n1 + arc + syl \]  
\[ E^5_4 + E^5_6 \rightarrow E^5_6 = hal + syl + gla + n1 \]

The total number of quinary invariant points hence becomes six, while two of which form at the intersection points of three curves and the other four points form at the intersection points of two curves. These quinary points at the same time are linked by means of quinary monovariant curves of different nature, which are also saturated with three solid phases in equilibrium. The eqs g–k represent the equilibrium solid phase composition of the quinary curves that extend between the determined invariant points in eqs a–f. The curves link the points that vary by a solid phase in equilibrium.

\[ E^5_7 - E^5_6 = gla + hal + bk \]  
\[ E^5_7 - E^5_9 = hal + gla + n1 \]  
\[ E^5_5 - E^5_4 = gla + syl + n1 \]  
\[ E^5_3 - E^5_8 = n1 + syl + arc \]  
\[ E^5_2 - E^5_3 = arc + syl + nk \]

The monovariant curves of the overall composition are classified into two types by the translation method; the ones generated from transformation of relevant invariant points of subsystems and the ones that extend between the invariant points of the overall composition. There are 14 quaternary points in the system, as shown in Figure 1, whose transformation and intersection generate quinary monovariant curves and invariant points given in eqs a–f, respectively. The main principle used in the selection of combining curves which form from the extension of invariant points of subsystems is that the points at the origin must vary by a solid phase and must be located in adjacent subsystems.

The equilibrium solid phase compositions of the curves generated from the latter quaternary points are identical with the composition of relevant points. Hereby, the 14 points of the quaternary composition, which are also listed in Table 2, generate 14 quinary curves with the identical solid-phase compositions. Hence, the total number of quinary curves becomes 19 curves by the addition of the ones in eqs g–k.

The determination of the composition of quinary divariant fields is straightforward by means of the translation method as the method foresees the extension of all geometrical figures of subsystems into the composition of the overall system when the system enters the global composition. The solid phase composition of this kind of fields is identical with the composition of relevant monovariant curves that transform into fields. 21 quinary fields are formed as there are 21 curves in the transition diagram, as shown in Figure 2. The solid phase composition of the fields that is formed between the quinary points and curves, which were not observed in this work, is determined using the solid phase composition of outlining points and curves. Quinary trivariant volumes which are saturated with a solid phase are generated from the extension of quaternary fields into the quinary composition.

Total phase equilibria diagram of the system is given in Figure 3. A reciprocal relationship between the determined points, curves, and fields is reflected in it. The dashed arrows and thick solid curves represent the quinary monovariant curves.

### RESULTS AND DISCUSSION

The difficulty of presentation of phase relations in the mineral assemblages was indicated by Eugster and Smith who stated, “the number of components involved in most mineral assemblages is large and makes complete graphic representation of the phase relations impossible.”

The most used techniques to represent a total phase diagram in a lower dimension are projections, sections, and pseudosections. Reducing the dimension of the total phase diagram inevitably leads to a loss of information. Therefore, it
must be decided which information of the total phase diagram is needed to document a given petrological observation satisfactorily. Analysis of the results obtained by Teeple shows that halite and sylvite are involved in three and four different quinary points, respectively. The author obtained diagrams of the system for the latter parts saturated with KCl and NaCl. “This type of diagram has been exceedingly valuable in interpreting data because the simple limitation we have fixed, complete saturation with NaCl, is a very usual one in our plant practice” is what he stated about the diagram he obtained for halite which is still in use in the utilization of Searles lake brines in California.

The overall position of the latter two phases in the diagram and their reciprocal relations with the rest of the phases in the system are shown and highlighted in Figures 4 and 5. These diagrams clearly show the whole set of phase relations in the overall Na, K/Cl, SO₄, CO₃−H₂O system at 35 °C including all the nine equilibrium solid phases. One may easily see points, curves, and fields involving halite and sylvite in total diagram of the system obtained in this work and the available data by Teeple verify the rest of the data obtained in this work. Fragmentation of the total phase equilibria diagram into the parts saturated with solid phases gives better clarification of the obtained results for the reader. Each of the parts saturated with solid phases has the same application as the diagrams presented by Teeple for the halite or sylvite parts. The diagrams, as shown in Figure 6a–i, were extracted from the total diagram of the system. They represent the parts of the system saturated with relevant solid phases. The parts saturated with halite and sylvite are shown in Figure 6c,i, respectively.

As the translation method, which relies on the compatibility principle, foresees the formation of geometrical figures of the quinary composition because of transformation and translation of quaternary geometrical figures, it clarifies difficulties in the investigation of complex systems. Formation of quinary geometrical figures because of the transformation and extension of quaternary geometrical figures elucidates the structure of the total diagram. Because the transformation of geometrical figures increases the dimension by a unit, the volumes which are generated from the extension of divariant fields require three dimensions. These volumes play an important role in the application as all the relevant points, curves, and fields are saturated with the same solid phase. On the other hand, the diagrams constructed for the parts saturated with a solid phase represent the composition of the relevant volumes.

The type of diagram used or developed by the Teeple is not in use anymore and far from the current version of diagrams used in the presentation of phase equilibria in quinary systems. However, what is obvious is the solid phase composition of geometrical figures in those diagrams is in good agreement with the solid phase composition of geometrical figures determined by the translation method. As Teeple emphasizes the lack of methodology of presentation of results of investigation of phase equilibria in multicomponent systems in 1929, this accentuate is still valid today even in the 21st century. The obtained results in this work are expected to alleviate this case for this quinary system. The diagrams can fully guide the process designs, which is used in the industry instead of trial and error. They do not leave any ambiguity in phase equilibria knowledge in the system as the entire system was considered in the investigation, and the obtained results were verified through the available literature data.

The total diagrams show the internal structure of the triangular prism and hence is not visualized due to dimension. The three-dimensional figure reflected on a plane is obviously beyond the mental comprehension of the authors and probably some of the readers as well. The volumes, as shown in Figure 6a–i, represent the geometrical figures relevant to individual solid phases, and the diagrams, as shown in Figure 7a–i, represent the results obtained from them. The latter diagrams draw the obtained results to the contemporary understanding of the quinary phase equilibria. The diagrams in Figure 7a–i were obtained from the crystallization regions in Figure 6a–i. They present the structures of phase equilibria diagrams of the
system saturated with relevant solid phases. There are nine diagrams of the system equivalent to the solid phases in the system at the investigated temperature.

The design and synthesis of crystallization-based separation processes can hardly be imagined without graphical illustration of phase behavior in the form of solid−liquid equilibrium phase diagrams. The subtle phase behaviors of chemical systems are transformed into visible pictorial features such as curves and surfaces though the phase diagrams. An effective way for understanding the reciprocal relationship of the variables along with the thermodynamic limits of the considered system is afforded by this. More importantly, the strategies and operations for carrying the feed mixture to the desired crystallization regions, where pure solids of the targeted components can be isolated, depend mainly on the perception derived from the visualization process. Initial crystallization-based separation schemes are composed of such operations, which include temperature shift, solvent addition/removal, and so on. The resultant process flowsheet can then be generated accordingly. Compared to the traditional methods that mainly rely on trial-and-error practice, process synthesis facilitated by phase diagrams is more reliable and requires less time, effort, and resources. The crystallization pathways are followed on the diagrams in Figure 7a–i.

When the initial and final states of the system are known, several routes through the solubility diagram can replicate an extractive process. Each of the routes is disintegrated into elementary steps where a single variable (temperature, composition) is altered, and a mass balance is set step-by-step. Then, the selection of the best theoretical process is carried out by drawing and comparing the flowcharts of the various paths. To check and adjust the assumptions of the theoretical investigation, a pilot unit can be considered. This quinary Na, K//Cl, SO₄, CO₃−H₂O system is a massive resource for the extraction of dissolved salts, as listed in Table 1. However, comprehensive exploitation requires more than the part saturated with halite or sylvite. Sometimes the part saturated with halite even is not adequate for the systems saturated with halite. The assumptions through the latter part may not be sufficient to elucidate the case as it happened in the work. The authors expected minerals kainite and kieserite but were not able to observe. Total phase equilibria diagrams and parts of the system saturated with other salts guide the cases like this.

The representation of monovariant curves, as shown in Figures 1−6a−i, stems from the essence of extension of the invariant points in subsystems to the composition of overall system. In other words, they show that the points are extended to higher level transforming into curves. The monovariant
Reciprocal relation of points, curves, and fields in the halite-saturated part of the systems given by Gale, as shown in Figure 8, and the diagram, as shown in Figure 7c, are in full agreement. There are three points saturated with halite as it is given by Gale. The three invariant points saturated with halite are also saturated with 3K₂SO₄·Na₂SO₄ + KCl + Na₂CO₃·H₂O, 3K₂SO₄·Na₂SO₄ + Na₂CO₃·H₂O + 2Na₂SO₄·Na₂CO₃, and Na₂SO₄ + 3K₂SO₄·Na₂SO₄ + 2Na₂SO₄·Na₂CO₃ phases. There are two monovariant curves which link these three points are saturated with 3K₂SO₄·Na₂SO₄+Na₂CO₃·H₂O and 3K₂SO₄·Na₂SO₄+2Na₂SO₄·Na₂CO₃ along with halite. The five divariant fields which are also saturated with halite are saturated with 3K₂SO₄·Na₂SO₄, KCl, Na₂CO₃·H₂O, 2Na₂SO₄·Na₂CO₃, and Na₂SO₄ phases. Comparison and analysis of the diagram in Figure 7c with diagram obtained with Gale in Figure 8 show consistency and full agreement.

The three ions except the ones in composition of the halite are shown at the corners in diagram in Figure 8 as the system was saturated with NaCl in the study by Gale. The point C representing the composition of the hot concentrated liquor on the diagram given by Gale was used in the process applied by Gale where only KCl crystallized out along the line CM. The initial phase which crystallizes from the system determines the diagram to be used during the process. Further processes of precipitates will be followed on the chosen diagram.

Considerable quantities of sodium carbonate, sodium sulfate, and sodium chloride crystallize during evaporation and are removed to become raw material for the soda products plant when processes are followed using the diagram, as shown in Figure 8. For elucidation of the extractive processes of the rest of the phases from brine diagrams, Figure 7 can be used. There are many studies where the parts of the quinary system saturated with a solid phase. All these studies gave partial results which elucidated the investigated systems with

Figure 7. (a–i) Phase equilibria diagrams of the quinary Na, K/Cl, SO₄, CO₃−H₂O system at 35 °C saturated with equilibrium solid phases.
The translation method is used in the determination of the phase equilibria in \((n+1)\)-multicomponent water−salt systems using the data in relevant \(n\)-component subsystems. It was derived from the compatibility principle of physicochemical analysis and functions, in accordance with the Gibbs phase rule. It gives the best results for the quinary systems which are extremely difficult to study with other methods. Uncertainty can be expected when there is a new phase on the overall composition of the system that is on the quinary composition for five-component systems. For the present study fortunately, this case was already overcome by the evidence data on the quinary composition and closure of the geometrical figures, in consistence with the Gibbs phase rule. This work was one of the exceptionally interesting studies where it was possible to find some quinary phase equilibria data, verifying the data obtained by the translation method. The system includes seven solid phases out of which two were investigated by Teeple before us. The latter two halite and sylvite parts which verified our obtained data did not leave any question about the reliability of the results in this work.

**CONCLUSIONS**

Investigation of phase equilibria in quinary systems and presentation of obtained results to the reader strain the mental capacity of researchers. Hence, the only exit from this case is bringing the obtained results to the understanding of the contemporary researchers in this field. The obtained results in this work, which shed light on the phase equilibria understanding in quinary systems to a considerable extent, elucidate the phase equilibria in the quinary Na, K//Cl, SO\(_4\), CO\(_3\), H\(_2\)O system at 35 °C. The obtained results comprise the parts of the system saturated with each of the nine solid phases in the system. They can be used as a guide and reference for the rational exploitation and extraction of dissolved salts in this quinary system. Analysis and discussion of results with respect to Teeple’s results introduce different methodologies in the investigation of this industrially important system. The results obtained by the translation method pave the way to further understanding the phase equilibria in this system and relieve future experimental investigation of the system.

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**Notes**

The authors declare no competing financial interest.

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