

# Estimation of the Solid-Liquid Phase Equilibria of the Quinary System $\text{Na}^+$ , $\text{K}^+$ , $\text{Mg}^{2+}/\text{Cl}^-$ , $\text{SO}_4^{2-}/\text{H}_2\text{O}$ and the Hexary System $\text{Na}^+$ , $\text{K}^+$ , $\text{Mg}^{2+}$ , $\text{Ca}^{2+}/\text{Cl}^-$ , $\text{SO}_4^{2-}/\text{H}_2\text{O}$ in a Temperature Range Below $140^\circ\text{C}$

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## ABSTRACT

The results of the estimation of the solid-liquid phase equilibria of the quinary system  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}/\text{Cl}^-$ ,  $\text{SO}_4^{2-}/\text{H}_2\text{O}$  and the hexary system  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}/\text{Cl}^-$ ,  $\text{SO}_4^{2-}/\text{H}_2\text{O}$  in a temperature range below  $140^\circ\text{C}$  are described. Therefore it is possible to define the phase diagram of the quinary system between  $-35.4$  and  $140^\circ\text{C}$  at high  $\text{MgCl}_2$  concentrations and the hexary system up to  $110^\circ\text{C}$ .

In general, the carnallite crystallization field shifts in the quinary system to higher  $\text{MgCl}_2$  concentrations with an increase of temperature. This is accompanied by a decrease of the saturation concentrations of  $\text{MgSO}_4$ ,  $\text{NaCl}$  and  $\text{KCl}$ .

The investigations of the hexary system show that a conversion of anhydrite into syngenite or polyhalite does not occur at high  $\text{MgCl}_2$  concentrations.

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## INTRODUCTION

The solid-liquid phase equilibria in the quinary and hexary system of the oceanic salts have been the subject of many investigations for more than a hundred years. These investigations have enabled a phase diagram to be constructed which contains the most important information for the production of  $\text{KCl}$  from rich sylvinitic ores. However, from consideration of the original data of the  $\text{NaCl}$ ,  $\text{KCl}$  saturated area in the phase diagram, it is evident that there is a lack of information about the equilibria both at low and at high temperatures (Autenrieth, 1955). The same can be said about the areas of high  $\text{MgCl}_2$  concentration. Very little information is known about the phase equilibria of the hexary system in the temperature range below  $110^\circ\text{C}$ .

Investigations into the solid-liquid phase equilibria in the system of oceanic salts are needed in a wider temperature and concentration range, particularly for the processing of raw salts of difficult composition and, for example, for the development of the use or recovery of carnallitic raw salts by solution

mining. For many years such investigations have been one of the main study areas at our institute, and the following should give an overview of our investigations of the phase equilibria in the quinary and hexary system of oceanic salts in the region of high  $\text{MgCl}_2$  concentrations.

## EXPERIMENTAL

All investigations were carried out using the isothermal stirring method. Special apparatus was used only for determination at high and at low temperatures. In all cases, complete chemical analyses of both the solutions and the solid phases were carried out. For the identification of the solid phases, additional microscopic methods, X-ray diffraction and thermal analysis were used.

The time taken to obtain equilibrium conditions varied in relation to the nature and composition of the solid phases. Usually, times between 98 and 240 h were used. In the case of the hexary system the times varied between 2 and 6 weeks at low temperatures.

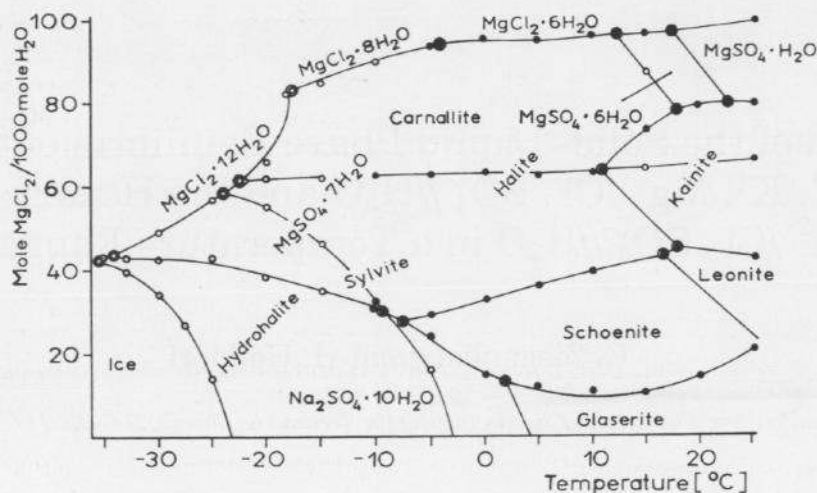


Fig. 1. NaCl(NaCl·2H<sub>2</sub>O)–KCl(KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O)-saturated four-salt solutions of the quinary system of oceanic salts in the temperature range between –35.4 and 25°C.

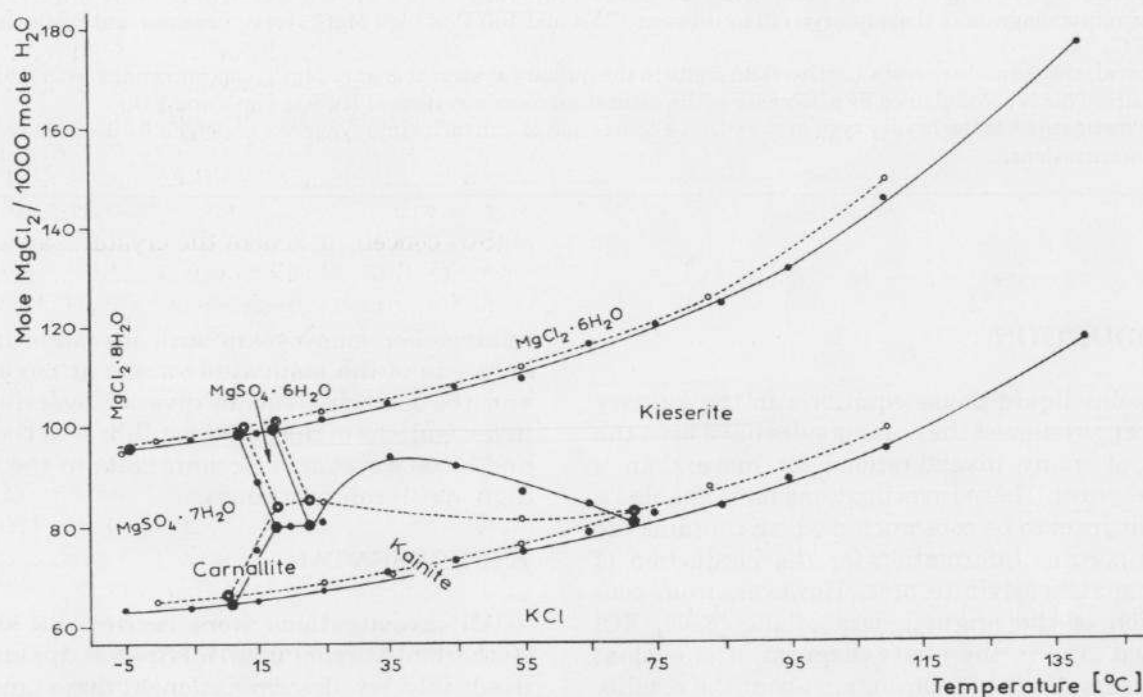


Fig. 2. Polythermal representation of the quinary system of oceanic salts between –5 and 140°C in the area of NaCl–Carnallite saturation. Solid lines, authors' data; broken lines, Autenrieth.

## RESULTS

The results of the investigations of the NaCl, KCl saturated area of the quinary system at low temperatures are summarized in Fig. 1 (Menzel and Holldorf, 1988). The paragneiss Ice–NaCl·2H<sub>2</sub>O–KCl–Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O is in the temperature range between –26.3 and –35.4°C, the boundary line to ice as

a solid phase. The point of intersection with the paragneiss NaCl·2H<sub>2</sub>O–KCl–MgCl<sub>2</sub>·12H<sub>2</sub>O–Na<sub>2</sub>SO<sub>4</sub>·10H<sub>2</sub>O distinguishes the ice-point of the system.

The stable existing area of carnallite begins at –22.2°C at the point NaCl, KCl, MgCl<sub>2</sub>·12H<sub>2</sub>O, KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O, MgSO<sub>4</sub>·7H<sub>2</sub>O. An increase of the temperature, combined with a rising MgCl<sub>2</sub>-concentration,

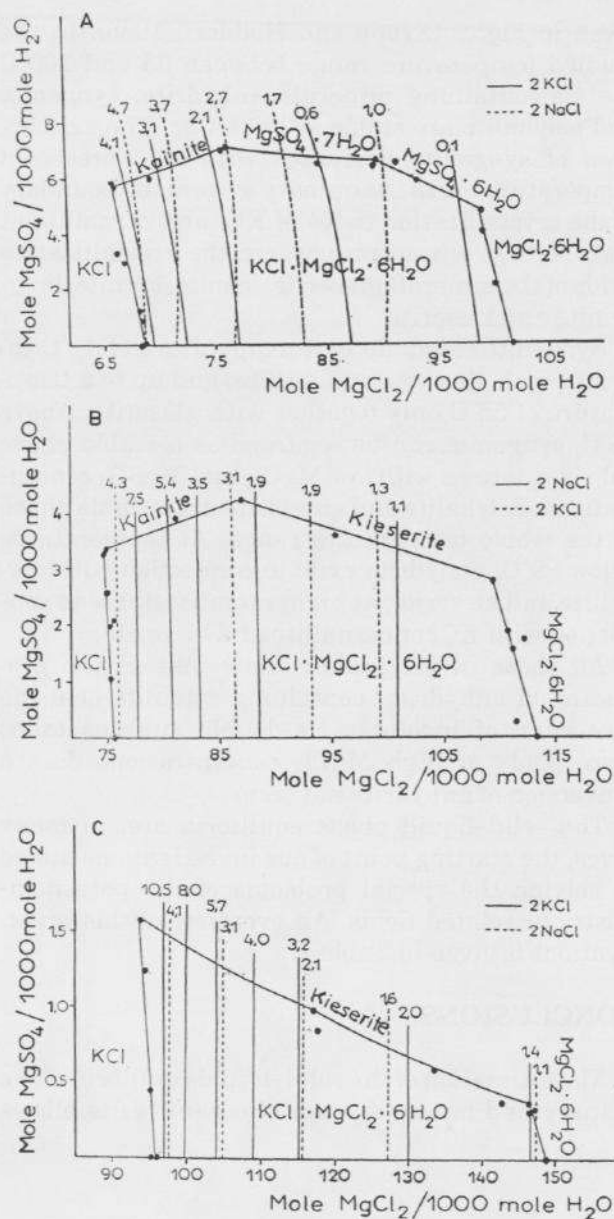


Fig. 3. NaCl-KCl- $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ -saturated area of the quinary system isothermal representation in  $\text{MgCl}_2$ - $\text{MgSO}_4$  coordinate system. A, 15°C; B, 55°C; C, 110°C.

tration leads to the point NaCl,  $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  at -17.2°C. The polythermal invariant transition point of  $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$  into  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  lies at -3.9°C.

In the temperature range below 140°C, at NaCl, KCl saturation the paragneiss of carnallite with  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  or  $4\text{H}_2\text{O}$  and with the sulfate containing minerals  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$  or  $6\text{H}_2\text{O}$ , kainite and kieserite can be observed (Fig. 2) (Beck et al., 1981; Ziegenbalg et al., 1991). In general, the carnallite crystallization field shifts to higher  $\text{MgCl}_2$  concentrations with an increase of temperature. This is

accompanied by a decrease of the saturation concentrations of  $\text{MgSO}_4$ , NaCl and KCl. The description of the paragneiss NaCl, carnallite, kieserite, kainite differs from the results of Autenrieth (1955). We think that this can be explained by the longer periods of formation of the equilibrium conditions, more experimental points and a better analytical procedure in our experiments (Fig. 2).

An isothermal representation shows that in the case of the paragneiss NaCl, KCl,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and NaCl,  $\text{KCl} \cdot \text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  an increase of the  $\text{MgSO}_4$  concentration is connected with a small decrease of the  $\text{MgCl}_2$  content (Fig. 3). While at 15°C carnallite exists in connection with the minerals kainite,  $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ , and at 55°C with kainite and kieserite, at temperatures higher than 72°C kieserite is the only stable sulfate-containing component.

In addition to the investigations aimed at describing the carnallite crystallization area, we have carried out experiments to characterize the formation areas of the minerals kieserite and langbeinite in the temperature range between 90 and 140°C (Ziegenbalg et al., 1991). At a transition from the reciprocal system  $\text{Na}^+$ ,  $\text{Mg}^{2+}/\text{Cl}^-$ ,  $\text{SO}_4^{2-}/\text{H}_2\text{O}$  to the quinary system, for example, at 140°C an increase of the KCl concentrations yields only small changes of the  $\text{MgSO}_4$  concentrations in the crystallization field of kieserite (Fig. 4). However, in the crystallization area of langbeinite the increase of the KCl concentrations leads to lower  $\text{MgSO}_4$  saturation concentrations. The investigations of the paragneisses NaCl-kieserite-langbeinite, NaCl-KCl-langbeinite, NaCl-KCl-kieserite and NaCl-KCl-carnallite allowed the definition of the phase diagram of the quinary system between 90 and 140°C at high  $\text{MgCl}_2$ -concentrations. Figure 5 shows the isothermal representation at 90°C. The succession of the saturation areas shows that an increase of the  $\text{MgCl}_2$  content yields both lower  $\text{MgSO}_4$  and KCl saturation concentrations. The isothermal invariant point NaCl-KCl-kieserite-langbeinite lies at 62.5 mole  $\text{MgCl}_2/1000$  mole  $\text{H}_2\text{O}$ . A polythermal analysis of the quinary system shows that the points NaCl-KCl-kieserite-langbeinite and NaCl-KCl-kieserite-carnallite shift to higher  $\text{MgCl}_2$ -concentrations with increasing temperatures. However, the quantity of the crystallization area of the kieserite does not change (Fig. 6).

To derive optimal processing conditions for raw salts with a high content on anhydrite, knowledge of the phase equilibria in the hexary system  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}/\text{Cl}^-$ ,  $\text{SO}_4^{2-}/\text{H}_2\text{O}$  is an important requirement. Some results of our investigations of this system in the saturation fields of NaCl and KCl are

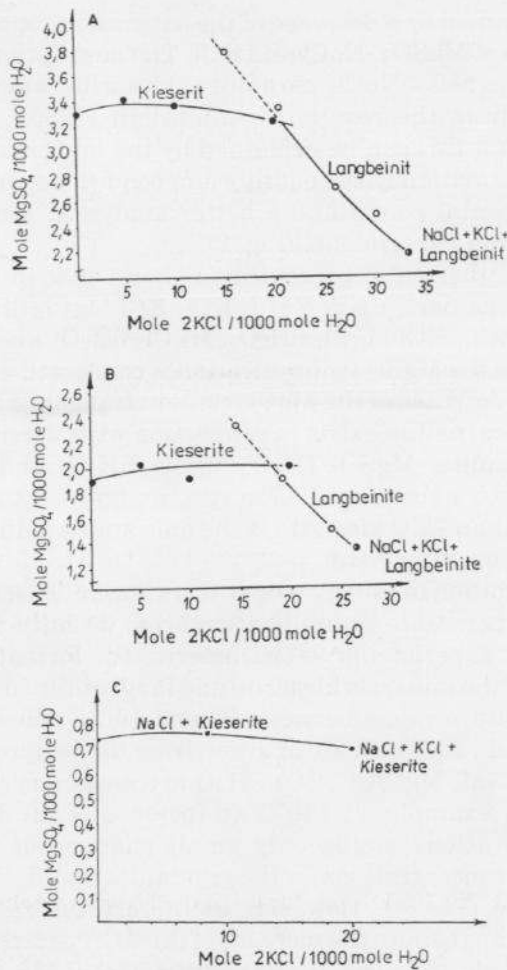


Fig. 4. Isothermal representation of the change of  $\text{MgSO}_4$  concentrations in dependence of the KCl content at  $140^\circ\text{C}$  in the NaCl-kieserite/langbeinite crystallization field. A, 50 mole  $\text{MgCl}_2/1000$  mole  $\text{H}_2\text{O}$ ; B, 70 mole  $\text{MgCl}_2/1000$  mole  $\text{H}_2\text{O}$ ; C, 98 mole  $\text{MgCl}_2/1000$  mole  $\text{H}_2\text{O}$ ;

given in Fig. 7 (Kropp and Holldorf, 1988). In the studied temperature range between  $35$  and  $100^\circ\text{C}$  the Ca-containing minerals anhydrite, syngenite and polyhalite are stable solid phases. The existing area of syngenite decreases with an increase of temperature. As in the quinary system the boundary of the crystallization fields of KCl and carnallite at high  $\text{MgSO}_4$  concentrations are the crystallization fields of the minerals glaserite, leonite, kainite, langbeinite and kieserite.

Syngenite exists up to a temperature of  $41^\circ\text{C}$  together with glaserite and leonite, and up to a temperature of  $55^\circ\text{C}$  only together with glaserite. Above  $55^\circ\text{C}$ , syngenite can be regarded as a stable phase only in solutions with low  $\text{MgCl}_2$  and  $\text{MgSO}_4$  concentrations. Polyhalite and anhydrite are a stable phase in the whole temperature range. At temperatures below  $89^\circ\text{C}$ , anhydrite exits in connection with carnallite and kieserite; at higher temperatures in connection with KCl or carnallite and kieserite.

All these investigations show that in the processing of anhydrite-containing sylvinitic ores the formation of insoluble Ca-double sulfates takes place. Only at high  $\text{MgCl}_2$  concentrations does a conversion of anhydrite not occur.

The solid-liquid phase equilibria are, in many cases, the starting point of our investigations aimed at solving the special problems of the potash industry or related fields. An overview of this investigations is given in Table 1.

## CONCLUSIONS

The estimation of the solid-liquid equilibria of the quinary and hexary system of oceanic salts allows

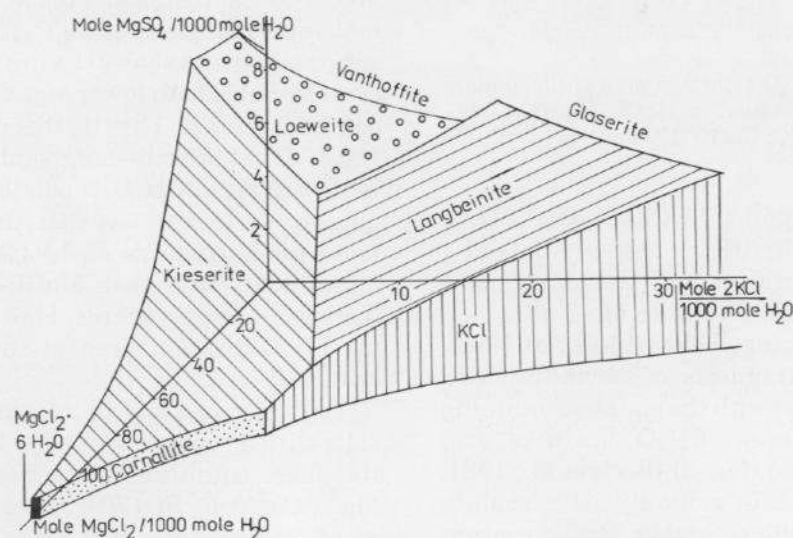


Fig. 5. The quinary system of oceanic salts in the area of NaCl saturation at high  $\text{MgCl}_2$  concentration at  $90^\circ\text{C}$ .

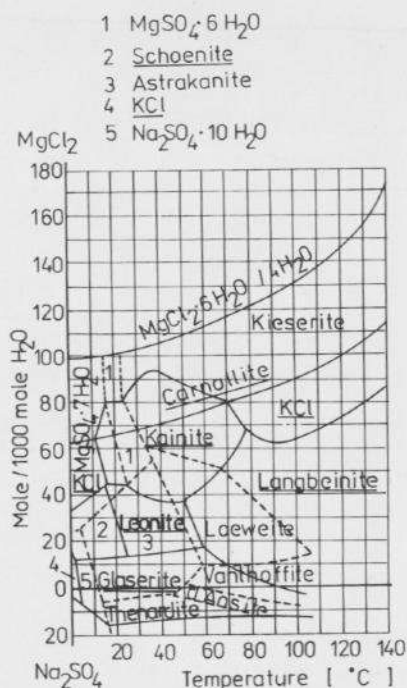


Fig. 6. Polythermal representation of the quinary system of oceanic salts at the saturation with NaCl and Mg or sodium-magnesium sulfates up to 140°C. Solid lines, areas of potassium salts; broken lines, areas of Na and magnesium sulfates.

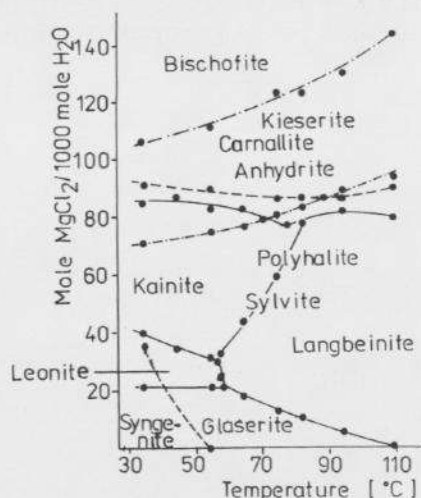


Fig. 7. Polythermal representation of the hexary system of oceanic salts at saturation of NaCl, KCl (carnallite), a sulfate-containing and a  $\text{Ca}^{2+}$ -containing solid phase. Dash/dotted lines, boundary line between the crystallization fields of KCl, carnallite and  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ ; solid line, boundary line between the crystallization fields of sulfate-containing solid phases; broken line, boundary line between the crystallization fields of Ca-containing solid phases.

TABLE 1

The determination of the solid-liquid phase equilibria is the basis for:

- Investigations into sealing off salt brine inflows in potash mines
- Investigations into  $\text{Mg}(\text{OH})_2$  precipitation from  $\text{MgCl}_2$  solutions
- Investigations of the mechanism of the conversion of anhydrite into gypsum in different anhydrite-water suspensions
- Investigations of injection processes
- Investigations concerning the recovery of different compounds from natural salt solutions

the definition of phase diagrams of the NaCl, KCl saturated areas in the temperature range between  $-35.4$  and  $140^\circ\text{C}$ . Thus it is possible to describe the processing of differently composed raw salts in a wide temperature and concentration range.

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