NEW PRINCIPLES FOR THE PROCESSING OF CARNALLITITES IN THE
DOMAIN OF MOLTEN SALT HYDRATES

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New concepts stimulated by environmental problems have been developed for
the processing of carnallite (KCl*MgCl2*6H2O) and of complex composed
MgCl2 solution at elevated temperatures in the concentration range of molten
salt hydrates. The main idea of the processes proposed is the separation of
MgCl2 as MgCl2*4H2O from the multi component salt-water mixture at
temperatures around 160°C. Although the temperature is relatively high the
processes are designed in a way, that the water vapor pressure does not exceed
0.1 MPa in any of the different manufacturing operations.

INTRODUCTION

The conventional processes for the manufacturing of KCl are based on the stable and
metastable solid-liquid phase equilibria of the five-component sea water system Na+, K+,
Mg2+/Cl-,SO42-//H2O at temperatures up to about 110°C. If starting materials are used, which
contain the double salt hydrate carnallite KCl*MgCl2*6H2O or carnallitites (a mineral, which
consists mainly of carnallite) MgCl2 is introduced into the process, which has than to be
removed from the process by special procedures. Environmental problems can be caused if the
concentrated MgCl2 solution is discharged to waste.

On the other hand MgCl2 is an interesting starting material for the production of MgO
or magnesium metal. The processing of the MgCl2 solution is expensive and inefficient,
because of the large amount of water, which have to be evaporated. Moreover the conventional
procedures for processing this solutions are faced with special problems which are mainly the
result of supersaturation phenomena.

To overcome this general disadvantage carnallite should be processed at elevated
temperatures in a hydrate melt without additional water. To derive an efficient process under
these conditions the appropriate solid-liquid-vapor phase equilibria have to be known in detail
at elevated temperatures (above 100°C).

Processes which proceed at elevated temperatures in the region of molten salt hydrates
offer several advantages in comparison with conventional processes. These are
- significantly smaller solution volumes during the processing
- technologies producing less waste and
- high efficiency for the recovery of heat (because of the high temperature level).

On the other hand, disadvantages should also be considered such as increased
corrosion and higher pressure.
Starting from the results of a comprehensive study of the solid-liquid-vapor equilibria of the five-component sea water system Na+, K+, Mg2+/Cl-, SO42-/H2O at elevated temperatures (up to 250°C) new concepts for the processing of carnallite and of complex composed solutions of MgCl2 have been derived.

PHASE EQUILIBRIA

Solid-liquid equilibria

The solid-liquid phase equilibria of the five-component sea water system Na+, K+, Mg2+/Cl-, SO42-/H2O have been studied at elevated temperatures (above 100°C) by using an analytical method. The results are published elsewhere (1-5).

The subsystem KCl-MgCl2-H2O, which is of particular interest was investigated in detail in the temperature range 120-250°C. A projection of the solid-liquid phase diagram of this system in the range of high MgCl2-content is plotted in Figure 1. The plain lines represent the bivariant equilibria solid-liquid-vapor (isotherms), while the bold lines are the monovariant equilibria (2 solid phases are in equilibrium with the liquid and the vapor phase).

At temperatures above 120°C the following solid phases are stable:

- KCl
- carnallite (KCl*MgCl2*6H2O)
- 1.5KCl*MgCl2*2H2O
- MgCl2*4H2O and
- solid solutions KClx*MgCl2*2H2O (0≤x≤1).

Carnallite and MgCl2*4H2O are melting incongruently at 167°C and 181°C, respectively. Three invariant equilibria (3 solid phases are in equilibrium with the liquid and the vapor phase) are stable within the temperature range 120-250°C. From the phase diagram the following solid phase combinations with the appropriate temperatures can be deduced for the invariant equilibria:

- KCl*MgCl2*6H2O / MgCl2*4H2O / 1.5KCl*MgCl2*2H2O (153°C)
- KCl / KCl*MgCl2*6H2O / 1.5KCl*MgCl2*2H2O (157°C)
- MgCl2*4H2O / 1.5KCl*MgCl2*2H2O / KCl*MgCl2*2H2O (solid solution) (165°C)

Vapor Pressure

The vapor pressure of the saturated liquid phase was calculated by using a modified BET equation and the parameters which have been deduced from the results of vapor pressure measurements in the system KCl-MgCl2-H2O at high temperatures and in the range of molten MgCl2-hydrates (6). The intersection curve between the liquidus surfaces and the surface for P≤O=0.1 MPa is plotted in Fig. 1 as dashed line. Obviously, saturated liquid phases with vapor pressures P≤O=0.1 MPa are also stable at relatively high temperatures in a relatively large concentration interval. The temperature maximum is located at about 193°C in the stability region of the solid solutions. In particular all liquid phases which are in equilibrium with MgCl2*4H2O have lower vapor pressures than 0.1MPa, which should be a very interesting feature for the processing of Carnallite and of complex composed solutions of MgCl2.
NEW PROCESSING PRINCIPLES

The processing principles will be explained by means of two examples. The balances for the different substances have been calculated by taking into account the phase equilibria of the five-component sea water system. For a better illustration the processes are discussed by means of the phase equilibria of the ternary system KCl-MgCl₂-FbO. In general the temperatures as well as the compositions of the liquids in the appropriate steps of the processes given can be altered in a certain range.

Processing of Carnallites in the range of molten salt hydrates

All proposals for the processing of carnallite in the range of molten salt hydrates made in the past have a common idea. The carnallite is decomposed in its own water of hydration at about 167°C (incongruent melting point of KCl·MgCl₂·6H₂O). The forming solid KCl is separated from the hydrate melt. From this hydrate melt synthetic carnallite is crystallized by cooling it down to about 120°C. The synthetic carnallite can be recycled. It remains a hydrate melt of MgCl₂·6H₂O with dissolved KCl and other contaminants, for example NaCl (if the mineral carnallite is used as the starting material, which always contains NaCl). The whole process has two important disadvantages:

1. The vapor pressure of the hydrate melt at the incongruent melting point of carnallite is larger than atmospheric pressure (p_H₂O=0.13 MPa) according to the phase diagram. Hence the decomposition of carnallite and the separation of the solid KCl have to be done in a pressure vessel, which makes the processes complicated and expansive.

2. The content of the alkaline chlorides in the MgCl₂·6H₂O is too large for the production of MgO or magnesium without further purification. In addition it is not possible to utilize the relatively large melting enthalpy of MgCl₂·6H₂O energetically.

To avoid this disadvantages we propose the following process. The different steps of the process are summarized in the flow sheet in Fig.2 and illustrated in Fig.1 by the dot-and-dashed lines. Carnallite or the appropriate mineral carnallitite is decomposed within a molten hydrate of MgCl₂ of the composition A at about 165°C (Fig. 1). For it, carnallite and melt are mixed in an appropriate ratio to form a molten hydrate of composition B and solid KCl as a result of the decomposition. After removing the KCl a synthetic carnallite is crystallized by cooling the liquid phase down to 150°C. The synthetic carnallite is separated and recycled. At this step the liquid phase composition has reached point C in the phase diagram. This liquid is concentrated by evaporation up to point A and returned to the decomposer. The MgCl₂·4H₂O crystallized during the evaporation represents the second final product.

Hence this process has the following advantages:

1. All stages of the process can proceed at vapor pressure p_H₂O≤0.1 MPa.

2. The amount of waste produced, is as low as possible.

3. The level of the impurities of both final products KCl and MgCl₂·4H₂O depends only on the efficiency of the solid-liquid separation.

4. A major part of the heat of fusion of the molten salt hydrate can be utilized energetically by using the high temperature level of the water vapor while concentrating the hydrate melt and crystallizing MgCl₂·4H₂O, respectively.

Processing of a complex composed solution of MgCl₂

The main feature of the conventional technologies for the processing of complex composed solutions of MgCl₂ is the removing of the impurities from the solution, which is in
general more disadvantageous than the separation of the final product from the mixture. The solution is concentrated by evaporation. During this process a mixture of NaCl and MgSO4·H2O is precipitated at temperatures of about 120°C and removed from the solution. In some cases the SO4-content of the solution is reduced by precipitation of K2SO4·2MgSO4 (Langbeinite). During the cooling of the concentrated solution synthetic carnallite is crystallizing and removed from the cold solution. The resulting solution contains - besides MgCl2 - various contaminants as MgSO4, KCl and NaCl depending on the initial composition and concentration. The most important disadvantage of this procedure is the resulting MgSO4 level of the MgCl2 solution because of supersaturation, which makes further purification - usually by different steps of precipitation - essential. This additional purification process is not very efficient and cases considerable loss of MgCl2.

The idea of the process proposed in this contribution is the separation of the final product - MgCl2 - from the complex composed solution. MgCl2·6H2O and MgCl2·2H2O are not suitable for this purpose as we can learn from the phase diagram of the system KCl-MgCl2-H2O. The concentration interval of KCl of the stabilization area of MgCl2·6H2O is too small for an efficient separation process and MgCl2·2H2O does not crystallize as pure salt hydrate but it forms solid solution with KCl·MgCl2·2H2O. Suitable for the separation of MgCl2 from a complex composed solution should be MgCl2·4H2O.

The different steps of the process proposed are illustrated in Fig. 1 by the dotted lines and are summarized in a flow sheet in Fig. 3. The complex composed solution of MgCl2 is concentrated by evaporation in a first step as far as close to the saturation of MgCl2·4H2O (point G in Fig.1) by increasing the temperature to about 160°C. During this step a thermal desulfatization and in some cases a crystallization of NaCl occurs (if the concentration of NaCl in the primary solution is high enough). After removing the solids in a second evaporation process MgCl2·4H2O is crystallized and separated. The remaining hydrate melt of composition A is mixed with one part of the primary solution (composition D) in an appropriate ratio to allow the crystallization of synthetic carnallite at 120°C which is separated. The remaining liquid phase of composition F is mixed with the other part of preheated primary solution. The resulting solution is given to the evaporation process.

The following advantages are gained by application of the process proposed in comparison to conventional processes:

- The supersaturation of MgSO4 has no negative influence on the quality of the final product. The separated MgCl2·4H2O can be used directly for the production of MgO or magnesium metal without additional purification.

- The water vapor pressure is lower than 0.1 MPa in all steps of the process, which is of particular importance for the different separation procedures.

- A large part of the heat can be recovered because of the high temperature level in the process.

The larger amount of energy which is necessary because of the higher degree of evaporation in comparison with conventional processes is not significant, if the overall process for example for the production of MgO is taken into account.
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Fig. 1: Projection of the MgCl₂-rich part of the phase diagram of the system KCl-MgCl₂-H₂O at 120-200°C. — boundaries between the liquidus surfaces; — isotherms; —— water vapour pressure p_H₂O=0.1 MPa.
Fig. 2: Flow sheet for the processing of carnallite.
Fig. 3: Flow sheet for the processing of complex composed MgCl₂ solutions.