

Solubilities in seawater-type systems: Some technical and environmental friendly applications

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Abstract

The crystallization sequence of salts during solar evaporation of seawater and brines is discussed. The supersaturation phenomena in highly concentrated seawater-type systems, which influence the crystallization sequence, are explained by differences between the Mg_2^+ -complexes in the solutions and in the solid phases. Methods to increase the yield of the solar sea salt production, to improve the salt quality and to utilize the waste brines, by using knowledge on the solubility diagrams, are developed. An environmental friendly multiproduct method is suggested for magnesium hydroxide and sea salt production.

INTRODUCTION

The sea water is an enormous resource for extraction of dissolved salts. Sea salt and magnesium compounds are derived in large quantities at present. Gypsum, potassium salts and bromine are recovered in smaller amounts (ref. 1,2).

Knowledge of the solubility diagrams of the seawater-type systems, as well as many other natural waters related to them, is of interest in several respects: i. Investigation of the crystallization sequence during evaporation of sea water. Such studies are important not only for avoiding scale formation connected with the seawater desalination and for improvement of sea salt production, but also for explanation of the natural salt deposits formation processes. ii. Creation of new methods and technologies for extraction of minerals from natural waters, recovery of other salts from seawater-type bitterns and brines and separation of salts from the products obtained after water evaporation or from the natural evaporite deposits. iii. Improvement of the present-day technologies in order to keep them in line with the modern ecological requirements.

CRYSTALLIZATION SEQUENCE OF SALTS FROM SEAWATER AND BRINES

The major components of natural and sea waters determining their solubility properties are: Na^+ , K^+ , Mg^{2+} , Cl^- and SO_4^{2-} . Fig. 1 shows data for the initial composition of Black Sea water as well as for the changes in the concentrations of the constituents by evaporation (ref. 3). It is usually assumed that the major constituents present in the seawater show constant relative proportions. This means that the variations in the composition of waters from different seas are due only to the changes in the amount of water present. It follows that the composition-density diagram shown in Fig. 1 is valid for every sea water type.

When seawater is evaporated, the first salts to precipitate are calcium carbonate and some amount magnesium carbonates. Gypsum starts to precipitate at solution density 1.09 and crystallizes mainly in the

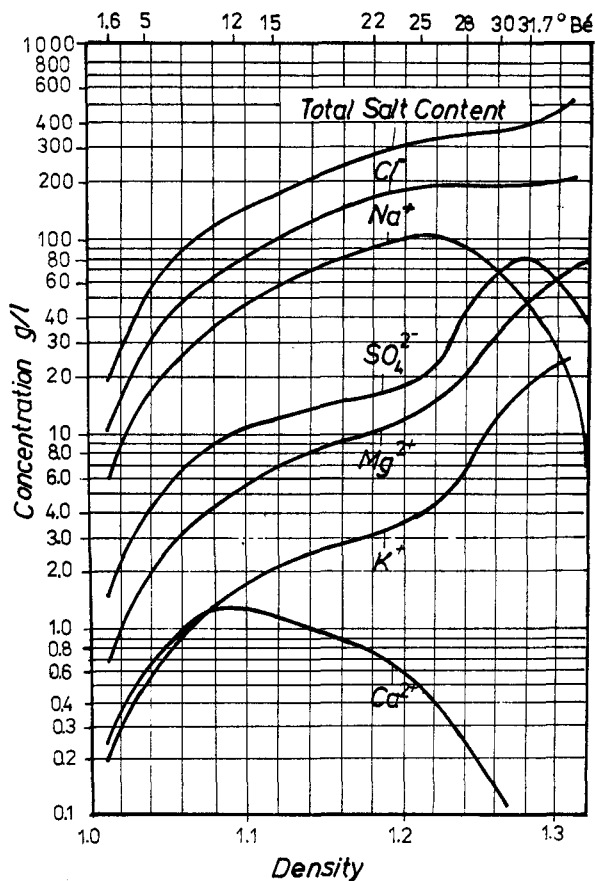


Fig. 1. Composition-density changes during evaporation of seawater at 25°C (the density of the Black Sea Water is 1.011).

interval from 1.10 to 1.21. The crystallization of sodium chloride starts at a density 1.2185. The sea salt crystals obtained up to 1.225 contain impurities of calcium sulfate. The purest NaCl crystals are obtained at densities between 1.225 and 1.235. A large amount of magnesium sulfate crystallizes together with the sea salt above solution density 1.235. Sea salt production is usually carried out until densities 1.245-1.25.

To increase the yield of the solar sea salt production and to improve the salt quality, the following method was developed (ref. 4). When the bittern reaches a density of 1.22 (see Fig. 2), the level of the bittern in the crystallization ponds must be augmented by 10 to 40 cm and then the crystallization is carried out to a density 1.28. After reaching this density, the brine must be thrown out and the crystallization ponds flooded again with bitterns having a density between 1.17 and 1.21. At this stage the crystallization process must be carried out only up to 1.245-1.25.

The waste brines from sea salt production are usually released back into the sea. This can harm marine organisms even if done only locally and on a temporary basis. In order to avoid this and to make use of the waste brines, methods for production of basic magnesium carbonate (ref. 5) and magnesium carbonate trihydrate (ref. 6) have been developed.

The magnesium ions are precipitated with sodium carbonate, at suitable conditions, as $4\text{MgCO}_3 \cdot \text{Mg}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ or $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$. Further solar evaporation of the solution leads to sodium sulfate crystallization. The liquid phase remaining after sodium sulfate crystallization is rich in sodium chloride and can be used preferentially in sea salt production (ref. 7). An almost wasteless process can be realized this way.

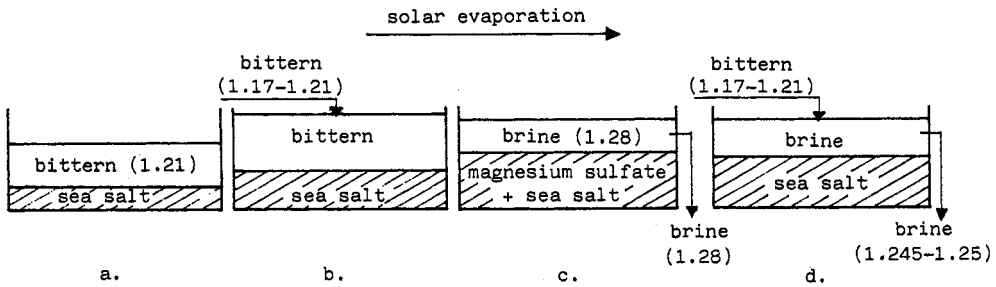


Fig. 2. Scheme of a method for increasing the yield of the solar sea salt and the salt quality:

- a. evaporation until solution density 1.22;
- b. addition of bittern (density 1.17-1.21) to augment the solution level with 10 to 40 cm;
- c. evaporation until solution density 1.28 and brine disposal;
- d. flooding again with bittern (density 1.17-1.21) and evaporation until solution density 1.245-1.25.

Another possibility for utilization of the brines remaining after the sea salt production is the separation of the constituents by fractional crystallization (ref. 1, 8-10). For improvement of these methods or development of new ones a knowledge of the solubility diagrams of the respective multicomponent systems over wide condition ranges is necessary. It must be noted that, along with the equilibrium solubilities, supersaturation phenomena may play important part, especially in these highly concentrated seawater-type systems.

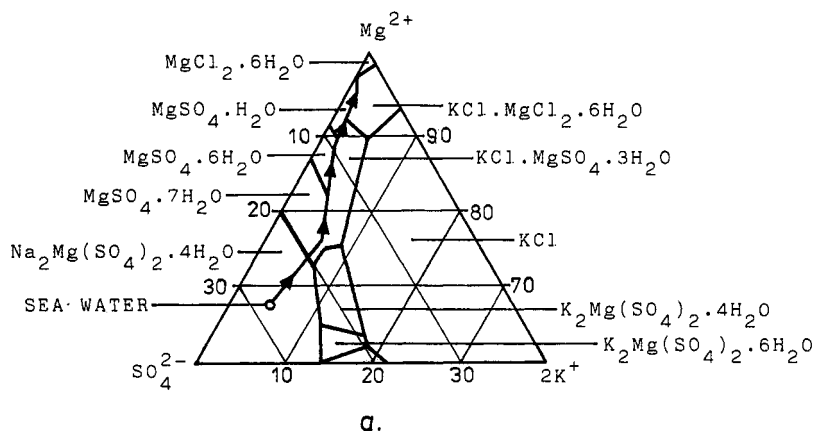
METASTABLE EQUILIBRIA

It is well known that the different simple and double magnesium salts tend to form extremely stable supersaturated solutions. Their existence can influence the crystallization sequence from multicomponent water-salt systems. Studies on the formation of evaporite mineral deposits can be discussed as an example.

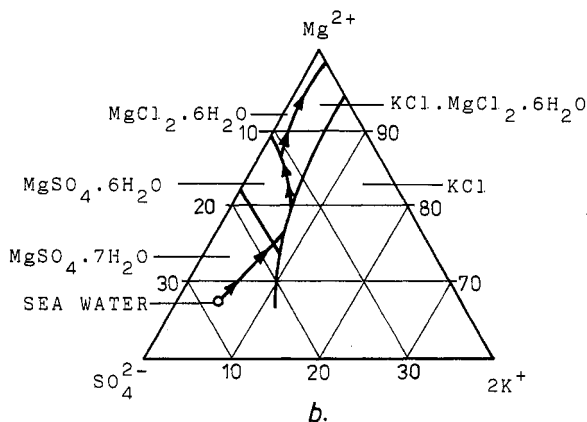
The first experimental investigations related to natural salt deposits were carried out by van't Hoff at the end of the last century (ref. 11). He studied equilibrium solubilities in the fivefold seawater-type system Na^+ , K^+ , Mg^{2+} , Cl^- , SO_4^{2-} , H_2O at 25 to 83°C. He also studied the conditions of formation of some calcium minerals after introducing calcium salts into these systems. The equilibrium solubility diagram obtained by van't Hoff for the fivefold system in its cross-section for saturated sodium chloride solutions is displayed in Fig. 3a.

In 1927 Kurnakow and Nikolaew (ref. 12) began studies on the evaporation of Sax lake which receives water from the Black Sea. These studies resulted in the discovery of the so called "solar sequence" for salt crystallization from seawater, as well as the "solar diagram" of evaporation (Fig. 3b). The "solar diagram" reflects solubilities in the metastable region. As seen from Fig. 3a and 3b there are no crystallization fields for bloedite ($\text{Na}_2\text{SO}_4 \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O}$) and kainite ($\text{KCl} \cdot \text{MgSO}_4 \cdot 3\text{H}_2\text{O}$) as well as for kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) in the "solar diagram". A crystallization field of sylvite (KCl), as a primary evaporite mineral is found to appear. The finding that sylvite instead of kainite is obtained during sea water evaporation was reported first by van't Hoff in his earlier works (ref. 13).

Differences between the equilibrium solubility diagrams and the respective "solar diagrams" were also found by Neitzel(14) for bitterns from the Great Salt Lake (USA). By evaporation of these bitterns under the conditions of day-night temperature variations he found out that



a.



b.

Fig. 3. Equilibrium solubility diagram at 25°C (a) and "solar diagram" (b) of evaporation of seawater in its cross-section for sodium chloride saturated solutions.

bloedite, leonite, loewite and vanthoffite crystallize only when the respective crystal nuclei are present in the solutions. Kainite is obtained mainly as a secondary mineral.

The existence of very stable supersaturation in highly concentrated seawater-type solutions was also shown recently by Emons and coworkers (ref. 15).

An explanation of the differences between the equilibrium solubility diagram of the marine-type system and the corresponding "solar diagram" is as follows (ref. 16): For nucleation of a given crystal phase, the supersaturated solution must contain sufficient amounts of the respective complexes constituting its crystal structure. The magnesium ions are known to exist in sea-type solutions predominantly as hexaaquacomplexes (see Fig. 4a). Highest crystallization rates and lowest supersaturations required for nucleation are exhibited by those magnesium salts, whose crystal structures contain hexaaquamagnesium complexes (Fig. 4b). The nucleation requires high supersaturations for salts with crystal structures in which the water molecules from the hexaaquamagnesium ions are partially (Fig. 4c) or completely replaced by other ligands. For that reason, these salts do not appear in the "solar diagram".

At higher ionic strength (very low water activities in relation to the ligand ion activities), e.g. very concentrated multicomponent solutions at higher temperatures, dehydration of the hexaaquamagnesium complexes occurs. The total equilibrium between the different possible magnesium complexes is shifted towards other octahedral magnesium complexes with

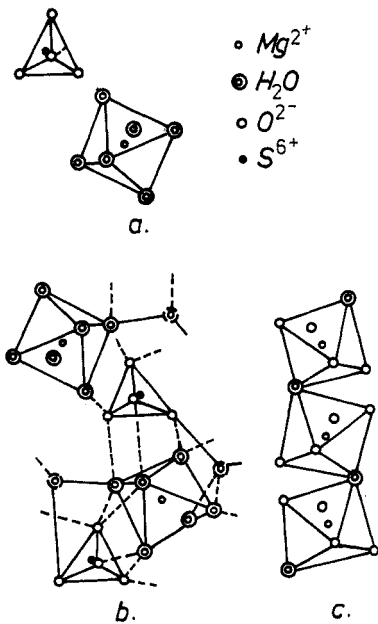


Fig.4. Structural units in:
 a. solution of $MgSO_4$;
 b. $MgSO_4 \cdot 7H_2O$ crystals;
 c. $MgSO_4 \cdot H_2O$ crystals.

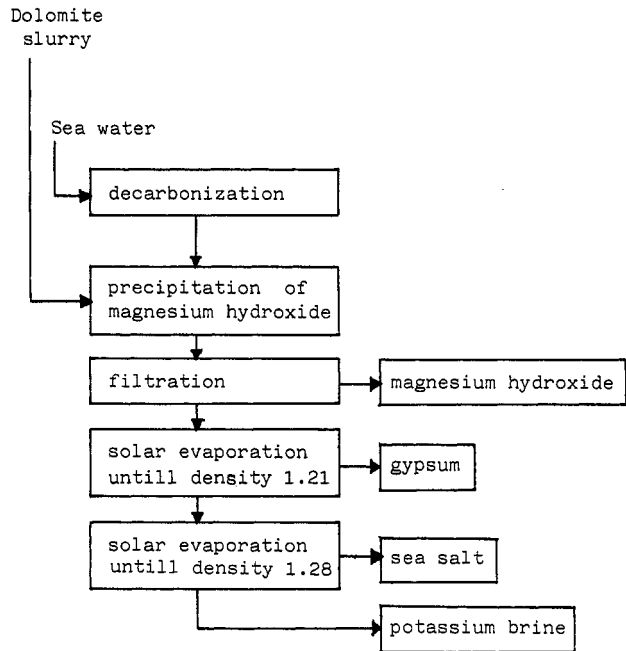


Fig.5. Scheme of the combined method for $Mg(OH)_2$ and sea salt production.

a lower number of coordinated water molecules. Thus the supersaturation required for crystallization of magnesium salts with less than six water molecules for each Mg^{2+} ion decreases with increasing concentration of the solution for example in the series: $Na_2SO_4 \cdot MgSO_4 \cdot 4H_2O$, $KCl \cdot MgSO_4 \cdot 3H_2O$, $MgSO_4 \cdot H_2O$, $K_2SO_4 \cdot 2MgSO_4$. In support of this claim, a number of data may be cited. Thus, for example, Emons and Stegmann (ref. 17), when studying solutions of the marine-type fivefold system at $85^\circ C$, have found that the trend towards langbeinite and kainite crystallization first appears in relatively high magnesium sulfate and magnesium chloride concentrations in the solution and increases with concentration. Moreover, these researchers have found that intermediate solution compositions exist at which only kainite and no langbeinite is found to crystallize. In highly concentrated seawater-type solutions the nucleation rates are usually also hindered by the very high solution viscosities.

STUDIES ON AN ENVIRONMENT FRIENDLY MULTIPRODUCT PROCESS

After sodium chloride, magnesium is the most important product currently derived from seawater. It is recovered commercially directly from sea water by precipitation as magnesium hydroxide with a dolomite slurry or with lime. This is the so called Dow process (ref. 18). Substitution of calcium ions from the lime for magnesium ions from the seawater takes place. The magnesium hydroxide is used for manufacturing of MgO-clinker for refractory materials. This method is so economical that a large part of the production of magnesium compounds all over the world is based on seawater. The only problem is the ecological one due to the enormous quantities of treated seawater which are released back into the sea. These waters contain at least four-times higher mass-concentration of calcium ions than the initial sea water as well as some unavoidable amounts of finely suspended $Mg(OH)_2$.

A combined multiproduct method is suggested for magnesium hydroxide and sea salt production (ref. 19), schematically shown on Fig. 5.

After removal of CO_2 seawater is treated with dolomite slurry or with lime as in the Dow process. The seawater free from magnesium ions is utilized for solar sea salt production. Due to the higher content of calcium ions, the gypsum crystallization starts earlier, at about a solution density 1.04, and continues up to about 1.21. An almost total precipitation of the sulfate ions occurs. The quantity of the gypsum obtained is considerably higher than that obtained by evaporation of ordinary sea water, making gypsum production more economical. The $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ obtained after thermal dehydration of this gypsum meets the requirements for building industry purposes.

Under continued evaporation, NaCl becomes saturated and in this case (of pretreated seawater containing no magnesium and sulfate ions) the process of crystallization of sodium chloride can be conducted up to solution density 1.28. The brines remaining after the sea salt production are rich in potassium and can be used for recovery of potassium salts.

The proposed multiproduct process has the following advantages. After magnesium hydroxide precipitation the sea water is utilized for solar sea salt production. This technology is environmental friendly and the cost of MgO production is lower than the present-day technology. The sea salt is of a considerably higher purity due to the preliminary precipitation of practically all magnesium ions, sulfate ions and colloidal organic substances. The yield of sea salt production is about 30 % higher due to the increase in the evaporation rate and to the possibility to extend the crystallization range up to solution density 1.28.

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