

Following of the seawater evaporation under saltwork and laboratory conditions

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1. INTRODUCTION

In addition to the field measurements and laboratory experiments mathematical models [1] are also included in modern studies of the seawater evaporation. They usually describe two main cases:

1. equilibrium evaporation, i.e. permanent contact of the brine with all previously formed solids
2. fractional crystallization, i.e. complete elimination of all precipitates at the moment of their formation.

In the first case [2] once precipitated salt can later react with solution, producing new solids and the corresponding changes in the composition of the liquid phase. Fractional crystallization, however, follows completely different path because back reaction with previously formed precipitates is not possible.

Whereas equilibrium evaporation is a usual situation, fractional crystallization can hardly be found under natural conditions. Among real systems only solar saltworks, in which seawater is evaporated in a series of pans and where once precipitated salt is really left behind, are similar to this case. Strictly speaking, however, they are somewhere between the cases 1 and 2.

Informations obtained by following of the seawater evaporation could be important for understanding of the physical chemistry of complex electrolyte solutions, processes that take place during (industrial) separation of inorganic salts from seawater and (to some extent) formation of

evaporites, i.e. rocks composed of minerals precipitated from the seawater as a consequence of evaporation.

2. EXPERIMENTAL

At the solar saltwork of Sečovelje (Slovenija), located on the Adriatic coast, brine samples of various densities ($d = 1.0255 - 1.23222 \text{ g/cm}^3$) were collected. In all of them concentrations of macroconstituents (Ca^{2+} , Na^+ , K^+ , Mg^{2+} , SO_4^{2-} and Cl^-) were determined using gravimetric, volumetric and spectroscopic methods. Additionally, mother liquor ("bittern") was additionally evaporated under laboratory conditions (up to $d \approx 1.3 \text{ g/cm}^3$) in order to obtain a set of highly concentrated salt solutions. For such a process two different temperatures (25 and 35°C) and subsequent equilibration of the liquid (in the presence or absence of the solid phase) were chosen. Depending on the type of equilibration "stable" and "metastable" samples were produced.

Eight years after the first study the whole procedure consisting of sampling, centrifugation, density measurement (by picnometer) and determination of macroconstituents (without laboratory evaporation) was repeated for comparison.

3. BRINES

Analysis of the two sets of brines indicates that values belonging to "distant" samplings are in very

good agreement. Moreover, points giving normalized concentrations of an individual ion in dependence on the solution density are located on the same line irrespective to which of the two series they belong. Such values were compared with calculated curves, based on empirical volume – density relationships. This type of expressions and the corresponding plots could be useful for interpretation of the experimental data (recognition of conservative behavior, calculation of precipitated or “lost” quantity of salts etc).

According to the mentioned approach [3] the whole density range of interest (up to 1.32 g/cm³) is divided in three segments: (1) up to the value of 1.2095, (2) between 1.2095 and 1.2197 and (3) over 1.2197 g/cm³, respectively. Corresponding equations, when transformed so to include density in g/cm³ instead of °Bé as originally given, are of the form:

$$V_1 = \frac{-0.00755d + 0.0326}{d - 1} \quad (1)$$

$$V_2 = \frac{-2.1547d + 2.7417}{d} \quad (2)$$

$$V_3 = \frac{0.107d + 217.893}{144357.2d - 173737.2} \quad (3)$$

where V_1 , V_2 and V_3 denote the volume in the first, second and third segment, respectively.

From the upper expressions, initial concentration and well-known volume concentration relationship expected concentration of each individual macroconstituent in the absence of precipitation can be calculated at a chosen density.

Very good agreement of calculated and measured values could be obtained only in the lower density range. In more concentrated brines differences between calculated and measured values appear, the later being lower even for Mg^{2+} which behaves conservatively. Solutions of very high density, however, were produced in a laboratory and this could be one of the reasons for the effect. Even in such a case better equations with clear physical meaning of all the constants would be welcome.

4. LABORATORY EVAPORATION

In a set of samples, obtained after isothermal evaporation of the highly concentrated brine ($d = 1.23222$) from the saltwork at 25°C, results were dependent on the subsequent treatment of the liquids. In each individual case density of the stabilized solution was lower than of the metastable one (difference: 3-15 g/l) in accordance with the literature [4] according to which “the metastable system exhibits the properties of a supersaturated solution and crystallizes by contact with the components of the stable system.” From the concentrations of individual constituents in the stable and metastable samples it could be concluded that, during equilibration of the aqueous phase with previously formed solids, sodium chloride precipitates whereas magnesium and potassium ions are released to the solution. The level of sulfate ions (except at the highest densities) does not seem to be influenced by the previous treatment of the sample. Upper conclusions are in agreement with the fact that in the solid phase, which was formed during equilibration period, only sodium chloride could be identified by x-ray diffraction.

Results obtained in the same way but using the temperature of 35 instead of 25°C were of the same type as described although direct comparison between the two sets of data was not possible because of some technical problems.

5. REFERENCES

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