Evaporative crystallization of salts from Electrodialysis concentrated brine at atmospheric and subatmospheric pressures

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Abstract. A large amount of concentrated brine was produced as by-product during the process of the electrodialysis seawater desalination. In this study, the crystallization sequences of different salts from the brine through evaporative crystallization at both atmospheric and subatmospheric pressures were investigated in detail. The profile of the boiling temperature with density and the relationship between the boiling temperature and the pressure were recorded. The combination of Powder X-Ray Diffraction and the polarizing microscope was employed to identify the salts in the solid form. It can be inferred that NaCl crystallized out firstly and then MgSO₄·6H₂O and CaSO₄ precipitate in order at both atmospheric and subatmospheric pressures, and it should be noticed that CaSO₄ crystallized as anhydrate at 70°C and 90°C while as dihydrate at 50°C. At the end of all the experiments the precipitation rates of CaSO₄ and NaCl have reached to more than 95% while MgSO₄ only reached to about 60%.

1. Introduction
The importance of seawater desalination in solving the global shortage of fresh water has long been recognized. Till 2020, the overall desalination capacity of China will reach 2.8 million m³/d, which can help release China’s fresh water shortage to a large extent. However, both the conventional thermal-based and membrane-based desalination processes have the disadvantage of a large amount of concentrated brine discharge, causing great deterioration to the coastal environment and the huge waste of the resources of salts [1-2]. Thus, it is essential to separate the salts from the concentrated brine before it is discharged directly into the sea.

Electrodialysis (ED) is an electro field driven membrane process with high brine concentration and low membrane fouling, which has become a perspective technology in the utilization of seawater desalination process due to its energy-saving feature compared to membrane distillation (MD) and reverse osmosis (RO) [3-4]. High concentration brine (NaCl, more than 180g/L) from ED can act as the feed fluid in multiple-effect evaporation, which has developed to be a mature and effective method to separate different kinds of salts from the concentrated seawater, and it is the preferential choice when a plant produces undesirable low heat energy. It has not only the advantage of high thermal efficiency but it can also be integrated with power plant or new energy such as solar energy and nuclear [5-7].

Meanwhile, multiple-effect evaporation in vacuum is a common method to produce refined salt, the progress of which includes four or five steps [8]. The first step usually operates under atmospheric pressure and the rest steps operated under sub atmospheric pressures, the corresponding temperatures...
of which are below the boiling evaporation temperatures under atmospheric pressure. In particular in this study, four temperatures, 110°C, 90°C, 70°C and 50°C, have been fixed based on the progress request of the multiple-effect evaporation. The brine derives from the ED concentrated seawater which contains very little divalent ions due to the low selectivity of the ion-exchange membrane but includes high concentration of monovalent ions such as Na⁺, K⁺ and Cl⁻. The present work aims at simulating the multiple-effect evaporation process, and assessing and validating the applicability of multiple-effect evaporation as an effective method to separate different kinds of salts from concentrated brine [9-10]. The salt crystallization sequences during the evaporation of the brine under atmospheric pressure and sub atmospheric pressures were investigated [11-14]. The link between the temperature and the obtained salts was elucidated. The profile of salts precipitation rate with the evaporation of water was also recorded to better understand the progress of the vacuum crystallization of salts.

2. Experimental section

2.1. Materials and apparatus
Sodium chloride, Calcium sulfate, Calcium chloride, Potassium chloride and Magnesium chloride (supplied by Tianjin Guagfu Chemical Reagent Ltd) were of analytical reagent grade and the mass purities were >99.5%. Deionized water was purchased from Tianjin Jiangtian Chemical Reagent Ltd. All the chemicals were used without further purification. The brine used in evaporative crystallization experiments was laboratory prepared and its composition is listed in Table 1, the relationship between the boiling point and the pressure is listed in Table 2.

**Table 1. Ionic Composition of the brine.**

| Destiny ρ/(g cm⁻³) | Na⁺/(g L⁻¹) | Ca²⁺/(g L⁻¹) | SO₄²⁻/(g L⁻¹) | Mg²⁺/(g L⁻¹) | K⁺/(g L⁻¹) | Cl⁻/(g L⁻¹) |
|---------------------|-------------|-------------|--------------|-------------|---------|----------|
| 1.1614              | 94.27       | 0.60        | 0.89         | 0.94        | 3.67    | 151.83   |

**Table 2. Relationship between the boiling temperature of the brine and the pressure.**

| Boiling temperature (°C) | 110 | 90   | 70   | 50  |
|--------------------------|-----|------|------|-----|
| Vacuum degree (MPa)      | 0   | 0.055| 0.078| 0.095|

![Sub atmospheric isothermal boiling evaporation apparatus.](image)
The setup of the evaporative crystallization experiment at atmospheric pressure and in vacuum was shown in Figure 1. A chemistry diaphragm pump (Vacuubrand, PC 510 NT) was used to control the pressure of the system. The crystallized salts were identified by powder X-ray diffraction pattern (PXRD, typed/max-2500, Rigaku, Japan) and a BX51 digital polarizing microscope (Olympus BX51, TOKYO, Japan).

2.2. Evaporative crystallization at atmospheric pressure
As shown in Figure 1, 1L of the brine was added into a boiling flask with 3-neck and agitated with an overhead stirrer. The desired temperature was controlled by a thermostatic bath (model 501 A, Shanghai Laboratory Instrument Works Co., Ltd., Shanghai, China) with an accuracy of ±0.01 K. The brine was kept boiling during the evaporation of water and the boiling points were monitored by a thermometer. The mass of the evaporated water, which was condensed at 278K, was recorded as soon as the salt nucleated, and then the crystals were separated with the solution through filtration. The crystals were dried and identified by PXRD and digital polarizing microscope. The ion concentrations of the filtrate were determined according to different ion analytical methods.

2.3. Evaporative crystallization in vacuum
The procedure of evaporative crystallization in vacuum was almost the same with that at atmospheric pressure except that the pressures were controlled under sub-atmospheric pressures. A chemistry diaphragm pump, shown in Figure 1, was applied to pose a vacuum system to make sure the prepared brine and the filtrate were evaporated at their boiling points (50℃, 70℃ and 90℃, respectively). The filtrate composition and the crystals content were determined, and the mass of evaporated water and the pressures were recorded as well.

3. Results and discussions

3.1. Salt identification
PXRD and digital polarizing microscope were widely applied to identify minerals, and in this study they were successfully used to determine the different salts. As shown in Figure 2, the obtained crystals in the end of the evaporative crystallization at 90℃ is the mixture of NaCl, MgSO₄·6H₂O and CaSO₄, which can be also verified by the digital polarizing microscope.

3.2. Crystallization of the salts from brine at atmospheric pressure
The first step of the multi-effect evaporation is operated under atmospheric pressure and kept in a high evaporation rates at boiling temperature. In this study, The brine is heated by the oil bath to reach the boiling temperature of 110℃, and then twelve liquid samples were taken through the flask at certain interval. The destiny and ionic composition of the liquid samples were analyzed.

Figure 2. The PXRD patterns of the obtained crystals at 90℃, and the standard patterns of NaCl, MgSO₄·6H₂O and CaSO₄.
It can be clearly seen that with the increasing of the density all ion concentrations kept a rising trend in the beginning, and then the Na⁺ concentration achieves the maximum when the density of the brine is equal to 1.2313 g/cm³ and the mass of the evaporated water is equal to 332 g. After that, the Na⁺ concentration declined gradually with the further evaporation of water, meanwhile a large amount of salt started to nucleate and grow. The identity of the salt was verified to be NaCl by PXRD, which indicates that NaCl crystallized first with the evaporation of water. There were only NaCl crystals in the solid samples until the density of the brine concentrated up to 1.2488 g/cm³, when SO₄²⁻ reached to its maximum concentration, MgSO₄ and CaSO₄ began to crystalize together with NaCl, and the SO₄²⁻ concentration decreased gradually with the further evaporation of water. Note that the Cl⁻ concentration kept increasing although it crystallized out in the form of NaCl. The concentration of K⁺ present a steadily increase during the process of evaporation without any consumption.

The values of the corresponding solid phases during the evaporation are illustrated in Figure 3. During the experiment, the continuously evaporation of water resulted in a mount of salts crystallizing out. The analysis of the solid phase showed that the precipitates were mainly composed of NaCl, MgSO₄ and CaSO₄. It can be clearly seen from Figure 3 that (i) the core composition is NaCl and it’s the first solid which precipitated from the saturated brine. In the beginning, the brine is unsaturation for NaCl, as the evaporation brine is saturation for NaCl when the evaporation ratio of water approach 26.30%, and the precipitation of NaCl is equal to 64.21g. (ii) The content of MgSO₄ and CaSO₄ kept in a low level in the solid form at the beginning, especially CaSO₄, the values are below 5%. But it then increased dramatically while further evaporation of water.

3.3. Crystallization of salts from brine at sub atmospheric pressure

The process of multi-effect evaporation is often operated under sub atmospheric where the secondary steam can be used as the heat resource for the next effect to reduce the energy consumption. In this study, the chemistry diaphragm pump was applied to achieve the sub atmospheric pressures of 0.055, 0.078 and 0.095MPa to simulate the pressures in the multi-effect evaporators. The corresponding boiling temperatures are 90°C, 70°C and 50°C, respectively. The evaporation process and the analysis of the brine and salts were similar to those at atmospheric pressure.

![Figure 3. Relationship between the evaporation and precipitation rate of solid at 110°C.](image)

![Figure 4. Relationship between the evaporation and precipitation rate of solid at 90°C.](image)
In the case of sub atmospheric evaporation at 90°C, the first salts sequence present at the density range of 1.1614 to 1.1901. In this sequence, the concentration of Na⁺ increased at the beginning of the evaporation. Then the concentration of Na⁺ decrease gradually due to the precipitation of NaCl. The general evaporation profile of the SO₄²⁻ and Mg²⁺ were similar to that of the atmospheric pressure, which showed a steady growth with the evaporation until the SO₄²⁻ reached to its maximum concentration at the destiny of 1.2155. The second sequence can be defined at the density range of 1.2036 to 1.2336. In this sequence, the concentration of Na⁺ still kept decreasing, due to the precipitation of CaSO₄ and MgSO₄·6H₂O while the concentration of Mg²⁺ continued to increase in solution. The K⁺ ion show a steadily increase during the overall evaporation without any loss. The water evaporation ratio and the solid forms were demonstrated in Figure 4.

In the case of sub atmospheric evaporation at 70°C, all the ionic concentration profiles were similar to that of 90°C. The foremost salts sequence showed at the density range of 1.1614 to 1.1881, while the second sequence of the sub atmospheric evaporation present at the density range of 1.1942 to 1.2252, and the third sequence showed at the density range of 1.1942 to 1.2252. Finally, the SO₄²⁻ precipitates into CaSO₄ and MgSO₄·6H₂O. The water evaporation ratio and the solid forms were demonstrated in Figure 5.

In the case of sub atmospheric evaporation at 50°C, all the ionic concentration profiles were similar to those of 90°C and 70°C. The first sequence can be divided from the density of 1.1614 to 1.1940, while the second sequence showed at the density range of 1.1985-1.2189. At last, a mixture of CaSO₄·2H₂O and MgSO₄·6H₂O was identified. The water evaporation ratio and the solid forms were demonstrated in Figure 6.

The chemical divide rule can be introduced to explain the ion concentration profiles, which is defined as whenever a binary salt is precipitated during evaporation, and the initial molar proportions of the two ions forming this salt is not equal in solution, further evaporation will result in an increase in the concentration of the ion present in great relative concentration in solution, and decrease in the concentration of the ion present in lower relative concentration [15]. Therefore, in the case of sub atmospheric evaporation at 70°C, at the starting density 1.1614, the molar proportion of Cl⁻ is initially greater than Na⁺ and Ca²⁺ is greater than SO₄²⁻ as like to the Cl⁻ and Mg²⁺. In view of that, in the process of evaporation of the brine, it is predicted that the precipitation of NaCl should due to an increase in the concentration of Cl⁻ and decline in Na⁺. The same effect may occurs when CaSO₄ salts start to precipitate where Ca²⁺ should enrichment up with reducing and MgSO₄ salts precipitate.

Figure 5. Relationship between the evaporation and precipitation rate of solid at 70°C.

Figure 6. Relationship between the evaporation and precipitation rate of solid at 50°C.
4. Conclusions
The present work systematically studied the evaporative crystallization of different salts from electrodialysis concentrated brine at atmospheric and subatmospheric pressures, respectively. The profile of the boiling temperature with density and the relationship between the boiling temperature and the pressure were recorded. During the evaporation of water, the ions concentration and the density of the brine were experimentally determined and the salts were identified by the combination of PXRD and the polarizing microscope. The salts crystallization sequences can be inferred that NaCl crystallized out firstly and then MgSO₄·6H₂O and CaSO₄ (70°C and 90°C) or CaSO₄·2H₂O (50°C) precipitate in order at all investigated pressures. The precipitation rate of CaSO₄ was greater than that of MgSO₄. At the end of the experiment the precipitation rates of CaSO₄ and NaCl have reached to more than 95% while MgSO₄ only reached up to about 60%.

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Reference
[1] Elimelech M and Phillip W A 2011 Science 333 712-717
[2] Hao Z, Fei H and Liu L 2014 Journal of geological 88 1614-1615
[3] Xu T and Huang C 2008 Aichem E Journal 54 3147-3159
[4] Simons R 1979 Desalination 28 41-42
[5] Banasiak L J , Kruttschnitt T W and Schäfer A I 2007 Desalination 205 38-46
[6] Kalogirou S A 2005 Progress in Energy & Combustion Science 31 242-281
[7] Ghyselbrecht K Silva A and Bruggen B V D 2014 Journal of Environmental Management 140C 69-75
[8] El-Dessouky H T and Ettouney H M 1999 Desalination 125 259-276
[9] Nafey A S, Fath H E S and Mabrouk A A 2006 Desalination 201 241-254
[10] Nafey A S, Fath H E S and Mabrouk A A 2008 Desalination 230 1-15
[11] Hans P 1980 Geochimica Et Cosmochimica Acta 44 1335-1347
[12] Harvie C E, Eugster H P and Weare J H 1982 Geochimica Et Cosmochimica Acta 46 1603-1618
[13] Jin Z M and Xiao X Z 1980 Acta Chim Sin. 38 313-321
[14] Zhou H, Cui S G and Sha Z L 2008 Acta Chimica Sinica 66 1483-1489
[15] Drever J I 1997 Journal of Environmental Quality 4 245-246