Electrodialysis with Brine Solutions Over-saturated with Calcium Sulfate

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Abstract
Electrodialysis (ED) experiments were carried out on brine solutions of various concentrations (similar to effluents from the desalination of brackish and industrial water) in order to increase their concentration to more than 20%. In this way, effluent volume could be reduced and disposal would be less costly. It was shown that the energy requirement to concentrate solutions from 70-300 mN (0.4-1.8%) up to 3.9 N (20%) was in the range 1.5-7.1 kWh/m$^3$, in contrast to approximately 25 kWh/m$^3$ by thermal evaporation. With the aim of preventing precipitation of CaSO$_4$ on the membranes, laboratory experiments were carried out on solutions of different compositions to determine the conditions that would lead to the precipitation of excess gypsum on gypsum seeds in a separate precipitator. A pilot plant ED unit was put in operation in which the brine that circulated through the ED brine cells passed through a CaSO$_4$ precipitator containing gypsum seeds. In 600 hours of operation, no gypsum precipitated on the membranes.

Introduction
Ecologically correct disposal of brine effluents that are the by-product of reverse osmosis (RO) of the desalination of brackish and industrial water is a persistent problem. It has traditionally been solved by piping the brine into the sea or into solar evaporation ponds or by thermal evaporation. All these solutions are expensive. In our study, we set out to solve this problem by increasing the concentration of the brine effluent concentration to about 20% through electrodialysis (ED). With this method, the volume of the brine effluent is reduced, and its disposal is thus cheaper.

However, there are two major technical problems:

1) How the ED unit can be operated up to a concentration of 20% salts without significantly diminishing the efficiency.

2) How CaSO$_4$ precipitation on the membrane during brine concentration can be prevented.

The efficiency of the ED process depends on the permselectivity of the membrane, back diffusion of salts from brine to the diluate, and leakage of current through the distribution system of the brine solution to the cells. The permselectivity of an ion-exchange membrane is maintained when most of the electrical current is conducted by the counterion and when the concentration of diffused electrolytes into the pores of the membrane is low, i.e., when the concentration of the external solution is low. When the solution concentration is increased,
the high concentration of diffused electrolyte in the membrane will sharply decrease membrane permselectivity. However, if a membrane separates the dilute from the concentrate, a concentration gradient is created across the membrane, and high permselectivity can be maintained as long as electrolyte concentration is low on one side of the membrane.

The problem of CaSO₄ precipitation can be prevented by continuous removal of gypsum from the brine in a separate precipitator, using gypsum seeds to precipitate the excess CaSO₄ in the oversaturated solution. In the present project, laboratory experiments were carried out on solutions of various compositions in order to determine the conditions that lead to precipitation of excess gypsum in the presence of gypsum seeds.

The thermodynamic solubility product (K_{sp}) for CaSO₄ is given by:

$$K_{sp} = a_{Ca^{2+}} \cdot a_{SO_{4}^{2-}}$$

$$= [Ca^{2+}] \cdot [SO_{4}^{2-}] \cdot \gamma_{Ca^{2+}} \cdot \gamma_{SO_{4}^{2-}}$$

$$= [Ca^{2+}] \cdot [SO_{4}^{2-}] \cdot \gamma^2 = K \cdot \gamma^2$$

where K is the product of Ca^{2+} and SO_{4}^{2-} concentrations, \( \gamma \) is the mean activity coefficient of CaSO₄ and square brackets represent molar concentration. An increase in the ionic strength of solution leads to a decrease in the activity coefficient and an increase in the solubility of CaSO₄.

Since the solubility of gypsum depends on the ionic strength of the solution, it changes dramatically with different sodium and magnesium chloride concentrations. Our experiments showed that solutions with high relative oversaturation (10-30%) are stable and that gypsum does not precipitate from such solutions, even for extended times. However, when seeds of gypsum are introduced at a concentration of 5-20 g CaSO₄/l, the excess CaSO₄ precipitates within 5-30 min. On the basis of these data, we designed and built a pilot-plant ED unit in which the brine circulating through the ED brine cells is passed through a CaSO₄ precipitator containing gypsum seeds. The Ca^{2+} and SO_{4}^{2-} ions that migrate into the brine cause oversaturation by only a few percent. When this slightly oversaturated solution is passed through our precipitator, the excess CaSO₄ is precipitated on the seeds. The resulting solution is stable, and as it passes through the ED stack there is no further precipitation of CaSO₄.

**Experimental**

In our pilot plant, the flow rate of the brine through an ED unit of 15 cell pairs is 600 liters/h, while the flow rate through the precipitator is 70-100 liters/h. The volume of the brine container is 70 liters and that of the precipitator, 130 liters. In the first experiment, the unit was operated for 200 h, with the polarity reversed for 1 h every 12 h. Later, it was operated

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* K. Kock, German Patents No. 0-33381941 (1983) and No. P-36190861 (1986).
for 170 h with reversal of polarity for 1 h every 24 h and 230 h with symmetric reverse polarity every 6-10 h. The brine composition was 0.25-1.1 N NaCl + 0.015 -0.13 N MgCl2 + 0.05-0.09 N CaSO4. Feed composition was 3.5 mN Ca, 1.2 mN SO4, 2.8 mN Mg, 5.2 mN Cl, 4.0 mN HCO3, and 0.8 mN NO3. The flow rate was 55 liters/h, and cell-pair voltage was 1 V. Sulfuric acid was added to the brine to keep the pH in the 2.8-3.5 range. When the stack was opened after 600 h, no CaSO4 precipitate was observed in the cells.

The experiments with gypsum precipitation under various solution and seed (CaSO4) concentrations were carried out with standard laboratory equipment. The experiments using the laboratory ED unit was carried out with cells of a surface area of 12 cm² and a cell thickness of 10 mm.

Results and Discussion

Fig. 1 shows that the electrical efficiency of the pilot plant ED unit decreased when the brine concentration increased. The reasons for this are: decrease in membrane permselectivity, increase in back diffusion, and increase in current leakage through the distribution system of brine to the cells, which became significant at low diluate concentrations. In the laboratory ED unit, where no current leakage occurred, higher electrical efficiency was obtained at lower concentrations (Fig. 2). Since the back diffusion increased at higher brine concentrations, it was preferable to operate the ED unit at high current densities to reduce this effect (Fig. 2). The electrical efficiency increased as the diluate concentration decreased from of 300 to 70 mN (Fig. 3). This behavior is the result of an increase in membrane permselectivity as the diluate concentration decreased. After permselectivity reached a maximum of 80%, the efficiency decreased, since a greater amount of the current passed through the brine distribution system and back diffusion became more significant. The energy requirement and the specific desalination area are given in Fig. 4, which shows that for desalination of a solution in the range from 50-300 mN, the energy requirement ranged from 1.5-7 kWh/m³.

The solubility of gypsum in ED brine solutions changes according to the solutions' concentration and composition of the solutions; e.g., the solubility of CaSO4 increases with the ionic strength of the solution. The solubility of CaSO4 is increased in ED brine solutions, since the high concentrations of NaCl and MgCl2 lead to a decrease in the activity coefficients of Ca²⁺ and SO₄²⁻.

Moderately oversaturated solutions of CaSO4 are stable for very long periods. However, when seeds of CaSO4 are added to an oversaturated dilute solution (60 mN), CaSO4 concentration decreased quickly to about 27 mN (Fig. 5). The rate of decrease in Ca concentration depended on the seed concentration. When the same experiment was carried out using a different brine solution, the concentration of CaSO4 in the brine decreased, depending upon the concentration and composition. We can calculate the concentration solubility product from the final CaSO4 concentration in solution after one day at equilibrium. We found that the concentration solubility product of CaSO4 in deionized water was 2.10⁻⁴. For solutions of 0.5 M NaCl, 0.1 M MgCl2 and 0.5 M NaCl + 0.1 M MgCl2, it was 7.10⁻⁴, 9.10⁻⁴.
and 14.10⁻⁴, respectively. In more concentrated solutions, the solubility of CaSO₄ is likely to increase.

The time of onset of CaSO₄ precipitation in an oversaturated solution (without seeding) depended on both the CaSO₄ concentration and the composition of the solution (Fig. 6). In highly concentrated CaSO₄ solutions (several hundred percents of oversaturation), precipitation occurs within minutes, while in less concentrated solutions onset of precipitation may be delayed overnight, even when the oversaturation exceeds 100%.

ED with a gypsum precipitation step was carried out with tap water in a 15 cell-pair unit. At a brine concentration of 0.35 M, the Ca²⁺ and SO₄²⁻ concentrations remained constant in the range of 50-65 mN during 190 h of operation (Fig. 7). This corresponds to a concentration solubility product of 8.3.10⁻⁴. The concentrations of Mg²⁺ and NO₃⁻ increased during electrodialysis because no solution was drained off. When the concentration of the brine was increased to 1.3 M (Fig. 8), the Ca²⁺ and SO₄²⁻ concentrations rose over time as a result of the decrease in the activity coefficient of the brine solution. The concentrations were in the range of 95 mN, which corresponds to a concentration solubility product of 22.5.10⁻⁴. After 600 h of operation, the stack was opened and checked for precipitate. No precipitation of CaSO₄ was found in the ED cells.

**Conclusions**

1. ED can be used to increase the concentration of brine solutions from less than 2% to more than 20% with an energy requirement of less than 7.1 kWh/m³.
2. Laboratory experiments designed to analyze gypsum precipitation kinetics showed that significant acceleration of precipitation can be achieved by seeding the over-saturated solution with 10-25 g CaSO₄/liter.
3. ED was successfully carried out in a pilot plant. The brine was circulated through ED brine cells and through a CaSO₄ precipitator under a reversal of polarity. No gypsum precipitation on the membranes occurred over 600 h of operation.
Figure 1. Electrical efficiency (%) vs. diluate concentration at different brine concentrations (pilot plant).

Figure 2. Electrical efficiency of desalination at different current densities of concentrated brine solution in the laboratory unit and the pilot plant.
Figure 3. Current efficiency, specific cell-pair resistance and current density during desalination of 0.34 N sodium chloride solution. Brine concentration was 200 g/l.

Figure 4. Specific energy requirement and output necessary to desalinate salt solution to 10 mN vs. its concentration. Cell-pair drop voltage was 0.71 and 0.45 volt. Number of cell pairs-15; dimension of each cell-150x150 mm. Brine concentration was 200 g/l.
Figure 5. Concentration of CaSO₄ in a solution of 62 mN CaCl²⁺ 62 mN Na₂SO₄ vs. time at different CaSO₄ concentrations.

Figure 6. Time to onset of gypsum precipitation vs. [Ca]x[SO₄].
Figure 7. Changes in ion concentrations in brine vs. time during electrodialysis with continuous CaSO_4 precipitation. Brine concentration was 0.20-0.35 M.

Figure 8. Changes in ion concentrations in brine vs. time during electrodialysis with continuous CaSO_4 precipitation. Brine concentration was 1.1-1.3 M.