Improved calcium sulfate recovery from a reverse osmosis retentate using eutectic freeze crystallization


ABSTRACT

A novel low temperature crystallization process called eutectic freeze crystallization (EFC) can produce both salt(s) and ice from a reverse osmosis (RO) stream by operating at the eutectic temperature of a solution. The EFC reject stream, which is de-supersaturated with respect to the scaling component, can subsequently be recycled back to the RO process for increased water recovery. This paper looks at the feasibility of using EFC to remove calcium sulfate from an RO retentate stream and compares the results to recovery rates at 0 and 20°C. The results showed that there was a greater yield of calcium sulfate obtained at 0°C as compared with 20°C. Operation under eutectic conditions, with only a 20% ice recovery, resulted in an even greater yield of calcium sulfate (48%) when compared with yields obtained at operating temperatures of 0 and 20°C (15% at 0°C and 13% at 20°C). The theoretical calcium recoveries were found to be 75 and 70% at 0 and 20°C respectively which was higher than the experimentally determined values. The EFC process has the added advantage of producing water along with a salt.

Key words | calcium sulfate, crystallization, desalination, environment, eutectic freeze crystallization, separations

INTRODUCTION

Reverse osmosis (RO) is a membrane technology that uses pressure and a selective membrane to remove ions from an aqueous solution (Nicos 2001). The technology is a leading desalination method with a global water production market of 53% (Mezher et al. 2011). The major limitations with an RO process result from the problems associated with scaling of various species (Kavitskaya et al. 2000) on the membrane surface as well as higher operating costs for streams with high total dissolved solids (TDS).

Calcium sulfate (CaSO₄·2H₂O) is a major scaling species in many RO processes. Treatment options are usually utilized in an attempt to remove or inhibit CaSO₄·2H₂O crystallization but the extent to which CaSO₄·2H₂O scaling can be prevented is often limited.

The removal of scaling components is therefore a very important step in an RO process. One method of removing a scaling component from a wastewater is via cooling crystallization, which uses the fact that the solubility of CaSO₄·2H₂O decreases with decreasing temperature (Hoang et al. 2007) below 38°C. Therefore, it should be possible to increase both the crystallization rate and the product yield, as compared with conventional crystallization processes, when crystallizing CaSO₄·2H₂O at low temperatures.

Eutectic freeze crystallization (EFC) is a novel water treatment method that operates at low temperatures. The process has the potential to remove scaling components from a wastewater stream while at the same time producing water in the form of ice. The operation is carried out at the eutectic point where separation is achieved via gravity with the ice floating to the top of the crystallizer while the denser salt sinks to the bottom of the crystallizer (van der Ham et al. 1998). EFC is most competitive when used in combination with other water treatment technologies and when applied to streams that have a high TDS, such as an RO retentate stream. This is because the more dilute the stream, the more ice must be removed before reaching eutectic conditions thus making the process more expensive. The process is also simpler to operate if salt is crystallized out of solution before ice as ice crystallization can lead to scaling (Pronk et al. 2008).

An economic analysis of an EFC process has shown that energy reductions of up to 65% can be achieved...
(van der Ham et al. 1998). Nathoo et al. (2009) give a detailed economic analysis of using EFC to treat brines and show that energy savings of up to 85% can be achieved when compared with evaporative crystallization. The major disadvantage of EFC is the high capital cost but this is expected to decrease significantly as the technology advances (Nathoo et al. 2009). EFC also has the added advantage of producing many pure salts rather than a mixed salt product that has to be disposed of at an additional cost.

The work conducted by Rahman et al. (2007) showed that a combination of a freeze concentration process, of which EFC is an example, and an RO process can offer a better overall desalination process when compared with conventional processes. The proposed hybrid process can potentially solve three major challenges associated with RO: limited overall water recovery due to scaling effects on membranes, increased operating costs at higher solution concentrations and the environmental impact of brine disposal. In similar research conducted by Madani & Aly (1989), the concept of a combined RO and direct contact freezing (DCF) process showed that the energy consumption could be reduced by approximately 17% and that an overall recovery of 97% could be achieved. The added benefit of such a setup was the reduced problem associated with brine disposal as the RO reject was essentially further desalinated using DCF.

This paper investigates the feasibility of using EFC as a means to remove a scaling component, CaSO₄·2H₂O, from an RO retentate stream saturated with respect to CaSO₄·2H₂O. The paper also looks at conventional crystallization at 20 and 0 °C with no solvent removal in order to ascertain whether EFC is a better CaSO₄·2H₂O removal option than the conventional methods. The major objectives of this study are therefore to determine the:

1. theoretical CaSO₄·2H₂O solubility and recovery curve of CaSO₄·2H₂O and ice for the industrial brine,
2. recovery of CaSO₄·2H₂O at 20 °C (reference temperature),
3. recovery of CaSO₄·2H₂O at 0 °C, and
4. recovery of CaSO₄·2H₂O under eutectic conditions for this specific brine.

**Thermodynamic stability of calcium sulfate**

Calcium sulfate typically crystallizes in three solid forms, namely the hemihydrate (CaSO₄·0.5H₂O), dihydrate (CaSO₄·2H₂O, gypsum) and anhydrous (CaSO₄) phases (Hoang et al. 2007).

In their investigation of the effect of temperature on the spontaneous crystallization of CaSO₄·2H₂O in synthetic supersaturated solutions, Klepetsanis et al. (1999) found that only CaSO₄·2H₂O was formed at temperatures between 25 and 80 °C. This was despite anhydrous calcium sulfate being the thermodynamically stable form at temperatures above 50 °C. However, the dihydrate form (CaSO₄·2H₂O) of the product crystals was only determined by thermo-gravimetric analysis after having filtered the sample at room temperature. This may have allowed a temporary anhydrous form to rehydrate back to the dihydrate form in the presence of humidity.

**Factors that affect the solubility and growth kinetics of CaSO₄·2H₂O**

**Temperature**

Temperature, through its effect on the solubility of the crystallizing salt, has an impact on both the rate of crystallization and the maximum theoretical yield of CaSO₄·2H₂O. The OLI Stream Analyzer thermodynamic modelling package (OLI Systems Inc. 2011) was used to model the relationship between temperature and the solubility of CaSO₄·2H₂O (see Figure 1).

The solubility of CaSO₄·2H₂O exhibits a maximum at 38 °C, meaning that the maximum amount of...

![Figure 1](https://iwaponline.com/wst/article-pdf/67/1/139/441422/139.pdf)
CaSO₄·2H₂O will remain in solution at this temperature. Above 38 °C, the solubility of CaSO₄·2H₂O decreases, which results in a greater fraction of CaSO₄·2H₂O being crystallized out at high temperatures. Similarly, high crystal yields can also be obtained at temperatures less than 38 °C, below which temperature the solubility also decreases.

In their investigation of the growth kinetics of gypsum in landfill leachate, Liu & Nancollas (1970) found that the CaSO₄·2H₂O crystallization rate decreased with a decrease in temperature for the temperature range 15–45 °C.

**Composition**

In addition to temperature, the composition of the aqueous solution significantly influences the solubility of CaSO₄·2H₂O. The presence of impurities in a system can also have profound effects on the characteristics of growth of a crystal either through retardation of the growth rate or disruptions in the crystal structure (Mullin 2001).

When comparing the experimentally derived solubility of CaSO₄·2H₂O in landfill leachate to that in pure aqueous solution, Tait et al. (2009) found that the CaSO₄·2H₂O solubility was approximately 3.3 times greater than that reported for the pure aqueous solution (see Table 1). Tait et al. (2009) used PhreeqC to calculate the solubility of CaSO₄·2H₂O in the leachate and they found it to be 7.09 g/L. This value differed from the experimentally determined solubility of 8.78 g/L and is tabulated in Table 1. The solubility of CaSO₄·2H₂O for this study was found to be 2.01 g/L at 20 °C and 1.64 g/L at 0 °C. These data are also given in Table 1.

The difference between the experimentally determined solubility and the solubility obtained from the PhreeqC thermodynamic modelling package indicates the complex nature of the aqueous streams. The results in Table 1 show that the solubility of CaSO₄·2H₂O differs between wastewaters and that thermodynamic models can at best only estimate the solubility of CaSO₄·2H₂O in complex systems.

**METHODS**

The theoretical CaSO₄·2H₂O solubility and recovery curve for the RO retentate stream was conducted using OLI Stream Analyzer (OLI Systems Inc. 2011) once the analysis of the brine was complete (objective 1). For objectives 2–4, laboratory experiments, rather than modelling, were conducted.

**Seed preparation**

**Solution preparation and analysis for seed preparation**

Before the recovery experiments could be conducted, synthetic seeds needed to produced. These synthetic CaSO₄·2H₂O seeds were produced in the laboratory using equi-molar (0.6 mol/L) solutions of analytical grade Na₂SO₄ and CaCl₂ made up using de-ionized water. The concentration of Ca²⁺ was analysed using atomic absorption spectrometry (AAS).

**Experimental setup for seed preparation**

The reaction for the seed preparation was performed in a 1.5 L glass jacketed crystallizer maintained at 70 °C by the circulation of thermostatted ethylene glycol solution through the outer jacket. The temperature in the crystallizer was measured and recorded with a temperature probe. A 4-bladed pitch-blade impeller attached to a digital stirrer was used to agitate the solution in the crystallizer. A 520s peristaltic pump (Watson Marlow) was used to add the Na₂SO₄ to the crystallizer. The product crystals were filtered through a 0.45 μm filter paper using a Buchner vacuum filter. The experiments were run in duplicate in order to maximize the amount of seeds made.

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**Table 1** | Experimental and simulated solubility of CaSO₄·2H₂O in different source solutions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Basis</th>
<th>CaSO₄·2H₂O solubility (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure aqueous solution with CaSO₄·2H₂O saturation&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Experimental</td>
<td>2.63</td>
</tr>
<tr>
<td>Landfill leachate wastewater&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Experimental Thermodynamic simulation&lt;sup&gt;c&lt;/sup&gt;</td>
<td>8.78  7.09</td>
</tr>
<tr>
<td>Reverse osmosis retentate, at 20 °C</td>
<td>Thermodynamic simulation&lt;sup&gt;d&lt;/sup&gt;</td>
<td>2.01</td>
</tr>
<tr>
<td>Reverse osmosis retentate, at 0 °C</td>
<td>Thermodynamic simulation&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1.64</td>
</tr>
</tbody>
</table>

<sup>a</sup>As reported by Seidell (1919).
<sup>b</sup>As reported by Tait et al. (2009).
<sup>c</sup>Using the thermodynamic modelling package PhreeqC (Tait et al. 2009).
<sup>d</sup>Present study: Using the thermodynamic modelling package OLI Stream Analyzer (OLI Systems Inc. 2011).
Experimental procedure for seed preparation

Synthetic CaSO₄·2H₂O seeds were prepared by the drop-wise addition of sodium sulfate (Na₂SO₄) to calcium chloride (CaCl₂), as described by Liu & Nancollas (1970) and Tait et al. (2009). The experimental procedure for the preparation of the synthetic CaSO₄·2H₂O seeds involved the addition of a fixed brine volume of 500 mL CaCl₂ to the crystallizer. The 500 mL of 0.6 mol/L Na₂SO₄ was added to the crystallizer at approximately 3 mL/min. The drop-wise addition of Na₂SO₄ allowed for a gradual reduction in the supersaturation of the system to produce seed crystals exhibiting a narrow size distribution.

The overhead agitator provided mixing for 2 hours, after which the crystals were filtered. The crystals were rinsed with de-ionized water and then ethanol. The entrained ethanol was evaporated in an autoclave maintained at 70 °C for 24 hours. The final product seed crystals were stored in an airtight container for use in the recovery experiments.

Recovery experiments

Solution preparation and analysis for recovery experiments

For the recovery experiments, a RO retentate stream was used as the feed for all the experiments. The cation and anion concentrations of the various species were analysed using inductively coupled plasma mass spectrometry (ICP-MS) and AAS. The brine sample was stored at 20 °C and filtered before the experiments were conducted.

Experimental setup for recovery experiments

Three 1.5 L glass, double-walled crystallizers equipped with an IKA overhead agitator were used for these experiments. A temperature logging device (Testo 175–177) was used to measure the solution temperatures of the crystallizers. The temperatures of the crystallizers were controlled with a Lauda RE207 thermostatic unit that continuously circulated the coolant (ethylene glycol and in the case of the EFC experiment, Kryo40) through the jackets of the crystallizers. A fixed brine volume of 1.0 L was added to the crystallizers and synthetic seeds were used. The EFC crystallizer setup was kept in a subzero, temperature-controlled laboratory at −1.5 °C.

For the filtration of the product solutions obtained from the 20 and 0 °C recovery experiments, 0.22 μm syringe filters were used. The final products formed during the EFC experiment were filtered in a cold room with the room being maintained at the same setpoint temperature as the thermostatic unit. The ice product was filtered using a Buchner funnel connected to a 1 L filtration flask. A 300 mL Millipore All-Glass filter holder connected to a vacuum pump was used to filter the salt. The pore size of the filter paper was 0.45 μm.

Experimental procedure for recovery experiments

The recovery experiments for 0 and 20 °C involved the addition of 0.42 g of synthetic CaSO₄·2H₂O seeds to the crystallizers. The amount of seeds added was based on the seed concentration range used by Liu & Nancollas (1970). The solutions were maintained at their respective temperatures (0 and 20 °C) by adjusting the setpoint of the refrigerated bath. The experiments were conducted for a maximum of 81.3 hours and samples were collected at pre-determined time intervals. Approximately 10 mL of sample was withdrawn from each crystallizer using the 20 mL capacity plastic syringe. Each sample was filtered using the 0.22 μm syringe filter (Millipore). The liquid samples were diluted with de-ionized water to prevent further crystallization and were later analysed for calcium. The product crystals were stored in an airtight container. The crystal products were rinsed using de-ionized water and then ethanol. The ethanol was evaporated by placing the filtered crystals in an autoclave for 12 hours. The product crystals were stored in an airtight container prior to further analysis. The experiments were repeated twice more for the experiments at 0 and 20 °C in order to determine the repeatability of the experiments.

The EFC recovery experiment was initiated by setting the thermostatic unit and setpoint of the freeze room to −1.5 °C. The data logging of the temperature was initiated when the solution was added to the crystallizer. There was not enough brine to run repeat EFC experiments. An initial liquid sample and samples after 2, 3, 4 and 5 hours were taken during the experiment. The samples were filtered using a syringe filter (pore size of 0.20 μm), and immediately diluted with de-ionized water to prevent any further calcium sulfate from crystallizing out of solution. The final ice and salt product were allowed to separate for ±10 min. The ice was then filtered under vacuum using a Buchner funnel and washed with water that was previously maintained at 0 °C while the saturated salt solution was filtered with the 300 mL Millipore filtration setup. The ice crystals were washed with 150 mL...
de-ionized water kept at 0°C. Samples of the ice product were taken before and after washing. These samples were then analysed using ICP-MS in order to determine the purity of the melted ice. This washing step was repeated three times. The Ca$^{2+}$ ion concentration for all experiments was analysed using AAS.

**RESULTS AND DISCUSSION**

**Brine analysis**

The results from the brine analysis showed that the stream was predominately made up of sodium (2,700 mg/L), potassium (615 mg/L), calcium (1,500 mg/L), sulfate (10,000 mg/L) and chloride (637 mg/L) ions with a TDS content of approximately 28 g/L. The cations and anions obtained from the brine analysis give an indication of the possible identities of the salts that could crystallize under EFC conditions. The salts would likely be sodium, potassium and calcium sulfate or chloride salts.

**Equilibrium recovery results**

The data used to plot Figure 2 were obtained from OLI Stream Analyser (OLI Systems Inc. 2011). Each data point in Figure 2 represents an equilibrium condition. Figure 2 shows the equilibrium recovery of Ca$^{2+}$ and ice as the temperature of the solution is decreased from 25 to -10°C. The recovery of a component crystallizing from the solution is therefore as a result of the system reaching a new equilibrium condition. The Ca$^{2+}$ recovery is 70% at 25°C and increases to 75% before ice begins to crystallize at -0.3°C. The recovery of calcium dramatically increases once ice begins to form with a 99% recovery of Ca$^{2+}$ being achieved at -3°C. The recovery of Ca$^{2+}$ is as a result of CaSO$_4$·2H$_2$O, the scaling component, crystallizing out of solution as a result of the concentrating affect during ice crystallization and a further decrease in temperature. In terms of water recovery, ice begins to crystallize out at -0.3°C and a 95% recovery is achieved at -3°C.

**Experimental recovery results**

Although the thermodynamic modelling results indicate that the RO retentate stream was saturated with respect to CaSO$_4$·2H$_2$O at 25°C, during the laboratory experiments the CaSO$_4$·2H$_2$O only crystallized when the solution was left to stand for approximately 1 month, indicating that the kinetics of the CaSO$_4$·2H$_2$O were slow. This could also be attributed to the presence of impurities in the stream. The kinetics of the CaSO$_4$·2H$_2$O crystallization can be improved by two methods; namely by seeding or by removing the solvent. For example, the work conducted by Tait et al. (2009) showed that a typical mine wastewater attained equilibrium within 2–5 hours after the addition of CaSO$_4$·2H$_2$O seeds. Concentrating a stream improves the kinetics of crystallization because the supersaturation of the crystallizing component increases.

The recovery of CaSO$_4$·2H$_2$O in the RO retentate was experimentally determined for 20°C, 0°C and under EFC conditions. The concentration change of aqueous Ca$^{2+}$ for 20 and 0°C is shown in Figure 3 over the full time frame of the experimental runs (81.3 hours).

It is clear that the calcium concentration remaining in solution at 0°C is lower than that at 20°C but the actual concentration difference between 0 and 20°C is marginal, on average the difference is approximately 2%. Also, the system has not reached equilibrium after 81 hours, thus indicating that a longer time is required for the system to reach equilibrium.

The recoveries of calcium at 20°C, 0°C and under EFC conditions (Figure 4) were calculated assuming that the change in mass of the Ca$^{2+}$ ion was only due to the crystallization of CaSO$_4$·2H$_2$O using the following formula:

$$\%\text{Recovery} = 100 - \frac{[\text{Ca}^{2+}]_0}{[\text{Ca}^{2+}]_i}$$  \hspace{1cm} (1)
where \( [\text{Ca}^{2+}]_{\text{aq}} \) is the aqueous concentration of calcium after time \( t \), measured in mg/L and \( [\text{Ca}^{2+}]_{\text{aq}}^{0} \) is the initial aqueous concentration of calcium also measured in mg/L.

The fluctuations in the aqueous calcium concentration (because of error in the analysis) result in recovery fluctuations. For the 20 and 0°C recovery curves, the majority of CaSO₄·2H₂O is obtained in the first 2.7 hours, for which the yields are 11 and 12% for 20 and 0°C respectively. The recoveries for these temperatures are generally the same, with 0°C recovery temperature being slightly higher than the 20°C recovery temperature. The recoveries are also low when considering that the theoretical recovery of CaSO₄·2H₂O should be 70% at 20°C and 75% at 0°C. This is due to the fact that the system had not yet reached equilibrium. It would thus be uneconomical to run a seeded crystallization process at 0°C in conjunction with the RO process for a residence time exceeding 1.3 hours (12.4% recovery) even though the greatest recovery (15%) is achieved at 69 hours.

EFC can utilize both the seeding and solvent removal methods, by the formation of ice, for an enhanced CaSO₄·2H₂O recovery. Figure 4(b) shows a zoomed in section of Figure 4(a) in order to see the recovery of calcium more clearly for the EFC experiments. The solution was initially seeded with 1 g CaSO₄·2H₂O and cooled to –1°C. The solution temperature was kept constant for 2 hours with no spontaneous ice crystallization occurring. This resulted in a calcium recovery of approximately 12%, which compares well to the value obtained during the 0°C recovery experiments. After the sample was taken for analysis at 2 hours, 1 g of ice seeds were added to the solution, resulting in the onset of ice crystallization. Due to the heat of crystallization, the temperature of the solution temporarily increased to –0.5°C and then decreased slightly to –0.6°C. The solution then remained at –0.6°C for the remainder of the experiment. The recovery of calcium during the EFC experiment increased significantly during the period of ice and salt crystallization (eutectic conditions) resulting in a 48% recovery after 5 hours of operating under eutectic conditions. The recovery of calcium obtained during the EFC experiment did not achieve the recovery predicted by the thermodynamics, which assume equilibrium.

The amount of water recovered, in the form of ice, after 3 hours of ice crystallization, was approximately 20%. The

![Figure 3](https://iwaponline.com/wst/article-pdf/67/1/139/441422/139.pdf)
ice recovery was limited to 20–25% because ice–salt separation could not be effectively achieved with greater solid contents in the batch operated crystallizer. Nonetheless, by removing 20% of the solvent in the form of ice, a calcium recovery of 48% can be achieved. The purity of the ice product was initially low, with a salt concentration of 2 g/L, but the purity of ice was significantly improved (0.001 g/L) after washing the ice with de-ionized water. The temperature of the solution reached a constant value of -0.6 °C. This differed somewhat from the equilibrium temperature (-0.3 °C) predicted using OLI Stream Analyser (OLI Systems Inc. 2012) and is probably due to a number of reasons such as:

- OLI Stream Analyser requires a charge-neutral balance and, as the analysis for a brine is never balanced, an extra amount of the dominant component in the stream is usually added in order to achieve a charge-neutral balance. This affects the accuracy of the modelled stream composition and thus any prediction;
- the brine analysis, although comprehensive, may not account for every component present in the stream thus reducing the accuracy of the thermodynamic modelling step;
- OLI Stream Analyser is limited by the accuracy of experimentally determined solubility data for a wide range of components collected from various sources.

Regardless, the results obtained from OLI Stream Analyser give a good first approximation. The results presented in Figure 4 indicate that CaSO₄·2H₂O can crystallize along with ice during EFC. The EFC waste stream, which would be de-supersaturated with respect to CaSO₄·2H₂O, can subsequently be recycled back to the RO process for an increased water recovery. Therefore, the limitations in water recovery within typical RO systems can be overcome by using a hybrid RO–EFC process.

CONCLUSIONS

This work has shown that there is a slightly greater recovery of CaSO₄·2H₂O obtained at 0 °C (15%) as compared with operating at 20 °C (13%) but that operating under EFC conditions will result in a greater recovery (48%) with only a 20% ice recovery rate. The recovery results obtained experimentally were found to be lower than the predicted equilibrium recoveries. The purity of the ice product formed during EFC was improved from 2 to 0.001 g/L with washing. The results have shown that EFC is a better technique for removing CaSO₄·2H₂O from a wastewater stream when compared with seeded crystallization with CaSO₄·2H₂O at either 0 or 20 °C. This is due largely to the fact that the stream is significantly concentrated during the EFC process which aids in the production of salt. Also, there is the added benefit of producing water during the EFC process.

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