



## Three strategies to treat reverse osmosis brine and cation exchange spent regenerant to increase system recovery



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### HIGHLIGHTS

- Three different strategies to treat concentrate and regenerant were investigated.
- With the application of EFC pure ice and pure salt were recovered.
- Combination of NF, RO and EFC allows near zero waste discharge.

### ARTICLE INFO

#### Article history:

Received 18 December 2013

Received in revised form 4 March 2014

Accepted 6 March 2014

Available online 30 March 2014

#### Keywords:

Eutectic freeze crystallization

Zero liquid discharge

Reverse osmosis

Cation exchange regenerant

### ABSTRACT

Concentrate streams from industrial processes entail an important risk for the environment, as they are often discharged into it. Therefore, efforts must be made to reduce the load of contaminants discharged to the environment. Eutectic freeze crystallization (EFC) is a novel technique which allows separation of salts and water from aqueous streams. In this research, three treatment options for reverse osmosis (RO) concentrate and cation exchange (CIEX) spent regenerant are investigated.

First, application of EFC to RO concentrate was investigated. The stream was rich in  $\text{HCO}_3^-$  and  $\text{Na}^+$ . Application of EFC to this solution, led to the formation of ice and  $\text{NaHCO}_3$  at  $-3.9^\circ\text{C}$  with 5.8 wt.%  $\text{NaHCO}_3$ .

Second, precipitation of  $\text{CaCO}_3$  by mixing the RO concentrate with the CIEX regenerant in a ratio of 2.8:1 and adjusting the pH to 11 was investigated. A 0.25 M NaCl solution remained after the treatment, which upon concentration could be used to regenerate the resin.

Third, application of EFC to a synthetic CIEX regenerant was also investigated. The multicomponent solution contained NaCl,  $\text{MgCl}_2$  and  $\text{CaCl}_2$ . Upon EFC treatment, ice formed first and then  $\text{NaCl} \cdot 2\text{H}_2\text{O}$  at  $-29^\circ\text{C}$ . The composition of eutectic point at  $-29.4^\circ\text{C}$  was 2.48 wt.% Na and 15.85 wt.% Cl.

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### 1. Introduction

Water scarcity is one of the main issues of this century. The application of membrane technology is playing an important role in the attempt to fight this problem. Nanofiltration (NF) and reverse osmosis (RO) membranes allow the use of alternative sources of water to produce high quality water. However, its application entails the production of a concentrate stream for which a destination has to be found. In principle, for low volume, the waste stream could be transported to the sea. However, for large capacity plants this is still a serious challenge. Alternatively, the remaining concentrate stream might be dewatered. In

literature evaporation is mentioned as an option to deal with the brine problem. In arid areas evaporation ponds are used [1,2], but in humid climates evaporation has to be realized by putting thermal energy into the process. Given the fact that evaporative crystallization (EC) is energy intensive and thus costly, it is worthwhile to explore the possibilities of alternative technologies. Eutectic freeze crystallization (EFC) is an alternative technology that is capable of separating aqueous solutions into pure water and pure solidified solutes. By cooling down the brine to the eutectic point (EP), ice and salt crystallize and these crystals can be easily separated due to their density difference. The energy required to separate the water as ice is significantly less than that required to separate it by evaporation, indicated by the fact that the heat of fusion of ice (6.01 kJ/mol) is less than the heat of evaporation of water (40.65 kJ/mol) [3]. In a previous study [4] it was shown that the energy cost to treat an industrial  $\text{KNO}_3\text{--HNO}_3\text{--H}_2\text{O}$  process stream with EFC was 69% lower compared to EC. Furthermore, Fernández-Torres et al.

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[5] performed a comparative life cycle assessment of EFC and EC. The two techniques were compared to a 4 wt.%  $\text{Na}_2\text{SO}_4$  solution, showing that EFC was strongly preferred than EC, due to the 6 to 7 times less energy required.

EFC can be used as the final step after any high recovery process where a mixture of salt and water is produced. For example, Randall et al. [6] applied EFC on brine (0.6 vol.% of feed water volume), which remained after extraction of gypsum from a HiPRO (High Recovery Precipitating RO) concentrate (1 vol.% of the feed water). The brine contained, among other ions, 7 g/L  $\text{Na}^+$ , 1 g/L  $\text{Ca}^{2+}$  and 16 g/L  $\text{SO}_4^{2-}$ . Their study shows that pure ice (>95% purity), pure calcium sulfate and pure sodium sulfate could be recovered from the brine. Ultimately, in the combined HiPRO, gypsum formation and EFC process, 99.6% of feed water was recovered as water, 0.3% as salts, and only 0.1% ended up as waste. Thus, the total salt and water recovery was nearly 99.9% [6].

The nearly zero liquid discharge (ZLD) concept has recently been investigated by various groups, and was the focus of several reviews [7–10]. Usually, membranes are used in the production of water in near-ZLD studies. Cation exchange (CIEX) resin may also be employed, to remove bivalent cations to prevent scaling. In a previous study feed water was first treated by CIEX, then it was treated by NF, and the concentrate was further treated by RO. The used pilot plant ran at total system recoveries between 91 and 98% [11]. In the case of working at 98% total recovery there is still a remaining 2% concentrate stream. Since EFC seemed a promising technique and requires less energy than for instance a three-stage evaporation system [4], it was chosen to treat the RO concentrate. This RO concentrate stream was relatively rich in  $\text{HCO}_3^-$  (0.9 wt.%) and  $\text{Na}^+$  (0.3 wt.%), thus, the production of  $\text{NaHCO}_3$  under eutectic conditions was expected.

Although the application of ionic exchange reduces scaling problems and makes a reduction of the brine stream possible, regeneration introduces a new waste material, the spent regenerant. In principle, the total salt waste stream increases because salts are needed to regenerate the ionic exchange column. This solution is normally disposed directly to the environment. Since the disposal of this solution to the environment is undesirable, the challenge is, therefore, to reuse the CIEX spent regenerant. In this case study, the resin is in the sodium form and  $\text{NaCl}$  is used to regenerate it. The resulting regenerant can be treated with  $\text{Na}_2\text{CO}_3$  to precipitate the calcium and to be able to re-use the regenerant. The possibility of treating the regenerant with the salt produced from the RO concentrate is investigated.

The CIEX spent regenerant is a multi-component solution containing a mixture of  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , among other ions. Another attractive alternative is to treat this stream with EFC in order to produce pure ice and recover pure salt. We know from literature that the solubility lines and eutectic points of the binary systems are:  $\text{NaCl-H}_2\text{O}$ : EP – 21.2 °C, 23.3 wt.%,  $\text{MgCl}_2\text{-H}_2\text{O}$ : EP – 33.6 °C, 32.3 wt.% and  $\text{CaCl}_2\text{-H}_2\text{O}$ : EP – 55 °C, 29.8 wt.%. However, actual eutectic conditions might deviate from the ones for pure systems for the multicomponent solution due to the presence of impurities (dissolved ions). This option has also been studied in this research.

## 2. Materials and methods

### 2.1. Scheme of the process

The RO concentrate and CIEX spent regenerant were obtained from a pilot plant described elsewhere [11]. When working at a 98% total system recovery, the pilot plant treats 120 L of tap water and produces 2.4 L/h RO concentrate and 100 L/week of regenerant, according to Fig. 1.

Three different strategies to increase the total system recovery have been studied:

- Strategy 1 Application of EFC to the RO concentrate. Pure ice and pure salt can be recovered. The salt produced can be used to treat the CIEX spent regenerant, or potentially be sold.
- Strategy 2 Mixing of the RO concentrate with the CIEX spent regenerant to precipitate  $\text{CaCO}_3$  and re-use the regenerant for regeneration of the CIEX resin.
- Strategy 3 Application of EFC to the CIEX spent regenerant. Pure ice and pure salt can be recovered.

### 2.2. Experimental methodology for Strategy 1

The starting solution for performing the experiments was the RO concentrate from the pilot plant described in detail elsewhere [11]. This RO concentrate was however, still rather diluted and far from the first expected eutectic point of  $\text{NaHCO}_3$  [12]. The RO concentrate was therefore, approximately 6 times concentrated by evaporation in order to get close to the expected eutectic point (it was pre-concentrated by evaporation just for practical reasons during the experiment, but it could had been pre-concentrated by freeze concentration). The concentration of the RO concentrate (pH 8.6) is shown in Table 1.

During the pre-concentration step, some salt formation already occurred. The subsequent EFC experiment was therefore conducted after filtering the salt from the solution with a 4.2  $\mu\text{m}$  pore size filter (Whatman 1442 090). Fig. 2 gives a detailed scheme of the procedure.

The filtered pre-concentrated solution was placed in a 1 L plastic beaker positioned inside a 2 L glass jacketed crystallizer (Fig. 3). An IKA stirrer with variable speed control was used to provide adequate mixing of the solution inside the crystallizer. Cooling was achieved indirectly with a Lauda RE207 thermostatic unit. Two PT-100 sensors connected to an ASL F250 precision switchbox measured the temperature of the solution and the coolant with a resolution of  $\pm 0.001$  °C. The values were recorded in a computer via the Lab View program. The temperature of the coolant was set at – 10 °C.

#### 2.2.1. Sample analyses

After ice formation, mother liquid samples were collected between each 0.2 and 0.6 °C decrease for analysis. The samples were filtered with a 0.22  $\mu\text{m}$  Millipore filter and analyzed with Ion Couple Plasma Atomic Emission Spectrometry (ICP-AES) with an accuracy of  $\pm 5\%$

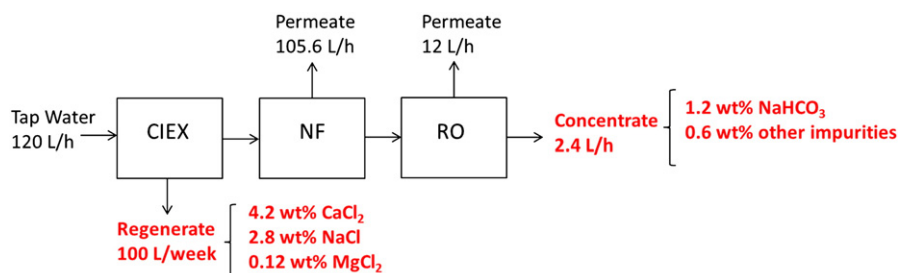


Fig. 1. Scheme of the ZLD process studied in this research.

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