



## A novel brine precipitation process for higher water recovery



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### HIGHLIGHTS

- Scale-forming compounds are removed from NF concentrate to enable higher water recovery in second stage NF or RO.
- Co-precipitation of phosphonate-based antiscalant by ferric chloride increases precipitation of scale-forming compounds.
- Precipitation process on NF concentrate enabled the secondary membrane to be run with 85% recovery.
- Studied all of the supersaturated compounds in the brine namely: calcite, magnesite, barite, dolomite, and huntite.
- Based on the optimized method, 82% of calcium, 61% of alkalinity, 98% of barium and 31% of the conductivity are removed.

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### ABSTRACT

A three-step demineralization process for removing scale-forming substances from brine solutions produced from nanofiltration (NF) of water was developed. The process is designed to remove substances that would lead to scale and membrane fouling during additional stages of NF or reverse osmosis (RO). Tests were performed to determine the most suitable dosages and mixing times for each reagent. The first step in the demineralization process employs ferric chloride for removing phosphonate scale inhibitors via co-precipitation with ferric hydroxide. The second step of the process increases the solution pH value to promote carbonate mineral precipitation. The third step involves barium sulfate precipitation promoted by barite seed crystals. Saturation indices for precipitation of mineral solids were simulated using the Phreeqc thermodynamic modeling program. Water recovery from the treated brines was modeled using the ROSA package for simulating permeate and concentrate compositions for NF processes. The three-step demineralization process allowed the recovery rate for the brine solution to be as high as the initial feed water, and achieved a total water recovery of >97%.

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### 1. Introduction

Over the last few decades, potable water scarcity has become a significant issue due to increasing population and changing rainfall patterns. It is estimated that more than one billion people are without clean drinking water, and almost 2.3 billion people live in regions with water shortages [1]. Therefore, water reuse and recycling schemes are becoming increasingly necessary to augment supplies of potable water [2].

High pressure membrane processes, such as reverse osmosis (RO) and nanofiltration (NF), are commonly used to produce potable water from non-potable source waters. RO and NF processes can remove both organic and inorganic species and produce extremely clean water [3]. The main drawback to RO and NF is the production of a concentrated brine stream requiring further treatment or disposal [3]. Concentrate disposal options include: ocean discharge, surface water

discharge, deep well injection, evaporation and land application [4]. The best option for concentrate disposal is site dependent, largely dependent on costs, and can be as high as 25% of the overall treatment costs [5]. Because of high costs and adverse environmental impacts of brine disposal, there is great need for methods that can minimize brine generation.

One method of reducing the brine volume from an RO or NF process is to pass the brine through a second high pressure membrane to increase recovery of clean water. However, this method is often not cost-effective and sustainable due to rapid fouling of the second membrane. To increase the lifetime of this second membrane, pre-treatment of the brine for removal of organic and inorganic species is required [6]. Although organic contaminants can be attenuated in the brine stream using oxidation processes, like ozone and UV-advanced oxidation, treatment of inorganic species is more challenging.

Lime slurry softening has been proposed as a treatment method for RO concentrates prior to second stage reverse osmosis [7]. Gabelich et al. performed a pilot-scale study using a solids contact reactor and achieved 92%, 97%, 88% and 67% removal for calcium, barium, strontium

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and silica. However, increasing the pH to over 10 resulted in magnesium hydroxide precipitation, which had poor settling characteristics. Several other studies used a two-step process for removing only calcite and gypsum [8,9]. However, in many cases, membrane concentrates are often supersaturated with respect to other potentially scale forming species, such as barite, magnesite, huntite and dolomite. Therefore, more robust treatment schemes are required.

Chemical softening of RO and NF brines is made more difficult when scale-inhibiting compounds, such as phosphonate antiscalants, are present. These compounds inhibit  $\text{CaCO}_3$  precipitation and reduce the particle size of precipitates. A recent study has found that a granular ferric hydroxide adsorbent can remove phosphonate antiscalants from RO concentrates [10,11]. However, the kinetics of the adsorption process were considerably slower than those for ion exchange, and extended contact times were required to achieve practical adsorbent loadings.

The goal of this research was to develop a treatment scheme for removing scale-forming compounds from membrane concentrate solutions that are supersaturated with respect to multiple carbonate and sulfate minerals. To remove antiscalant compounds that interfere with mineral precipitation, ferric chloride was added to promote co-precipitation of ferric hydroxide and the phosphonate antiscalants. The effectiveness of three pH adjusting chemicals, lime, caustic soda, and soda ash, on promoting carbonate mineral precipitation was determined. The effect of mixing time and several seeding agents on precipitation rates were also investigated.

## 2. Experimental

All of the experiments are conducted at 22 °C and the mixing rate was 250 rpm.

### 2.1. Materials

Ferric chloride hexahydrate, hydrochloric acid, and anhydrous sodium carbonate were procured from Fisher scientific, and calcium hydroxide, barium sulfate and sodium hydroxide were obtained from ACROS Organics. All chemicals were ACS reagent grade or higher. Silica (0.2–0.3 mm) and garnet (#60) were procured from Red Flint Sand & Gravel, LLC. Pall membrane filters (GH PolyPro 0.45  $\mu\text{m}$  50 mm) were used for filtration of the solutions after each treatment step. A phosphonate-based antiscalant with the dose of 1.5 mg/L (PermaTreat 191, PermaCare-191) is added to the CAP water.

### 2.2. Brine generation and system description

Water from the Central Arizona Project (CAP) as delivered to Tucson, Arizona was collected before each experiment. The water was treated using a Dow Filmtec™ (NF270-400) NF membrane operating at 85% recovery. The brine characteristics are shown in Table 1. Concentrations are given as ranges as a consequence of conducting the experiments throughout the year with different CAP water qualities. The supersaturation levels of mineral solids in the brine are shown in Table 1. The saturation index (SI) for each solid was calculated as:

$$SI = \log \frac{\prod a_i^{v_i}}{K_{sp}} \quad (1)$$

where  $K_{sp}$  is the solubility product for the mineral dissolution reaction,  $a_i$  is the activity of ion  $i$  and  $v_i$  is the stoichiometric coefficient for species  $i$  in the mineral dissolution reaction.

Experiments were conducted using a jar test apparatus (PB-900 Programmable Jar tester, Phipps & Bird) containing 6 reaction vessels. The dimensions of the vessels were 11.5 cm  $\times$  11.5 cm  $\times$  21 cm, and each test was conducted on 1 l of solution.

**Table 1**

Brine characteristics generated from CAP water at 85% recovery with an NF membrane.

Analyte	Concentrations (mg/L)	
pH	8.3–8.4	
Alkalinity (as $\text{CaCO}_3$ )	270–330	
Sodium	287–321	
Magnesium	145–162	
Potassium	14–16	
Calcium	339–346	
Barium	0.7–0.8	
Phosphorous	0.5–0.8	
Chloride	108–118	
Sulfate	1770–1899	
	SI values	Log $K_{sp}$ values
$\text{CaCO}_3$ (Calcite)	1.5–1.54	– 8.48
$\text{BaSO}_4$ (Barite)	1.75–1.81	– 9.97
$\text{CaMg}(\text{CO}_3)_2$ (Dolomite)	2.95–3.06	– 17.09
$\text{CaSO}_4$ (Gypsum)	– 0.26	– 4.58
$\text{CaMg}_3(\text{CO}_3)_4$ (Huntite)	1.42–1.73	– 29.97
$\text{MgCO}_3$ (Magnesite)	0.84–0.94	– 8.03

### 2.3. Methods

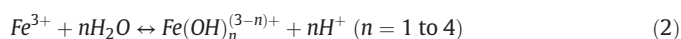
Anions were analyzed using a Metrohm Professional IC (Model 850 Anion HP Gradient). A Metrohm ASUPP7-250 (4 mm ID  $\times$  250 mm) column was used for this purpose. All reagents and standards were prepared in ultrapure water (18 M $\Omega$  cm). The eluent solution for anions was 3.2 mM of sodium carbonate and the Metrohm Suppression Module (MSM) solutions were 1% nitric acid for regeneration and ultrapure water for rinsing. Cations were analyzed using an Agilent 7900 ICP-MS. All of the reagents and tuning solutions were procured from Agilent. Samples were acidified using 2% nitric acid before analysis. Alkalinity was measured using Gran Function Plot Method available in USGS online free software.

Scaling indices were calculated using the Phreeqc aqueous phase thermodynamic modeling package from the U. S. Geological Survey. The Phreeqc model uses extended Debye–Huckel and the Davies equation for modeling solution phase activity coefficients [12]. The scaling potential of the treated brine solutions was evaluated using the ROSA software package from DOW Filmtec. The ROSA software simulates membrane treatment operations by applying empirical separation factors for different ions and operating conditions.

## 3. Results and discussion

### 3.1. Ferric chloride addition

The effect of ferric chloride dose on removal of the phosphonate antiscalant is shown in Fig. 2. The phosphorous concentration in solution was used to track antiscalant removal, since its exact structure is a proprietary trade secret of the manufacturer. Ferric chloride addition results in hydrolysis reactions that produce ferric hydroxide, according to [11]:



Both phosphate and phosphonate antiscalant compounds are known to form chemical adsorption complexes with ferric hydroxide [10]. These complexes involve replacement of an  $\text{OH}^-$  or  $\text{H}_2\text{O}$  ligand bound to one of the Fe atoms with a phosphate or phosphonate ligand. This results in formation of a Fe–O–P bond that removes the antiscalant compound from solution, as illustrated in Fig. 1. This chemical adsorption process allows selective removal of the antiscalant in the presence of high concentrations of other anions, such as, chloride and sulfate, which do not form these inner-sphere complexes. The declining solution pH values with increasing  $\text{FeCl}_3$  dose were indicative of ferric

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