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Effect of solution composition on seeded precipitation of calcium for high recovery RO of magnesium-bearing wastewater, surface water or groundwater

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ABSTRACT

The accelerated seeded precipitation (ASP) of calcium salts from simulated municipal wastewater RO brines using calcium carbonate seed is compared to the much more effective but more expensive ASP using calcium phosphate seed. The aim of this study was to identify the test water compositional limitations of ASP using calcium carbonate seed, and to elucidate the chemistry responsible for the different performance of calcium carbonate and calcium phosphate as seed materials in the ASP of calcium from municipal wastewater and magnesium-bearing groundwater.

The results of seeded precipitation of calcium from simulated wastewaters and groundwater using $CaCO_3$ seed was found to only be effective in the absence of phosphate and at conditions where the driving force for $MgCO_3$ formation was low. Seeded precipitation using $CaHPO_4$ seed greatly outperformed $CaCO_3$ seeded precipitation at high carbonate-high magnesium concentration conditions where inhibition was the greatest for $CaCO_3$ seeded precipitation.

SEM images of the seed particles after seeded precipitation showed $CaCO_3$ seeds that appeared to be covered with a thin layer of precipitate. SEM images of the solid formed after $CaHPO_4$ seeded precipitation, however, showed seed that had a thick covering of very small particles.

1. Introduction

Municipal wastewater and groundwater are valuable water resources for inland locations in Australia at times of water shortage, and play an integral role in sustainable water management strategies of water authorities in inland regions. Due to their salt content, however, their indiscriminate use for irrigation can lead to soil sodicity and crop failure, and many water authorities have included desalination in their strategic plans for the delivery of fit-for-purpose recycled water to their community.

Desalination in inland regions poses a major challenge – the management of the resultant brine concentrate. Extraction of excessive quantities of low salt water from the feedwater during the reverse osmosis (RO) desalination process leads to salt concentrations that are greater than the solubility of certain salts, such as calcium carbonate, calcium sulfate or calcium phosphate, resulting in the formation of mineral scale on the membranes and the reduction in clean water flux through the membranes. To avoid the development of this scale, the recovery of low salt water during the reverse osmosis treatment is kept to values of typically 70–80% of the wastewater volume, depending on the wastewater constituent concentrations. The management of the resulting 20–30% of the feed volume can be a major burden to the water authority, and represents a major underutilization of the wastewater, particularly at times of drought when wastewater and groundwater resources are called upon more strongly in order to meet the water needs of the community.

Waste brine management and wastewater utilization can be improved by the use of interstage treatment of the RO concentrate to remove scale precursor ions. Interstage treatment involves operating the RO at water recoveries that are not conducive to scale formation, treatment of the resulting RO concentrate to remove the scale precursor ions via precipitation and solid-liquid separation, and then further treating the RO concentrate via another RO stage or by recycling to the feed stream to extract more low salt water. The solid-liquid separation process adopted depends largely on scale and economic considerations. This can be sedimentation and microfiltration as was piloted by Gabelich et al. [1], ceramic filtration as piloted by Sanciolo et al. [2], moving bed filter or any

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other solid-liquid separation process that can achieve the desired low turbidity (<1 NTU) for the subsequent RO treatment.

Antiscalants can be added downstream of the ASP stage, i.e. at the second RO stage, as their use in the first stage may hinder the interstage precipitation and removal of scale precursor ions if the ASP process operates at low supersaturation. Alternatively, antiscalant can be added at the first RO stage and removed by adsorption on $CaCO_3$ seed prior to interstage treatment [3]. In some circumstances, the judicious choice of antiscalant may allow antiscalant use in the first RO stage without adverse effects in the downstream ASP stage. Sanciolo et al. [2], for example, adopted ASP involving $CaHPO_4$ precipitation on $CaHPO_4$ seed and used an antiscalant that is not effective against $CaHPO_4$ scale formation but is effective against $CaCO_3$ scale formation (Flocon 135) in the first RO stage, thus providing some protection against $CaCO_3$ scale without adversely affecting $CaHPO_4$ precipitation in the ASP stage.

The removal of scale precursors in high recovery RO has been achieved via ion exchange [4], chemical precipitation [1] or seeded precipitation [5]. Interstage demineralization of RO concentrates has been shown to be effective for mildly brackish river water treatment [5,4] for tap water treatment [6] [7], and for groundwater treatment [8]. Literature studies involving the application of interstage demineralization to high recovery RO of municipal wastewater, however, are very few [9,2].

The choice of seed material to be used in ASP is often dictated by the composition of the solution to be treated, with the composition of the seed *usually* being that of the salt to be precipitated. Lin and Singer [10], for example, compared the use of quartz, dolomite and calcite as seed materials for calcium carbonate precipitation from calcium carbonate solution, and found that only calcite had the ability to initiate calcium carbonate precipitation. Similarly, Lioliou et al. [11] investigated seeded precipitation from stable calcium carbonate supersaturated solutions using calcite and quartz seed and found that calcite induced precipitation but quartz did not. The choice of seed material is, however, more difficult when one is dealing with solutions that contain interfering substances. Our earlier work on high recovery RO of municipal wastewaters [2], that were supersaturated with respect to calcium carbonate, showed that the removal of calcium from the 70% water recovery RO concentrate produced from this wastewater via accelerated seeded precipitation (ASP) using calcium carbonate seed was not effective. The use of calcium phosphate seed ($CaHPO_4$), however, allowed the reduction of the calcium concentration from 250 mg/L to 10 mg/L. The poor performance of calcium carbonate seed was attributed to the presence of magnesium and phosphate at levels that interfere with the seeded precipitation process [12–24]. The high concentration of calcium, magnesium and phosphate in the wastewater was attributed to the combined effect of high evaporation rate, low flow and groundwater infiltration.

The presence of small quantities of phosphate has been found to markedly slow the precipitation of calcium carbonate from supersaturated solutions [20]. The inhibitory effect of phosphate on calcium carbonate precipitation has been attributed to the chemisorption of aqueous $CaHPO_4$ species [21], which blocks the active calcium carbonate surface sites, preventing or slowing further calcium carbonate deposition. Similarly, the presence of magnesium ions has been found to retard calcium carbonate precipitation [25] and inhibit calcium carbonate crystal growth [19]. A competitive adsorption model involving Ca^{2+} and Mg^{2+} was found to give a good fit to the experimental data. The inhibitory effect of magnesium ions on unseeded precipitation has also been attributed to the increase in interfacial tension of the newly formed nuclei [16].

Our previous studies of calcium carbonate precipitation in simulated RO brines at pH 10 [26] confirmed the slowing influence of magnesium and phosphate ions on calcium precipitation in the absence of seed, and served to elucidate the solution conditions responsible for calcium carbonate supersaturation in RO brines at this pH. Solutions were equilibrated at pH 10 for 2 h prior to filtration through 0.45 μm filter and it was found that the filtrate of solutions without magnesium or phosphate had low residual calcium concentrations. The filtrate of solutions containing magnesium had the highest residual calcium concentration. The presence of phosphate on its own was also found to lead to elevated calcium concentrations at the end of the experiment. The combined addition of magnesium and phosphate was found to result in higher residual calcium levels than with these two components added individually. Seeded precipitation experiments using $CaCO_3$ seed also showed that the presence of magnesium and phosphate also significantly affects seeded precipitation of calcium from RO brines.

In this paper, calcium carbonate seeded ASP is tested at different concentrations of magnesium and carbonate, in the presence and absence of phosphate ion, and compared to the much more effective but more expensive ASP using calcium phosphate seed. The aim of this study was to elucidate the test water compositional limitations of interstage ASP using calcium carbonate seed, and the chemistry responsible for the different performance of calcium carbonate and calcium phosphate as seed materials in the ASP of calcium from municipal wastewater and magnesium-bearing groundwater RO concentrates to achieve high RO water recovery.

2. Methods

2.1. Seed materials

The particle size of the $CaCO_3$ (Ajax chemicals) and $CaHPO_4$ (BDH chemicals) used as seed were determined using a Malvern Zetasizer Nano-ZS. The powders were dispersed in ASP treated (10 g/L $CaCO_3$ or $CaHPO_4$, pH 10) RO brine that had been filtered through a 0.45 μm cellulose acetate membrane filter. The composition of this RO brine is given in a previous publication [2]. The powders were polydisperse with a high proportion of the particles (>30%) with a diameter larger than 6000 nm, and exhibiting poor suspension stability. The $CaCO_3$ seed particles with diameters below 6000 nm were found to have diameters between 13 and 450 nm with the most frequent diameters being between 20 and 250 nm. The $CaHPO_4$ seed particles with diameters below 6000 nm were found to have diameters between 350 and 2000 nm with the most frequent diameter being between 600 and 1100 nm. The surface area was determined using a Micromeritics TriStar Surface Area and Porosity analyser to be 0.96 m^2/g for $CaCO_3$ seed and 2.3 m^2/g for $CaHPO_4$ seed.

2.2. Solutions

2.2.1. Seeded precipitation trials

The solution magnesium, phosphate and carbonate concentrations used are shown in Table 1. The solution Mg^{2+}:Ca^{2+} ratio and CO_3^{2-}:Ca^{2+} ratio are shown in Table 2. Ten millilitre aliquots of the required stock salt solutions were delivered to a 200 mL glass reaction vessel and made up to 100.0 mL with deionised water. All solutions were made 6.25 mM with respect to Ca^{2+}, 10.2 mM

Table 1
Parameter settings for the 3 × 2^3 full factorial seeded precipitation experiments (mM) using no seed, 10 g/L $CaCO_3$ seed, or 10 g/L $CaHPO_4$ seed at pH 10.0.

Parameter	Low	High
Mg^{2+}	7.6	15.2
HPO_4^{2-}	0	0.58
CO_3^{2-}	10.2	30.6