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This is the Accepted version of the following publication

Sanciolo, Peter, Ostarcevic, Eddy, Atherton, Paul, Leslie, Greg, Fane, Tony, Cohen, Yoram, Payne, Marrack and Gray, Stephen R (2010) Enhancement of Reverse Osmosis Water Recovery Using Interstage Calcium Precipitation. *Desalination*, 295. pp. 43-52. ISSN 0011-9164

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# Enhancement of Reverse Osmosis Water Recovery Using Interstage Calcium Precipitation

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**Abstract** The feasibility of removing calcium scale precursor ions from reverse osmosis (RO) concentrate by accelerated seeded precipitation (ASP) was investigated with the goal of increasing product water recovery and minimizing the volume of concentrate disposal from inland municipal wastewater desalination plants. Three seed materials were tested in laboratory trials – calcium carbonate, calcium sulfate and calcium phosphate. Calcium carbonate and calcium sulfate seed were not effective. The addition of calcium phosphate seed particles at 20 g L<sup>-1</sup> or phosphate ion in stoichiometric excess of the calcium concentration (250 mg L<sup>-1</sup> Ca = 6.25 mM Ca<sup>2+</sup>, 650 mg L<sup>-1</sup> HPO<sub>4</sub><sup>2-</sup> = 6.7 mM) decreased the calcium content in the RO concentrate to 10 mg L<sup>-1</sup>. Evaluation of the accelerated seeded precipitation process using in-situ generated calcium phosphate seed at the pilot scale was performed on a 25 kL day<sup>-1</sup> pilot plant consisting of dissolved air flotation, ultrafiltration and reverse osmosis. The treated concentrate was filtered by a ceramic filtration system. Preliminary cost analyses indicates that high recovery RO using calcium phosphate precipitation can only be justified in inland situations where restrictions on concentrate disposal drive smaller evaporation pond storage volumes to offset the higher chemical and energy running costs.

**Keywords** Reverse osmosis, scale formation, precipitation, calcium phosphate, high recovery RO

## 1. INTRODUCTION

Conventional RO treatment of municipal wastewater can only recover approximately 70% to 85% of the water for reuse, leaving 15% to 30% as waste saline brine, requiring costly disposal and representing a waste of water resource. Operating RO systems at water recoveries that are above, or at the upper bounds of this recovery range, can result in the formation of calcium, barium, strontium or silica scale on the membrane surface, resulting in an increase in energy and cleaning requirement, and a decrease in the lifetime of the RO membranes. For a municipal wastewater, the major contributors to scale formation were found to be calcium, carbonate and phosphate [1].

Membrane mineral scaling limits the achievable product water recovery, and higher water recoveries can be achieved by decreasing the concentration of scale precursor ions in the RO concentrate. This demineralization, often referred to as intermediate concentrate demineralization (ICD), has been found to be a promising strategy for enhancing water recovery [2]. This ICD can take place via chemical precipitation or seeded precipitation. Chemical precipitation ICD is a process which is analogous to the classical lime-soda or caustic softening processes (i.e., precipitation softening), and has been applied to the enhancement of water recovery in the RO treatment of mildly brackish surface water [3]. Seeded precipitation ICD, also known as

accelerated seeded precipitation (ASP) is a process whereby precipitation is initiated by crystal seeding, which provides crystal growth sites for precipitation reactions [4]. Demineralization via ASP has been shown to be effective for mildly brackish surface water treatment [5, 6] and in tap water treatment [7].

It is generally found that seed materials that have a high degree of chemical similarity to the salts that are to be precipitated on their surface tend to be effective for ASP. Lin and Singer [4], for example, compared the use of quartz, dolomite and calcite as seed materials for calcium carbonate precipitation, and they found that only calcite had the ability to initiate calcium carbonate precipitation. Municipal wastewaters typically contain considerable quantities of calcium, carbonate and sulfate ions, and therefore have potentially high calcium carbonate and calcium sulfate scaling tendency. The logical approach for ASP treatment of municipal wastewater would, therefore, be to use calcium carbonate (calcite) or calcium sulfate (gypsum) as seed.

The ASP removal of calcium from municipal wastewater using calcium carbonate seed is difficult due to the presence of considerable quantities of phosphate and magnesium. These constituents have been reported to be powerful inhibitors of calcium carbonate precipitation in numerous studies [8, 9, 10, 11, 12]. Removal of scale precursor ions has also been achieved via unseeded precipitation of calcium carbonate by alkali addition [3]. It is known that unseeded precipitation is also sensitive to solution conditions [13, 14, 15]. As a consequence of the presence of these interfering constituents, ASP treatment of municipal wastewater using calcium carbonate as seed has been found to require large seed doses and extended precipitation periods [16].

The use of calcium sulfate seed has been successfully employed in the removal of calcium to the calcium sulfate solubility limit from agricultural drainage water containing magnesium concentrations that interfere with calcium carbonate precipitation [17]. Calcium sulfate seed may, therefore, be a good candidate for ASP calcium removal from municipal wastewater. One of the main goals of the current research is to identify a suitable seed material for the accelerated seeded precipitation of calcium from municipal wastewater RO concentrates.

Prior research in this area has used sedimentation clarifiers and filtration to remove the seed from the treated brine prior to further RO treatment [2]. Clarifiers require a large footprint and are prone to problems associated with gas bubble formation. Sedimentation is also not suited to high solids loadings since the rate of sedimentation decreases with increasing solids concentration [18] due to interaction between the particles that can slow sedimentation. The current research used a ceramic filtration system that has a smaller footprint than a clarifier and also offers the added advantage of allowing operation at higher solids (seed) concentration, thereby offering the potential to lower phosphate ion additions. Ceramic ultrafiltration was used rather than conventional ultrafiltration with organic membranes for this application due to the ability of ceramic membranes to withstand the harsh cleaning required to remove the expected calcium phosphate fouling. It is, however, much more energy intensive as mitigation of fouling due to cake formation is accomplished with the use of very high flows, rather than backwashing as is the case for conventional ultrafiltration with organic membranes.

This paper presents a laboratory scale investigation of calcium removal from municipal wastewater RO concentrate via ASP using a variety of seed materials, and the results of subsequent pilot plant testing of the ASP process using the most effective seed material from the laboratory tests. The ASP stage was integrated into an RO process using ceramic ultrafiltration to remove the precipitated calcium and provide a calcium depleted stream for further RO processing to recover additional water. The process was tested on highly saline ( $9,500 \text{ mg L}^{-1}$  total dissolved solids), calcium rich ( $220 \text{ mg L}^{-1}$ ) municipal wastewater from Donald, a small inland town in Victoria, Australia. The elevated salinity and calcium content of this municipal wastewater is attributed to high evaporation rates and ingress of saline groundwater.

## **2. METHODS**

### **2.1 Wastewater composition**

The chemical composition of the wastewater used in the laboratory and pilot plant trials is shown in Table 1. This municipal wastewater was sourced from the Donald Wastewater Treatment Plant, Donald, Victoria, Australia.

## **2.2 Laboratory scale experiments**

Brine was sourced from a RO system desalting secondary municipal wastewater at 70% water recovery after the addition of  $3 \text{ mg L}^{-1}$  Flocon 135 antiscalant and acid dosing to achieve a pH of 6.5. Experiments were conducted on 100.0 mL aliquots of brine under constant stirring, prior to pH adjustment using 1 M NaOH. The  $\text{CaCO}_3$  (AR grade, Ajax Chemicals) and the  $\text{CaHPO}_4$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (LR, BDH chemicals) used as seed were dosed without drying. Phosphate ion addition was performed by adding the required volume of 0.4M  $\text{KH}_2\text{PO}_4$  solution. Carbonate ion addition was performed by adding the required volume of 1.0M  $\text{NaHCO}_3$  solution.

**Table 1:** Wastewater composition

Parameter	Units	Laboratory experiments <sup>a</sup> (sampled mid 2009)	Pilot Plant Trial <sup>b</sup> (sampled mid 2011)
pH	pH Units	8.8	7.0
Phosphorus, reactive as P	mg P L <sup>-1</sup>	5.9	<0.01
Total Dissolved Solids	mg L <sup>-1</sup>	3100	9500
Fluoride, as F	mg L <sup>-1</sup>	0.39	0.68
Chloride, as Cl	mg L <sup>-1</sup>	1700	5600
Sulfate, as SO <sub>4</sub>	mg L <sup>-1</sup>	170	970
Bicarbonate Alkalinity as CaCO <sub>3</sub>	mg CaCO <sub>3</sub> L <sup>-1</sup>	340	370
Carbonate Alkalinity as CaCO <sub>3</sub>	mg CaCO <sub>3</sub> L <sup>-1</sup>	64	<2
Hydroxide Alkalinity as CaCO <sub>3</sub>	mg CaCO <sub>3</sub> L <sup>-1</sup>	<2	<2
Total Alkalinity as CaCO <sub>3</sub>	mg CaCO <sub>3</sub> L <sup>-1</sup>	410	370
Chromium 6+, as Cr	mg L <sup>-1</sup>	<0.01	<0.01
Chromium 3+	mg L <sup>-1</sup>	<0.01	<0.01
Ammonia, as N	mg N L <sup>-1</sup>	17	11
Nitrate, as N	mg N L <sup>-1</sup>	1	0.16
Nitrite, as N	mg N L <sup>-1</sup>	0.32	0.91
Silica, reactive as SiO <sub>2</sub>	mg L <sup>-1</sup>	13	15
Aluminium	mg L <sup>-1</sup>	<0.1	<0.1
Barium	mg L <sup>-1</sup>	0.03	0.06
Boron	mg L <sup>-1</sup>	0.5	1.4
Chromium	mg L <sup>-1</sup>	<0.01	<0.01
Copper	mg L <sup>-1</sup>	0.01	0.03
Iron	mg L <sup>-1</sup>	<0.2	<0.2
Lead	mg L <sup>-1</sup>	<0.01	<0.01
Manganese	mg L <sup>-1</sup>	0.02	1.7
Nickel	mg L <sup>-1</sup>	<0.01	0.02
Strontium	mg L <sup>-1</sup>	3.8	5.3
Zinc	mg L <sup>-1</sup>	0.02	0.14
Calcium	mg L <sup>-1</sup>	96	220
Magnesium	mg L <sup>-1</sup>	140	360
Potassium	mg L <sup>-1</sup>	71	46
Sodium	mg L <sup>-1</sup>	890	2800

<sup>a</sup> this wastewater was put through RO treatment at approximately 70% water recovery to generate the brine used in the laboratory experiments

<sup>b</sup> UF filtrate, pre-treated by dissolved air flotation with ferric chloride flocculant (50 to 100 mg L<sup>-1</sup>), turbidity of feedwater before treatment was approximately 300 NTU

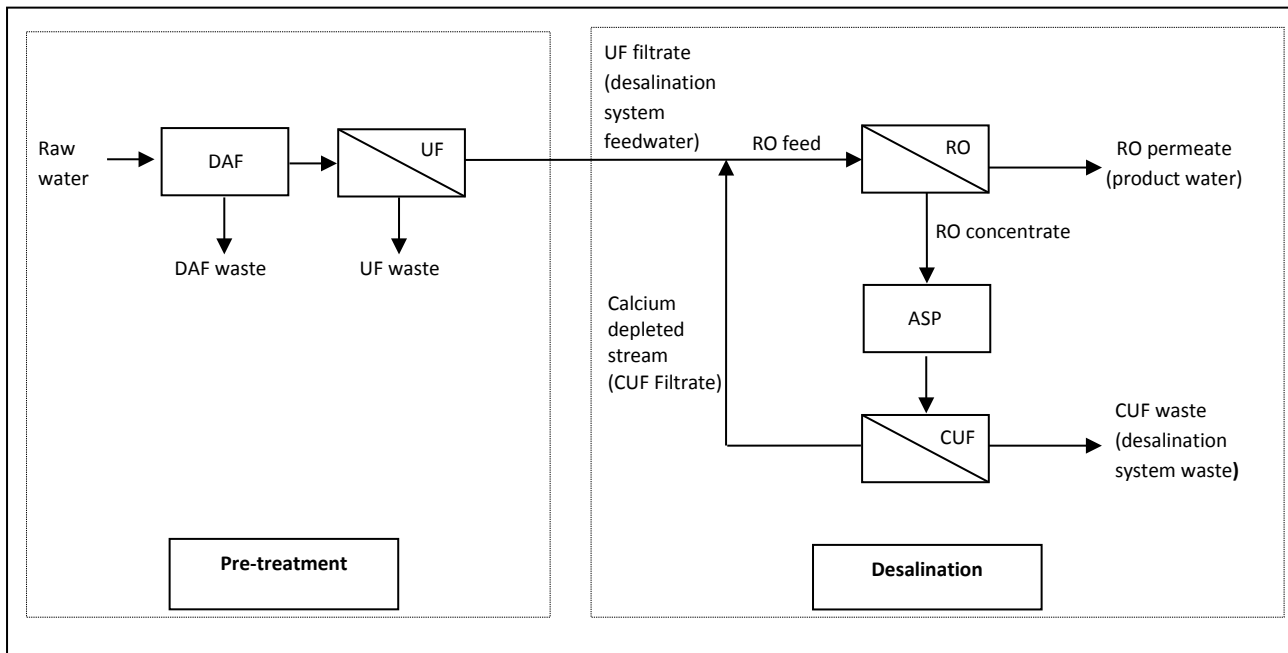
Alum treatment for phosphate removal was performed by treating 100 mL of brine with Alum to 200 mg L<sup>-1</sup> Al<sup>3+</sup> (as Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.18H<sub>2</sub>O) at pH 6.5. Suspended solids (AlPO<sub>4</sub> and Al(OH)<sub>3</sub> precipitate) were removed by filtration using a 0.45 micron cellulose acetate filter, prior to addition of 10 g L<sup>-1</sup> calcium carbonate at the resulting pH (~7), and subsequent pH adjustment to 10.0.

For analyses involving atomic absorption spectroscopy measurement of calcium, the brine was sampled using a syringe, and filtered through 0.45 micron acetate filter and acidified prior to analysis using a nitrous oxide - acetylene flame and 5,000 mg L<sup>-1</sup> potassium addition to standards and samples. For analyses using calcium ion selective electrode measurements, standards were prepared with background electrolyte approximately matching the pH of the brine samples and the

concentration with respect to  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ . This electrolyte was made using analytical grade  $\text{Na}_2\text{SO}_4$  (BDH),  $\text{NaCl}$  (Merk),  $\text{MgCl}_2$  (Merk) and  $\text{KCl}$  (Ajax). The wastewater and brine composition (Table 1) were determined by a commercial analytical laboratory (NATA accredited to ISO/IEC 17025).

### 2.3 Pilot plant trials

The pilot plant train consisted of pre-treatment using dissolved air flotation (DAF) and ultrafiltration (UF), followed by desalination using reverse osmosis (RO), accelerated seeded precipitation (ASP) and ceramic ultrafiltration (CUF) as shown in Figure 1. The desalination process flows used are summarised in Table 2.



**Figure 1:** Diagrammatic representation of process stages and streams. DAF: Dissolved Air Flotation; UF: Ultrafiltration using Hydracap membrane modules; RO: Reverse osmosis using Filmtec SW membrane elements; ASP: Accelerated seeded precipitation using pH elevation and phosphate ion addition; CUF: Ceramic Ultrafiltration.

**Table 2:** Process flows, 48% RO water recovery

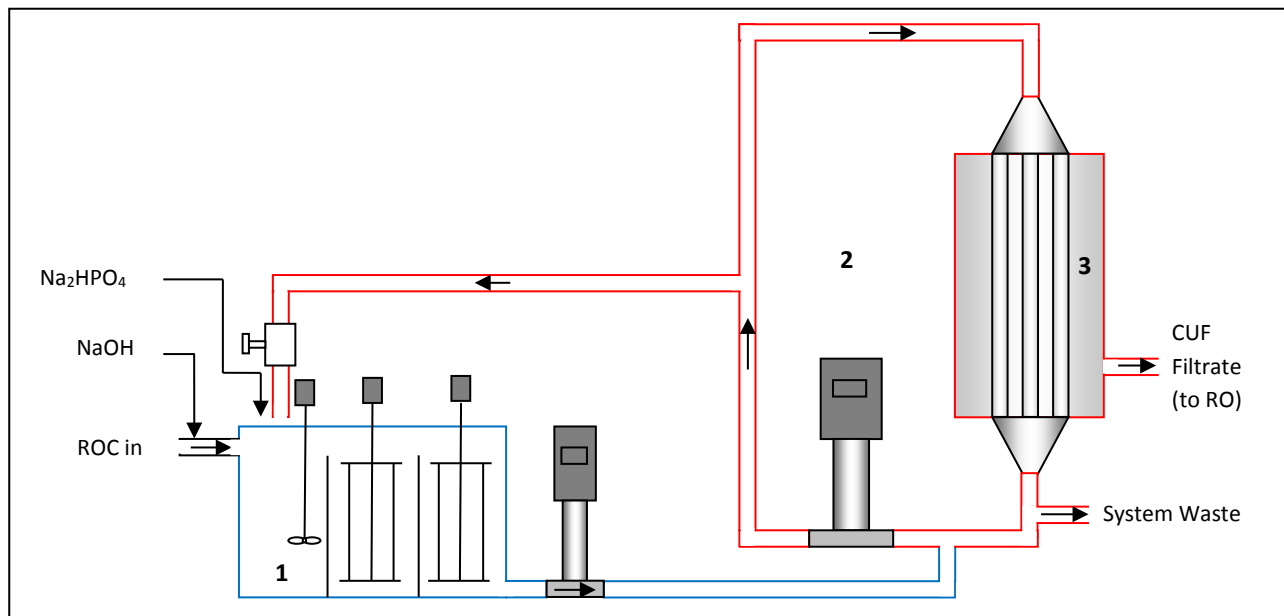
Stream	Flow ( $\text{L hr}^{-1}$ )	
	70% System water recovery	90% System water recovery
UF Filtrate	1026	806
RO Feed	1512	1512
RO Permeate	726	726
RO concentrate	786	786
CUF filtrate	486	706
Desalination System Waste	300	81

*DAF plant:* Removal of algae from the municipal wastewater feedwater was performed using a DAF plant (1.5 m x 1.0 m x 1.0 m). Ferric chloride was used as coagulant at 50 to 100  $\text{mg L}^{-1}$  dose rate, depending on turbidity of the feedwater. This treatment was found to reduce the turbidity by approximately 50 to 60% from approximately 300 NTU.

*UF Plant:* The feedwater to the RO was further pre-treated by ultrafiltration using 4 HYDRACap 60 (Hydranautics) membrane capillary (inside out) modules. This treatment was found to reduce the turbidity to below 1 NTU.

*RO Plant:* Reverse osmosis was performed using Dow, - Filmtec membrane elements (6 x 4 inch diameter seawater elements (SW4040), 6 x 2.5 inch diameter seawater elements (SW2540), in series configuration). Sea water elements were selected rather than brackish water elements due their potential for operation at the higher osmotic pressure and high applied pressure conditions expected at high water recovery (BW element maximum pressure: 41.1 bar, SW element maximum pressure: 68.9 bar). The average operational flux was 12 L m<sup>-2</sup> h<sup>-1</sup>.

*ASP-CUF plant:* The ceramic ultrafiltration system was designed to return some of the in-situ generated solids back to the precipitation tanks as shown in Figure 2.



**Figure 2:** Diagrammatic representation of the ASP-CUF system 1: 100 L flash mixer, 200 L flocculation tanks, 200 L maturation tank. 2: ceramic filter recirculation loop (flow = 70,000 L h<sup>-1</sup>); 3: ceramic filter

Addition of caustic soda was performed in the lines to the flash mixer and flocculation tanks. Filtration of the precipitated calcium salts from the brine was performed using Jiangsu Jiuwu Hitech Co., Ceramfil® Inorganic Ceramic Membranes consisting of multi-channel tubular elements composed of alpha-Alumina/Zirconia with a 50 nm pore size (Model CMF09060-OD25), assembled in 3 pressure vessels in series, each pressure vessel containing 19 ceramic membranes. The total surface area of the ceramic filtration system was 11.4 m<sup>2</sup>. The ceramic filter system was equipped with an internal solids recycling loop designed to minimise caking by providing a high flow rate within the ceramic filter elements (typically 70,000 L h<sup>-1</sup> for a filtrate flow of approx. 700 L h<sup>-1</sup>). The filtration system was also equipped to return the ceramic filter concentrate to the ASP flocculation tanks, allowing higher seed dose in the flocculation tanks.

*Analytical techniques:* On site monitoring of calcium levels was performed using a calcium ion selective electrode. Validation of this method on the test waters prior to the trial was performed by comparison of the calcium selective electrode results with those obtained using atomic absorption spectroscopy.

### 3. RESULTS AND DISCUSSION

#### 3.1 Test water composition

It can be seen from Table 1 that the wastewater used for the laboratory experiments contained 96 mg L<sup>-1</sup> of calcium and 340 mg L<sup>-1</sup> (as CaCO<sub>3</sub>) of bicarbonate alkalinity which at pH 8.8 corresponds to an LSI value of 1.5, suggesting that the solution is disposed to calcium carbonate precipitation. It

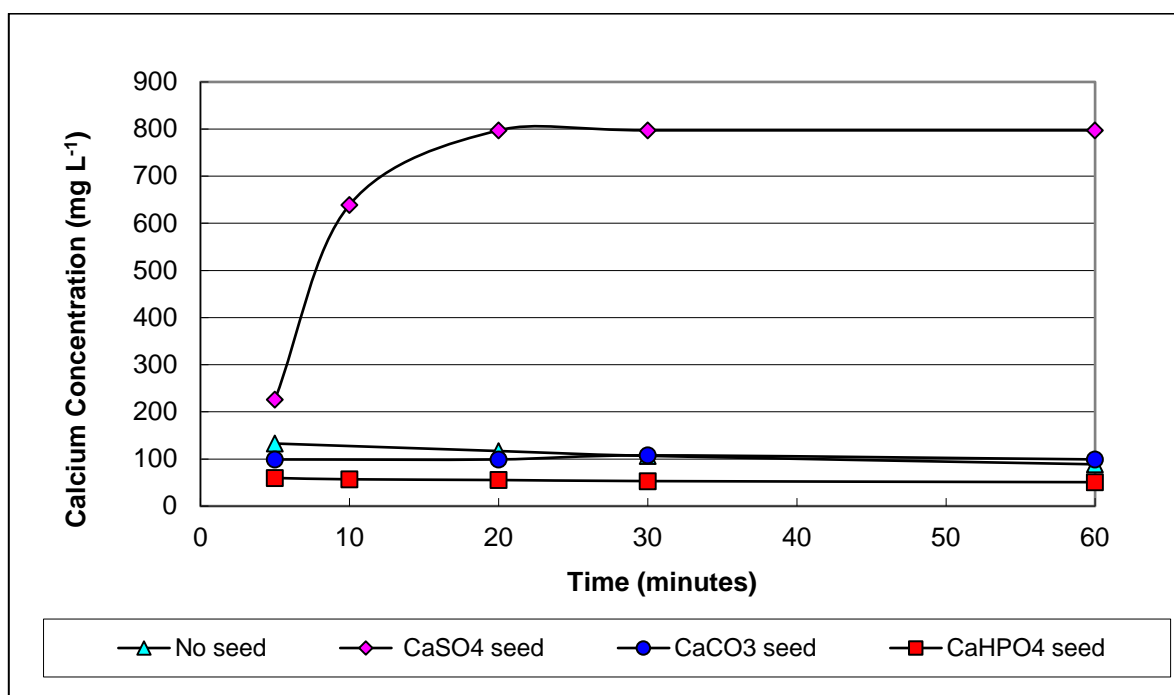
can also be seen, however, that the wastewater also contains  $140 \text{ mg L}^{-1}$  of magnesium and  $5.9 \text{ mg L}^{-1}$  of reactive phosphorous – two powerful inhibitors of calcium carbonate precipitation. [ 8, 12].

The brine generated in the pilot plant trials was approximately a factor of three more saline and contained twice as much calcium and magnesium as the brine used in the bench experiments. The feedwater LSI at pH 7.0 was -0.004 which was lower than the feedwater used in laboratory studies due to the lower alkalinity and pH. In addition, the phosphate level of the pilot plant feedwater was below  $0.01 \text{ mg P L}^{-1}$  due to pre-treatment with ferric chloride coagulant during the dissolved air flotation pre-treatment used in the pilot plant trials. Notwithstanding the differences in the two waters, the purpose of the bench experiments was to generate information on the response of RO brine to seeded and ion precipitation doses prior to testing at the pilot stage.

### 3.2 Laboratory scale experiments

#### 3.2.1 Batch mode seed requirements.

The wastewater contained high calcium, carbonate and sulfate ion concentrations (Table 1), suggesting that calcium carbonate or calcium sulfate crystals may serve as seed to accelerate the precipitation of these ions. The alternative seed material for this test water was calcium phosphate, selected in order to assess the feasibility of precipitative removal of calcium phosphate in order to facilitate calcium carbonate precipitation at elevated (alkaline) pH. . The effectiveness of these seeds in reducing the calcium concentration of the RO concentrate at pH 10 is shown in Figure 3.



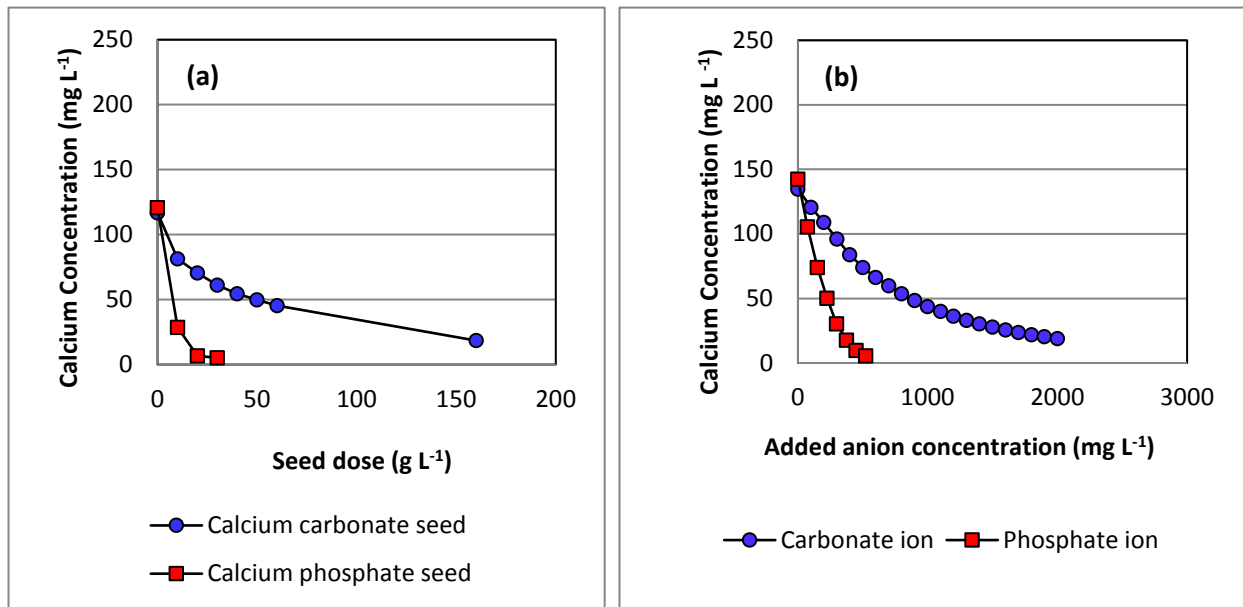
**Figure 3:** Effect of seed type, 10 g/L seed dose, pH10. The calcium concentration in the RO concentrate before pH adjustment to 10.0 was  $250 \text{ mg L}^{-1}$ .

The three seed materials tested can be seen to have very different effect on the precipitation behaviour of calcium in the RO concentrate. Increasing the pH of the brine from the native pH (8.8) to pH 10.0 in the absence of seed raised the LSI from 1.5 to 2.3, and reduces the concentration of soluble calcium to approximately  $125 \text{ mg L}^{-1}$ . This residual level of calcium is higher than would be expected from a solution with such a high LSI value due to the presence of magnesium, phosphate the Flocon antiscalant, which inhibit calcium carbonate precipitation. This interference can also be seen in the case of calcium carbonate seed addition, where a mild and slow decrease the calcium concentration was observed. Calcium phosphate seed addition, however, was found to considerably decrease the calcium concentration to  $50 \text{ mg L}^{-1}$ . Addition of calcium sulfate seed



was found to increase the calcium concentration from approximately 130 mg L<sup>-1</sup> (no seed) to 800 mg L<sup>-1</sup> within 20 minutes, indicating dissolution of the seed. The observed increase in calcium concentration is greater than that expected if the added calcium sulfate were dissolving to its pure water equilibrium solubility limit (~200 mg L<sup>-1</sup>,  $K_{sp}(\text{CaSO}_4) = \sim 2.4 \times 10^{-5}$  [ 19]). This is consistent with the high calcium sulfate supersaturation found for other highly saline waters [ 20].

The effect of various doses of calcium carbonate and calcium phosphate seed, at pH 10.0, is shown in Figure 4(a).



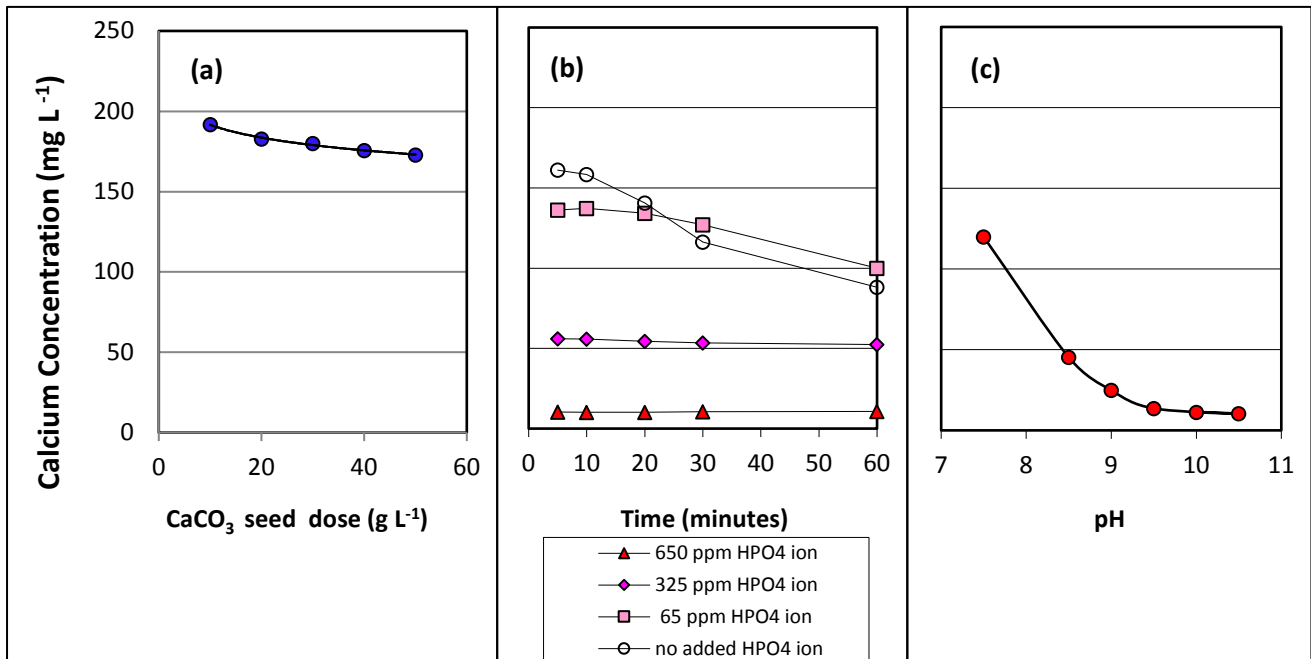
**Figure 4:** Effect of seed addition (a) or anion addition (b) at pH 10.0, RO brine, pH maintained at 10.0 after seed addition, one minute equilibration between additions, the calcium concentration before treatment was 250 mg L<sup>-1</sup>.

Subsequent addition of seed was found to further reduce the calcium concentration. Calcium phosphate seed was found to be more effective at reducing the calcium concentration, 20 g L<sup>-1</sup> being sufficient to reduce the calcium concentration to below 10 mg L<sup>-1</sup>. A seed dose of 20 g L<sup>-1</sup> would, however, be expected to be prohibitively expensive when one considers that reuse of the seed may be difficult due to carbonate fouling of the seed surface [ 15]. It can be seen from Figure 4(a) that to achieve the same calcium levels would require more than ten times this dose of calcium carbonate. It is noted that phosphate molar concentration in the test brine was only ~1/10 of the molar calcium concentration, indicating that the low calcium concentrations achieved with phosphate seed addition were achieved by the combined precipitation of calcium phosphate and calcium carbonate. It is not clear why the interferences that are known to hinder seeded precipitation of calcium carbonate using calcium carbonate seed [6, 10] do not also interfere with seeded precipitation of calcium carbonate using calcium phosphate seed to the same extent. One explanation may be that the calcium phosphate seed adsorbs or precipitates the interfering components, allowing the calcium carbonate to precipitate more freely.

### 3.2.2 Batch mode anion requirement to generate seed in-situ

An alternative mode of treatment to the seeded precipitation shown in Figure 4(a) is to precipitate the calcium and generate the seed in-situ by adding carbonate or phosphate ion. This mode of operation would be expected to allow easier automation, and would be particularly suited to water that is lean in carbonate or phosphate ions. The brine was titrated at the bench with carbonate or phosphate solutions and the calcium concentration was determined one minute after anion addition. The results are presented in Figure 4(b). Phosphate addition, whether as a preformed seed (Fig 4 a) or as an ion (Fig 4.b), is more effective at reducing calcium content than carbonate. Calcium phosphate precipitation can be seen to be favoured over calcium carbonate precipitation

for the test brine. The addition of 500 mg L<sup>-1</sup> (5.2 mM) of phosphate ion was found to decrease the calcium concentration to below 10 mg L<sup>-1</sup> from approximately 140mg L<sup>-1</sup>, whereas more than 2500 mg L<sup>-1</sup> (42 mM) of carbonate ion would be required to achieve similar results. These results are not surprising in the light of the fact that the antiscalant used in the production of the RO brine (Flocon 135) is stated by the manufacturers to provide protection against calcium carbonate precipitation but not against calcium phosphate precipitation.



**Figure 5:** Effect of alum pre-treatment, phosphate ion dose and pH, and calcium carbonate seed addition to alum treated brine at pH 10.0 (a), effect of reaction time at different phosphate ion doses at pH 10.0 (b), and effect of pH at 650 ppm HPO<sub>4</sub> ion addition, 5 minutes contact time (c). Ca concentration before treatment and pH adjustment was 250 mg L<sup>-1</sup>.

### 3.2.3 Effect of pre-treatment to remove phosphate

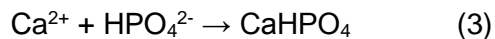
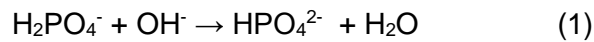
In order to test the feasibility of removal of the interference from phosphate, the brine was pre-treated with 200 mg L<sup>-1</sup> Al<sup>3+</sup> at pH 6.5 to remove the phosphate. The phosphate removal for the alum treatment was found to be 82%. The calcium concentration one minute after repeated 10 g L<sup>-1</sup> additions of calcium carbonate seed at pH 10.0 is shown in Figure 5(a). Here it can be seen that alum treatment followed by 10 g L<sup>-1</sup> calcium carbonate seed addition decreases the calcium concentration from approximately 250 mg L<sup>-1</sup> to approximately 190 mg L<sup>-1</sup>, and further seed additions only marginally decrease the calcium concentration. Calcium removal shown in Figure 5(a) is poorer than that for seeded precipitation without alum pre-treatment (see Figure 4a).

### 3.2.4 Effect of phosphate ion concentration on rate of calcium precipitation

The rate of calcium precipitation at pH 10.0 at different phosphate ion additions is shown in Figure 5(b). It can be seen that the calcium concentration slowly decreases in the absence of phosphate ion addition at pH 10.0. The composition of the brine suggests that the precipitating species is calcium carbonate or calcium hydroxide. The addition of 65 mg L<sup>-1</sup> phosphate mildly decreases the calcium concentration at low reaction times, but is detrimental at longer reaction times, suggesting that the chemical species being precipitated are different. This data is consistent with the precipitation of calcium phosphate and inhibition of calcium carbonate and calcium hydroxide at less than stoichiometric quantities of phosphate. The addition of phosphate in stoichiometric excess of the calcium concentration (250 mg L<sup>-1</sup> Ca = 6.25 mM Ca, 650 mg L<sup>-1</sup> HPO<sub>4</sub><sup>2-</sup> = 6.7 mM) rapidly decreases the concentration to below 10 mg L<sup>-1</sup>.

### 3.2.5 Effect of pH

In the near neutral to alkaline pH region, increasing the pH results in an increased driving force for calcium phosphate precipitation due to the formation of HPO<sub>4</sub><sup>2-</sup> ion from H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ion as follows:



To investigate the effect of pH on calcium precipitation, the brine was dosed with 650 mg L<sup>-1</sup> phosphate ion and then adjusted to various pH values between 7.5 and 10.5. The results are shown in Figure 5(c). It can be seen that the optimum pH range for calcium precipitation using added phosphate ion was above pH 9.5

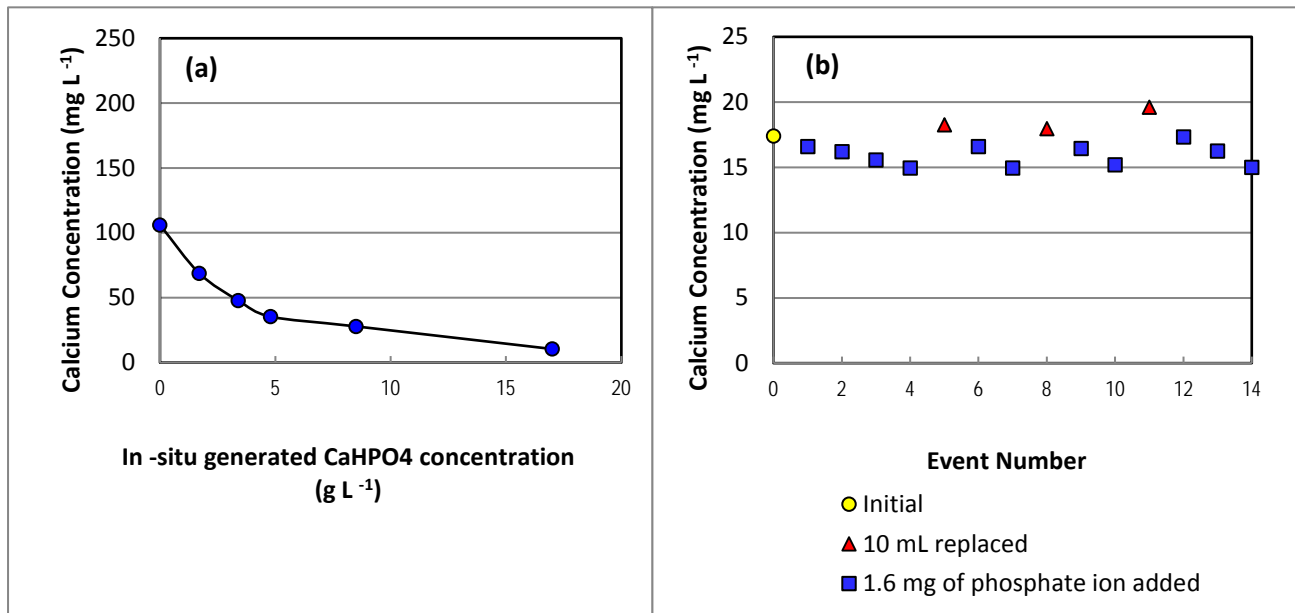
### 3.2.6 Effect of in-situ generated calcium phosphate concentration

The precipitated solids produced after the addition of phosphate ion are expected to be largely calcium phosphate. To determine if the precipitated solids can be reused as seed in the pilot plant, and thus minimise phosphate ion addition, the solids generated in varying quantities of RO concentrate brine (250 mg L<sup>-1</sup> calcium) at 600 mg L<sup>-1</sup> added phosphate, and pH 10.0, were concentrated by filtration down to less than approximately 10 mL (i.e., to a thick paste). The recovered solids were redispersed in 100 ml of untreated brine with the aid of a two minute ultrasonication. The pH was adjusted to 10.0 with NaOH, giving a nominal calcium phosphate concentration of 17 g L<sup>-1</sup>. The calcium concentration was measured after 5 minutes of equilibration. The results were compared to the calcium level resulting from pH adjustment to 10.0 alone in Figure 6(a). Here it can be seen that the addition of 17 g L<sup>-1</sup> of recycled solids to raw water achieves the same level of calcium removal as the addition of 650 mg L<sup>-1</sup> HPO<sub>4</sub><sup>2-</sup> ion. The residual calcium concentration can be seen to increase linearly at a rate of 2 mg L<sup>-1</sup> for every g L<sup>-1</sup> decrease in added solids in the added solids range between 4.25 and 17 g L<sup>-1</sup>. A sharper increase in residual calcium concentration was found to occur between 0 and 4.25 g L<sup>-1</sup> added recycled calcium phosphate. The results shown in Figure 6(a) indicate that recycling of the solids can decrease the phosphate ion addition requirement. At 17 g L<sup>-1</sup>, no phosphate addition was required to achieve a target calcium concentration of 10 mg L<sup>-1</sup>. This result, however, is for freshly precipitated solid that are only used once.

### 3.2.7 Phosphate requirement with seed reuse

To determine the phosphate requirement with seed reuse at high seed concentration, the solids resulting from the precipitation treatment of 2,000 mL of brine using 650 mg L<sup>-1</sup> phosphate ion addition at pH 10.0 were concentrated into 100 mL by filtration, giving a nominal CaHPO<sub>4</sub> concentration of 17 g L<sup>-1</sup>. Ten millilitre samples of this suspension were replaced with untreated brine, and the resulting increase in concentration was then titrated with phosphate. The results are

shown in Figure 6(b). It can be seen that 6.4 mg (events 1 to 4) of  $\text{HPO}_4^{2-}$  additions were required to decrease the calcium concentration from the initial 17 mg  $\text{L}^{-1}$  to 15 mg  $\text{L}^{-1}$ . Subsequent replacement of 10.0 mL of this suspension with 10.0 mL of raw brine containing 250 mg  $\text{L}^{-1}$  Ca (event 5) increases the concentration to 18 mg  $\text{L}^{-1}$  rather than the 41 mg  $\text{L}^{-1}$  expected if no precipitation were taking place. The difference between these two figures represents the quantity of calcium being removed by accelerated seeded precipitation using 17g  $\text{L}^{-1}$  in-situ generated seed material. Two further 1.6 mg additions of  $\text{HPO}_4$  ion (events 6 and 7) were required to decrease the concentration back to 15 mg  $\text{L}^{-1}$ . The quantity of  $\text{HPO}_4^{2-}$  required to treat the 10.0 mL of raw water added between event 5 and event 8 was, therefore, 3.2 mg  $\text{HPO}_4 / 10.0 \text{ ml of raw water} = 320 \text{ mg } \text{L}^{-1}$ . This is approximately half equimolar to the calcium content. The next replacement of 10.0 mL of this suspension required the same phosphate ion addition (events 8 to 10), but the subsequent replacement (event 11) required 3 phosphate ion additions (events 12 to 14) to reduce the calcium concentration to 15 mg  $\text{L}^{-1}$ , equating to 420 mg  $\text{L}^{-1}$  phosphate requirement. This increase in requirement may be attributable to the loss of seed with each replacement (10% at each replacement), and/or to a change in composition of the seed from predominantly calcium phosphate to increasing quantities of calcium carbonate and calcium hydroxide. These results demonstrate the potential for recycling of calcium phosphate seed to reduce phosphate ion addition required for removal of calcium, although the long term viability of this strategy was not demonstrated in the short term laboratory experiments.



**Figure 6:** Effect of in-situ generated recycled seed dose (a), and repeated replacement of 10 mL of high solids suspension (17 g  $\text{L}^{-1}$ ) with untreated brine, without return of solids, with phosphate ion addition, 100 mL total volume (b).

### 3.3 Pilot Plant Trial

The pilot plant trial were designed to achieve high system water recoveries (90%) by taking the concentrate from the RO process operated at low water recovery (48%), removing most of the calcium, blending this calcium depleted stream with a UF-filtered raw water stream, and then feeding this back to the same RO plant component that had produced it (see Figure 1 and Table 2). This blending roughly halves the calcium concentration reaching the RO. The RO, in turn, approximately doubles this concentration back up to the original raw water concentration. Under this flow regime, the propensity for calcium scale formation is minimised by keeping the calcium concentration below or at that of the raw water, thereby allowing high system water recoveries.

The aims of this trial were to determine if low calcium concentrations can be achieved in a continuous manner on a large scale, the chemical requirements for calcium concentration reduction, whether incorporation of the ASP stage into the RO process can allow high desalination system water recovery to be achieved without scale formation, and to perform a preliminary costing of high system water recovery desalination. The results of this trial point to the challenges that need to be met in future research on high recovery RO treatment of municipal wastewater using ASP.

**Table 3:** Phosphate addition rates (mole h<sup>-1</sup>)

Run time (hours)	System Water Recovery			
	70%		90%	
	Phosphate addition rate (mole hr <sup>-1</sup> )	HPO <sub>4</sub> : Ca ratio	Phosphate addition rate (mole hr <sup>-1</sup> )	HPO <sub>4</sub> : Ca ratio
1	18	3.5	17	4.2
2	18	3.5	17	4.2
3	15	2.9	14	3.5
4	15	2.9	15	3.7
5	14	2.7	15	3.7
6	13	2.5	16	4.0
7	13	2.5	17	4.2
8	14	2.7	17	4.2
9	15	2.9	-	-
10	15	2.9	-	-
11	15	2.9	-	-
12	15	2.9	-	-
13	15	2.9	-	-
14	15	2.9	-	-

### 3.3.1 Accelerated seeded precipitation stage performance:

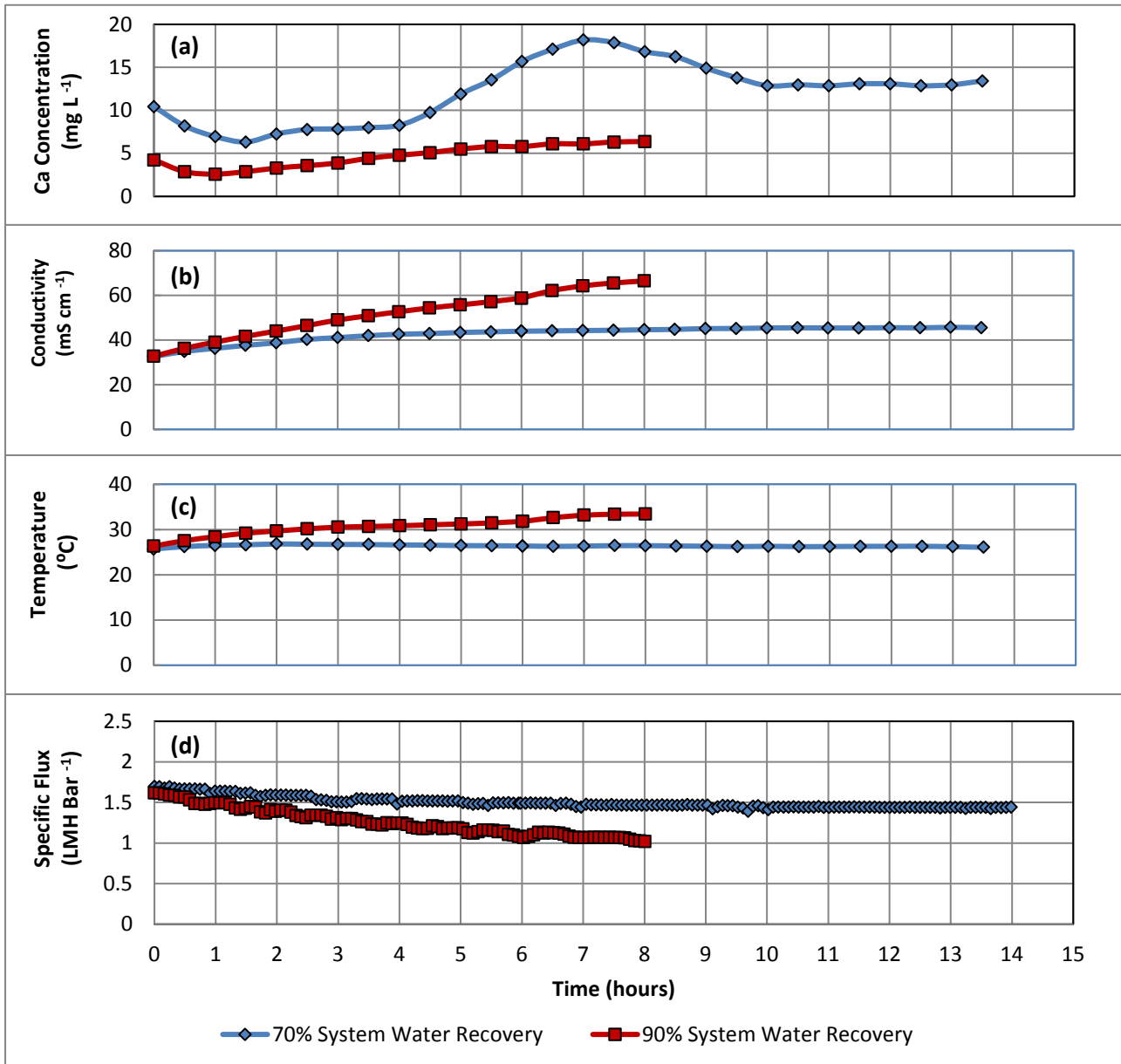
The calcium concentrations achieved in the ASP stage are shown in Figure 7.

The use of a calcium selective electrode was found to a convenient and reliable method of monitoring the calcium concentration. The feedwater calcium concentration on the day of the trial was 198 mg L<sup>-1</sup>, and this was reduced to less than 20 mg L<sup>-1</sup> during the ASP stage. The phosphate addition rate and the resulting phosphate to calcium ratio achieved are shown in Table 3. Due to the different UF filtrate feed flows to the RO in the 70% and 90% system water recovery periods (see Table 2), the quantity of calcium entering the ASP stage was different – 5.1 mole hr<sup>-1</sup> and 4.0 mole h<sup>-1</sup> respectively. Comparison of the calcium concentration achieved at similar phosphate to calcium ratios shows very similar residual calcium concentrations (compare the 70% system water recovery data at 1 and 2 hours operation time, with the 90% system water recovery data at 3, 4 and 5 hours). The higher residual calcium concentrations in the 70% water recovery period may be attributable to the lower phosphate to calcium ratios used during this period. The phosphate to calcium ratio was kept high in the 90% system water recovery period in preparation for planned subsequent phosphate optimisation at higher recycled solids concentrations. The development of turbidity in the CUF filtrate, however, prevented this optimization. The increases in CUF turbidity necessitated the disconnection of the CUF filtrate from the RO, thereby reducing run time and preventing investigations which require longer time periods, such as seed dose and chemical optimisation, and RO scale formation assessments.

### 3.3.2 Turbidity of filtrate from ceramic ultrafiltration system

Two increases in CUF filtrate turbidity occurred, as shown in Figure 8. These increases in turbidity necessitated the disconnection of the ASP-CUF system from the RO. One turbidity increase

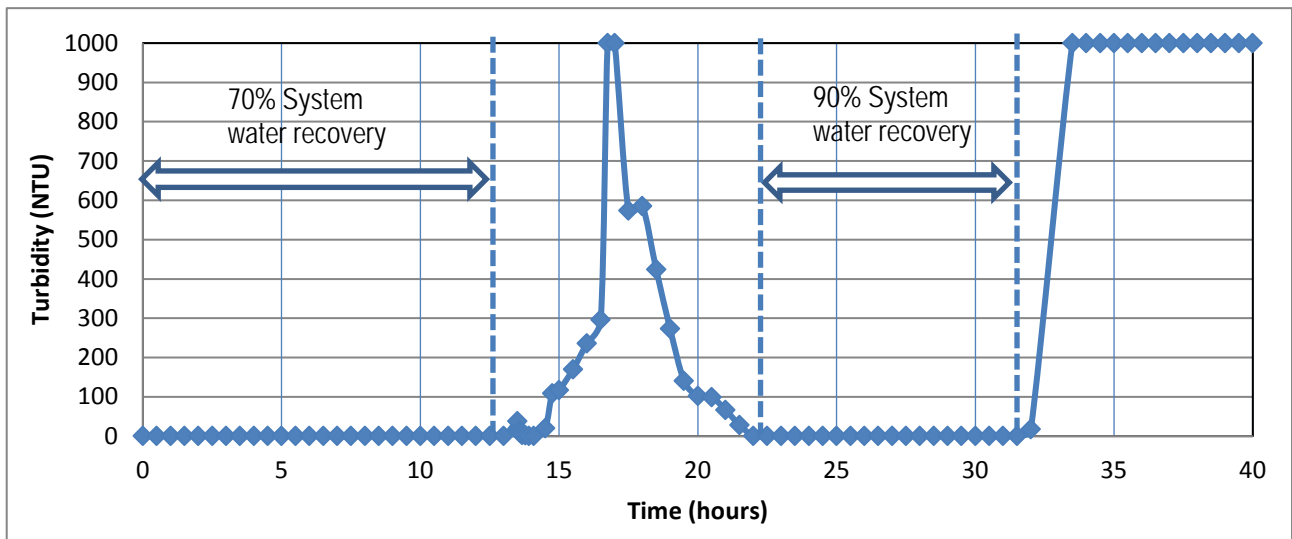
occurred after approximately 13.5 hours of operation at 70% system water recovery. The other turbidity increase occurred after 8 hours of operation at 90% system water recovery. During these periods, the temperature of the CUF filtrate was found to increase from the feed temperature of 12 °C to 28 °C at 70% system water recovery, and 34 °C at 90% system water recovery.



**Figure 7:** Pilot plant results, calcium concentration in CUF filtrate (a), conductivity of CUF filtrate (b), temperature of CUF filtrate (c), and RO process specific permeate flux (d), feed calcium to ASP was 5.1 mole hr<sup>-1</sup> for 70% system water recovery and 4.0 mole hr<sup>-1</sup> for 90% system water recovery, phosphate ion addition was as per Table 3.

The higher temperature is the result of the high internal filter flow rates used the CUF system to minimise the chance of filter cake formation (70,000 L h<sup>-1</sup>), and due to the increase in temperature of the RO feed resulting from the blending of the warm CUF filtrate and the cooler UF filtrate. An increase in temperature is known to enhance precipitation of calcium phosphates due to the lower solubility of these salts at the higher temperature. The increase in CUF filtrate turbidity can then, tentatively, be attributed to precipitation of calcium species on the filtrate/permeate side of the ceramic filter when the calcium and the anionic insoluble calcium salt precursor ions (e.g. CO<sub>3</sub><sup>2-</sup>,

$\text{HPO}_4^{2-}$ ) were exposed to higher temperatures in this region of the filtration equipment. Since the increase in temperature is imparted to the retentate/concentrate stream by the pump, this mechanism of solids formation on the filtrate/permeate side of the ceramic filter would require an induction period that is sufficiently long as to allow the free ion to travel to the filtrate side before precipitation takes place. Further testing is required to test this speculative explanation. If the cause is the increase in the temperature increase, the use of a heat exchanger, lower cross flow velocities and/or higher feed flows may minimise this effect and allow longer periods of operation using ceramic filters. The use of two separate RO plants, rather than using one RO plant in recirculation mode (as in the current study, see Figure 1), would also be expected to minimise the temperature increase



**Figure 8:** Turbidity of filtrate from ceramic ultrafiltration (CUF) system.

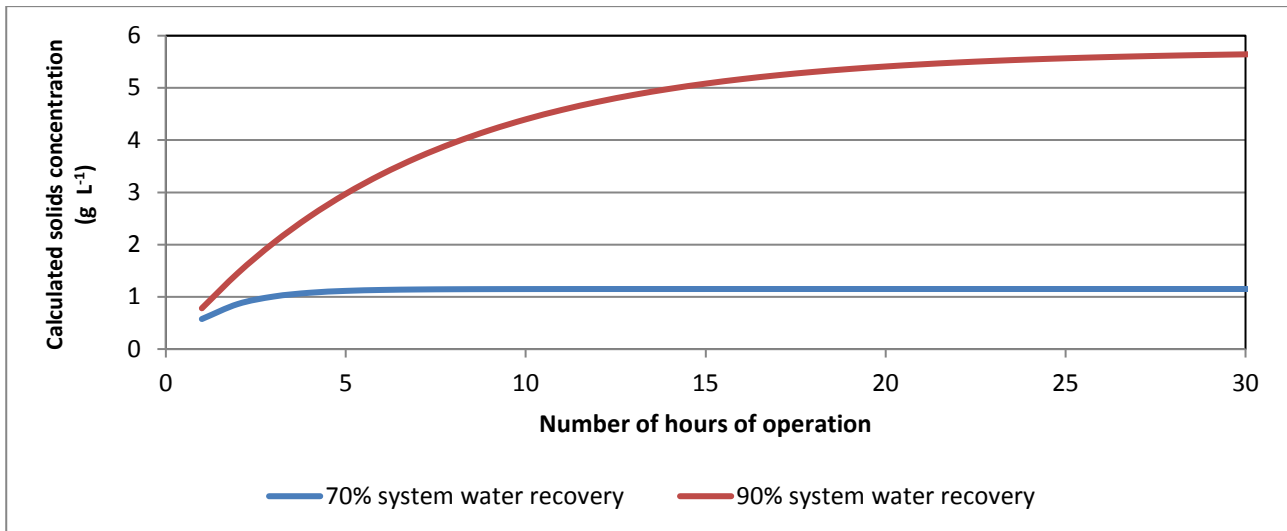
### 3.3.3 Fouling of ceramic filters

Only slight adjustment of the CUF filtrate flow valves was necessary during the trial, indicating that the fouling tendency was low for the ceramic filter at the high recirculation flow ( $70,000 \text{ L h}^{-1}$ ) and relatively low solids loading (up to  $\sim 4 \text{ g L}^{-1}$  after 8 hours at 90% system water recovery) operating conditions used. The fouling tendency would, however, be expected to increase with increasing solids concentration. The optimum solids concentration was found to be approximately  $17 \text{ g L}^{-1}$  in laboratory experiments (see Figure 6(a)).

### 3.3.4 Recycled seed concentration:

The laboratory trials indicated that the recycling of the in-situ generated seed will reduce the required quantity of phosphate ion to below equimolar to the calcium concentration. The rate of build up and the maximum achievable seed concentration, however, depend on how much calcium is entering the system and how much is lost from the system.

*At 70% system water recovery:* With a UF filtrate calcium concentration of  $198 \text{ mg L}^{-1}$ , the quantity of calcium entering the system at  $1026 \text{ L h}^{-1}$  was  $203 \text{ g h}^{-1}$  as calcium ion, which equates to  $690 \text{ g h}^{-1}$  of  $\text{CaHPO}_4$ . This weight of  $\text{CaHPO}_4$  would be expected to be confined to the ASP flocculation tanks ( $500 \text{ L}$ ) and the ceramic filter system ( $100 \text{ L}$ ). In the first hour, the loss of solids expected from the system in the waste stream ( $300 \text{ L h}^{-1}$  for the first 8 hours of operation) would be  $345 \text{ g}$ , leaving  $345 \text{ g}$  of  $\text{CaHPO}_4$  with a concentration of  $0.57 \text{ g L}^{-1}$  in the first hour of operation. Application of this calculation ( $690 \text{ g h}^{-1}$  of  $\text{CaHPO}_4$  entering the system per hour with 50% being lost in waste per hour) to subsequent hours reveals that the maximum calcium phosphate seed concentration achieved was  $1.1 \text{ g L}^{-1}$  after approximately 5 hours (see Figure 9).



**Figure 9:** Calculated seed concentration in ASP-CUF system at the achieved system water recoveries.

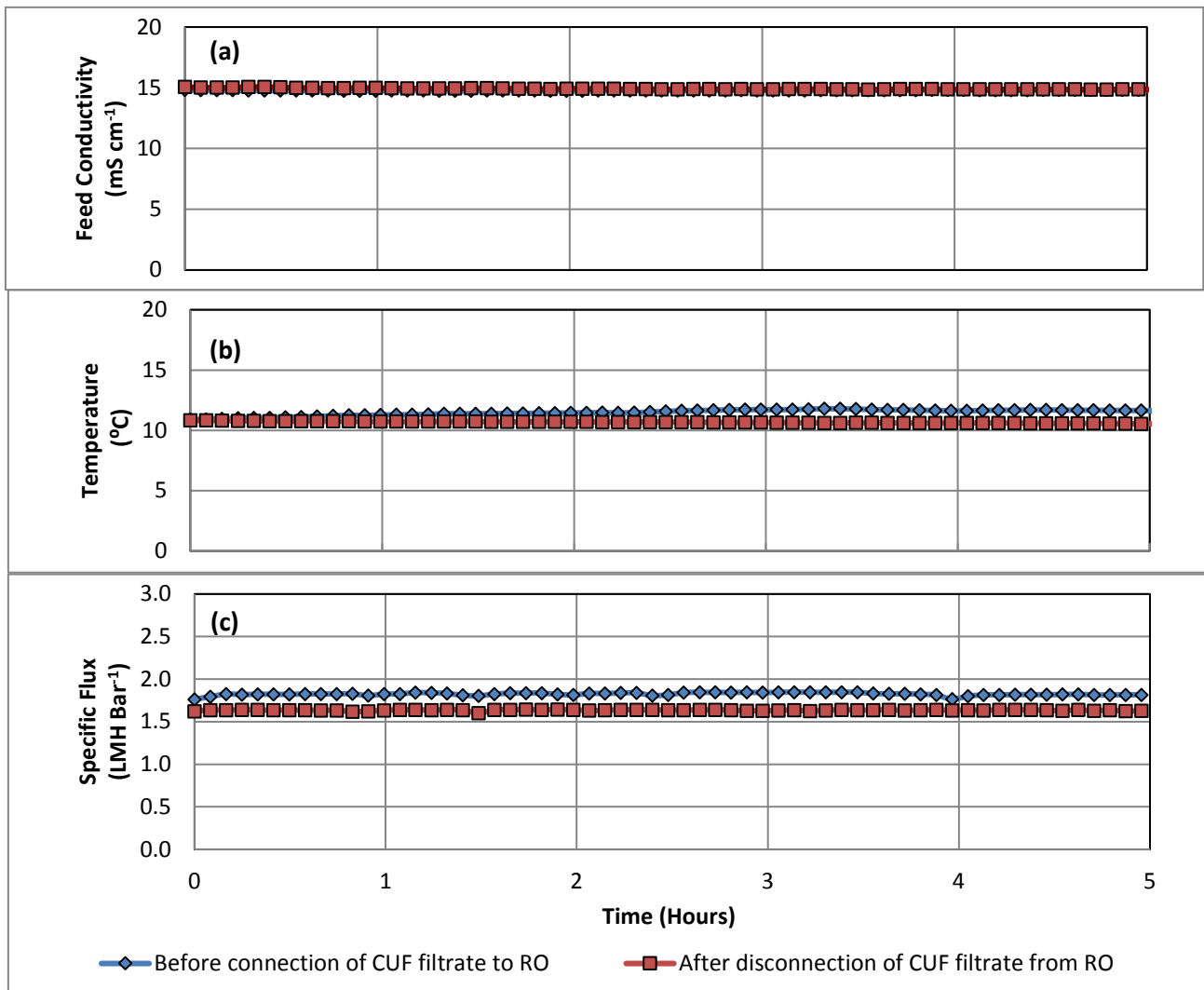
*At 90% system water recovery:* Similarly, with a UF filtrate calcium concentration of  $198 \text{ mg L}^{-1}$ , the quantity of calcium entering the system at  $806 \text{ L h}^{-1}$  was  $160 \text{ g h}^{-1}$  as calcium ion, which equates to  $542 \text{ g h}^{-1}$  of  $\text{CaHPO}_4$ . In the first hour, the loss of solids expected from the system in the waste stream at 90% system water recovery was 74 g, leaving 468 g of  $\text{CaHPO}_4$  with a concentration of  $0.78 \text{ g L}^{-1}$  in the first hour of operation. Application of this calculation ( $542 \text{ g h}^{-1}$  of  $\text{CaHPO}_4$  entering the system per hour with 13.7 % being lost per hour in the waste) to subsequent hours reveals that the maximum calcium phosphate seed concentration achieved was approx.  $5.7 \text{ g L}^{-1}$  after approximately 30 hours (see Figure 9). After the 8 hours of operation in the current study, the expected solids concentration was approximately  $4 \text{ g L}^{-1}$ .

It is important to note that laboratory experiments have shown that solids concentrations of approximately  $17 \text{ g L}^{-1}$  are required to reduce the phosphate requirement to approximately one half of equimolar to the incoming calcium level (see Figure 6). This seed concentration could be achieved by taking more than the required quantity of CUF filtrate and diverting some to waste. The ceramic filtration unit was set up to be able to do this and operation in high solids mode was planned for the latter stages of the run. The premature end of the run due to high CUF filtrate turbidity prevented this investigation, and further optimisation of the phosphate addition rate.

### 3.3.5 RO performance

The specific permeate flux was found to decrease with time soon after integration of the ASP-CUF system stage into the RO process (see Figure 7(d)). This decrease in specific flux can largely be attributed to the increase in osmotic pressure resulting from the increase in salt concentration and temperature (see Figure 7(b) and Figure 7(c)). Comparison of the specific flux for the constant ionic strength and temperature periods during which the CUF filtrate was disconnected from the RO feed (see Figure 10), however, reveals a decrease in specific flux from  $1.8 \text{ LMH Bar}^{-1}$  (before integration of ASP-CUF stage) to  $1.65 \text{ LMH Bar}^{-1}$  (after disconnection of the ASP-CUF system from the RO). This represents an 8% decrease in specific flux over two days. This flux decrease may be attributed to calcium phosphate scale formation on the membranes due to the excess of phosphate leaving the ASP stage. Dow Filmtec recommends that a drop of 10% in the normalised specific flux is an indication of fouling.





**Figure 10:** RO performance before and after integration of ASP stage into RO process, RO feed temperature (a), RO feed conductivity (b), and specific permeate flux (c).

### 3.3.6 Cost considerations

The premature end of the pilot plant trail, due to unacceptably high CUF filtrate turbidity, prevented the increase in seed concentration to useful levels ( $17 \text{ g L}^{-1}$  according to laboratory results). This, in turn, prevented minimization of the phosphate addition rate, and maximisation of raw water flows to the system. It is, therefore, difficult to make realistic estimates of the cost of the integration of ASP into conventional RO process in order to achieve higher system water recoveries. From the limited, unoptimized, pilot plant data available, the process is very expensive. The chemical costs for the desalination process (i.e. DAF and UF pre-treatment not included) were \$21 per kL of product water, while the energy costs were \$4 per kL of product water (\$1.15 due to RO, \$2.85 due to CUF). This energy cost is approximately 13 times that of conventional RO run at 75% water recovery. If the chemical requirement could be reduced to that indicated in laboratory experiments (i.e. phosphate ion requirements that are one half of equimolar to the calcium content) the chemical cost could be reduced to \$2.6 per kL of product water. The specific energy for the CUF system is also expected to be less at a larger scale. At the ML scale the CUF filtrate specific energy ( $4.5$  to  $5 \text{ kWh kL}^{-1}$ ) is expected to be approximately one third of the energy expenditure during the pilot plant trial ( $13.5 \text{ kWh kL}^{-1}$ ), potentially reducing the total desalination energy cost to \$0.95 per kL of product water. It may, therefore, be possible to reduce the total running cost to \$2.6 (chemical cost) + \$1.15 (RO) + \$0.95 (CUF) = \$4.7 per kL of product water.

**Table 4:** Estimated evaporation pond capital expenditure costs for a desalination plant producing 1 ML d<sup>-1</sup> product water.

	<b>Conventional RO (75% water recovery)</b>	<b>High Recovery RO (90% water recovery)</b>
<b>Feed flow required to produce 1 ML d<sup>-1</sup> of product water (ML)</b>	1.333	1.111
<b>Volume of waste brine produced (ML d<sup>-1</sup>)</b>	0.333	0.111
<b>Area of evaporation pond required (ha)<sup>a</sup></b>	12.15	4.05
<b>Total Cost<sup>b</sup> (\$M)</b>	12.15	4.05

<sup>a</sup> Assuming an average evaporation rate of 10 ML ha<sup>-1</sup> yr<sup>-1</sup>

<sup>b</sup> Assuming a cost of \$1M ha<sup>-1</sup>

These costs may be partly mitigated by the value of generated calcium phosphate. Calcium phosphate is commonly used as fertiliser and the cost of crude grade calcium phosphate is approximately \$0.8 kg<sup>-1</sup>. To produce 1 kL of product water at 90% water recovery, 1.111 kL of wastewater must be treated. The quantity of calcium precipitated from 1,111 L of 200 mg L<sup>-1</sup> Ca wastewater = 200 x 1111 mg = 222 g of Ca. This equates to 755 g of CaHPO<sub>4</sub>. The desalination process could generate approximately \$ 0.6 worth of calcium phosphate from every kL of product water produced.

*Evaporation pond requirements:* At equal product water production rate, the pondage requirement of the 90% RO operation is expected to be one third that of conventional RO operated at 75% as shown in Table 4.

Due to the high running costs of the process, the use of ASP to achieve high water recoveries in the desalination of municipal wastewater would be most suited to locations where there is a desperate need for fresh water and where land costs and regulatory requirements make the construction of large evaporation ponds prohibitively expensive.

#### 4. CONCLUSIONS

Laboratory trials in the early stages of this project showed that removal of calcium from municipal wastewater RO concentrate via ASP using calcium carbonate is very inefficient. This was attributed to the presence of magnesium, phosphate and antiscalant in the RO concentrate. The laboratory studies, however, showed that in-situ generation of calcium phosphate seed by addition of phosphate ion at pH 10, followed by reuse of this seed at 17 g L<sup>-1</sup>, is a more efficient and effective means of removal of the calcium from the test municipal wastewater. The quantity of phosphate required in these laboratory experiments was one half the quantity (in moles) of calcium in the wastewater.

The pilot plant used in these studies consisted of dissolved air flotation, ultrafiltration, reverse osmosis, accelerated seeded precipitation and ceramic ultrafiltration. The plant was operated at 70% and 90% system water recovery for long enough for the major impediment to its operation and to the prolonged achievement of high water recovery to manifest itself – turbidity forming after the ceramic ultrafiltration (CUF) system that prevented further RO processing to extract more clean water. The generation of a turbid CUF filtrate was tentatively attributed to the heating in the ceramic filter recirculation loop due to pump energy input, giving rise to the generation of a supersaturated calcium solution due to the decreased solubility of sparingly soluble calcium salts at the higher-temperature, and the precipitation of calcium from this supersaturated solution after it passed through the ceramic filter.

The increases in CUF turbidity during this trial necessitated the disconnection of the CUF filtrate from the RO, thereby reducing run time and preventing investigations which require longer time periods, such as seed dose and chemical optimisation, and RO scale formation assessments. Comparison of the specific flux during the operation of the RO before integration of the ASP-CUF system stage into the RO process with the specific flux after the ASP-CUF system had been

disconnected from the RO process, however, revealed an 8% decrease in specific flux, suggesting scaling may have taken place. This scaling may be due to formation of calcium phosphate on the membranes due to the excess of phosphate used during the trial. This may be mitigated by optimisation of phosphate dosing. This was not performed due to short run time resulting from the generation of turbid CUF filtrate.

Only slight adjustment of the CUF filtrate flow valves was necessary during the trial, indicating that the fouling tendency was low for the ceramic filter at the high recirculation flow ( $70,000 \text{ L h}^{-1}$ ) and relatively low solids loading (up to  $\sim 4 \text{ g L}^{-1}$  after 8 hours at 90% system water recovery) operating conditions used. The fouling tendency would, however, be expected to increase with increasing solids concentration. The optimum solids concentration was found to be approximately  $17 \text{ g L}^{-1}$  in laboratory experiments.

Preliminary cost estimates for the ASP process indicate that the ASP-RO process was considerably more expensive than conventional RO, but that there are considerable cost savings associated with lower evaporative pond required to manage the waste brine. The chemical running costs associated with the ASP stage suggested from the laboratory experiments were \$2.6 per kL of product water. The un-optimised pilot plant ASP stage chemical usage costs were \$21 per kL of product water. These chemical running costs may be partly mitigated by the use of the generated calcium phosphate as fertiliser. The value of the generated calcium phosphate was calculated to be \$0.6  $\text{kL}^{-1}$  of product water. The energy running costs of the plant were estimated to be \$3.8  $\text{kL}^{-1}$  of product water, which is 13 times the energy cost of conventional RO run at 75% water recovery. At an equal product water output, the cost of evaporation pond construction at 90% water recovery were estimated to be one third those of conventional RO run at 75% water recovery.

Addition of another process stage to the conventional RO desalination process to achieve higher water recoveries is expected to incur an added cost associated with the additional chemicals and energy inputs. The benefits of this added cost, however, are that the quantity of waste brine produced is less and the quantity of product water is more at higher water recoveries. At equal clean water production rates, the evaporation pond requirement for a plant operated at 90% water recovery is one third that of one operated at 75% water recovery. Economic justification for aiming to achieve higher water recoveries in the desalination of municipal wastewater can only be made if the benefit of the lower evaporation pond requirement outweighs the higher chemical and energy running costs. This is most likely to be the case in locations where there is a desperate need for fresh water and where land costs and regulatory requirements make the construction of large evaporation ponds prohibitively expensive.

## **ACKNOWLEDGEMENTS**

The authors wish to thank GWMWater and the Smart Water Fund for funding this project, and Dow Filmtec for donation of the SW membrane elements used in this research

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