

## Concentrating primary reverse osmosis concentrate by direct contact membrane distillation

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### ABSTRACT

In the present work, a thermally driven membrane process—direct contact membrane distillation was investigated for concentrating the primary reverse osmosis concentrate to minimize the water loss. The primary reverse osmosis concentrate used in the work was obtained from the RO process of the direct drinking water preparation system designed for the 29th Olympic Games with 50% recovery. The feed water was Beijing tap water. Membrane fouling during the DCMD process was discussed, and acidification and accelerated precipitation softening was used as the pretreatment method to control the calcium scaling. Experimental results showed that acidification can alleviate and even eliminate  $\text{CaCO}_3$  scaling, but  $\text{CaSO}_4$  crystallization still occurred and led to a sharp decline of module efficiency. Accelerated precipitation softening enabled a high removal efficiency of  $\text{Ca}^{2+}$ , so both the  $\text{CaCO}_3$  and  $\text{CaSO}_4$  scaling was efficiently controlled. After proper pretreatment to control calcium scaling, the primary reverse osmosis concentrate could be concentrated 40 times and then the whole recovery was enhanced to 98.8%.

**Key words** | direct contact membrane distillation, high-recovery desalination, reverse osmosis concentrate

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### INTRODUCTION

Reverse osmosis has been widely used for desalination of brackish water in the industrial and civil area (Agashichev & El-Dahshan 2003; Afonso *et al.* 2004; Feng *et al.* 2006; Kosutic *et al.* 2007; Hrayshat 2008; Radjenovic *et al.* 2008). However, membrane scaling forces operation at a low recovery level. Currently, the recovery of primary reverse osmosis (PRO) is only 50–75%. Even with the use of water soluble polymeric antiscalants, mineral salt scaling remains an impediment to achieving high product water recovery (Vrouwenvelder *et al.* 2000). So each year, a large amount of PRO concentrate discharges and leads to a significant loss of water resource and a disposal challenge.

Researchers have been working to enhance the recovery of reverse osmosis, however, membrane fouling

becomes severe and the operating pressure become much higher. Thus, it is not possible to enhance the recovery by reverse osmosis itself. Integrated reverse osmosis and other membrane processes or chemical processes enabled a high recovery. It was reported that a combined process of high-rejection nanofiltration and reverse osmosis was used for seawater desalination, and the recovery was enhanced to 60%, while the recovery of the conventional reverse osmosis process for seawater desalination was only 30–40%. In addition, multi-stage reverse osmosis was also established to achieve high recovery (Gabelich *et al.* 2007; Rahardianto *et al.* 2007).

In the present work, a hydrophobic membrane process—direct contact membrane distillation (DCMD) was used to concentrate the primary reverse osmosis

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concentrate to enhance the recovery. DCMD is the simplest configuration of membrane distillation (MD). MD is a thermally driven process that only vapor can transport through non-wetted hydrophobic porous to the permeate side. Compared with pressure-driven membrane processes, MD is less dependent on the initial salinity of the feed as well as a higher salt rejection. In addition, it is operated at ordinary pressure with less demanding on the membrane's mechanical strength (Lawson & Lloyd 1997).

However, membrane fouling caused by CaCO<sub>3</sub> and CaSO<sub>4</sub> scaling still exists in the DCMD desalination of PRO concentrate. Thus, it is important to have a deep understanding of the membrane fouling mechanism in the process, and on the basis of this, a fouling control strategy should be put forward.

Acidification is common to control the formation of CaCO<sub>3</sub> and has been described in many studies. The control mechanism is based on the following reaction:



Accelerated precipitation softening is a seeded precipitation process. The added seeds can provide a preferential surface area for heterogeneous nucleation and growth of mineral salts, so the precipitation kinetics and the efficiency of solid–liquid separation can be significantly improved. Various seeded precipitation softening for RO process pretreatments were reported in the literature (Gilron *et al.* 2000, 2005; Oren *et al.* 2001; Rahardianto *et al.* 2007). Rahardianto *et al.* (2007) integrated RO and APS for high water recovery desalting of mildly brackish water, and the results indicated that the recovery up to 98% was feasible with the PRO–APS–SRO sequence. In a compact accelerated precipitation softening (CAPS) proposed by Gilron *et al.* (2000, 2005) for RO pretreatment of surface water, CAPS allowed high RO recoveries by reducing the scaling potential and also reduced the contaminant load of colloids and dissolved organic microorganisms.

Accordingly, the objective of this work was to: (1) apply DCMD in concentrating the PRO concentrate, (2) investigate the fouling phenomenon during the DCMD process, and (3) compare the two pretreatment methods: acidification and APS for fouling control in the DCMD process.

## EXPERIMENTAL

### PRO concentrate

The PRO concentrate in the experiments was obtained from the RO unit of the direct drinking water preparation system designed for the 29th Olympic Games. The RO system was operated at 50% recovery with Beijing tap water pretreated with ozone oxidation, catalyze oxidation and active carbon filtration. The quality of PRO concentrate is shown in Table 1.

### Membrane and membrane modules

The PVDF hollow fiber membrane used in the experiments was self-made. The characteristics of the membrane are seen in Table 2.

The membrane module was made by a polyester tube and two UPVC T-tubes. The outside/inside diameters of the module were 20 mm/15 mm respectively and the effective length of the module was 100 mm. The module was equipped with 50 hydrophobic hollow fiber PVDF membranes. The total efficient area of the module was calculated for the internal diameter of hollow fiber membrane and amounted to 94.20 cm<sup>2</sup>.

### Reagents

Calcium carbonate powder (>99.0%, A.C.S. Reagent) was used as a calcite seed in the APS treatment. All the other reagents were analytical grade.

**Table 1** | Quality of the PRO concentrate

Parameters	Value	Parameters	Value
Turbidity (NTU)	0.25	Mg <sup>2+</sup> (mg/L)	43.1
Conductivity (μS/cm)	960	Cl <sup>-</sup> (mg/L)	52.1
pH	7.7	SO <sub>4</sub> <sup>2-</sup> (mg/L)	63.5
Na <sup>+</sup> (mg/L)	30.0	HCO <sub>3</sub> <sup>-</sup> (mmol/L)	9.25
K <sup>+</sup> (mg/L)	10.9	CO <sub>3</sub> <sup>2-</sup> (mmol/L)	0.35
Fe <sup>2+</sup> (mg/L)	0.037	SiO <sub>3</sub> <sup>2-</sup> (mg/L)	11.8
Ca <sup>2+</sup> (mg/L)	118.2	TOC (mg/L)	1.0
Total hardness(mg/L), as CaCO <sub>3</sub>		470.7	

**Table 2** | Characteristics of the PVDF membrane

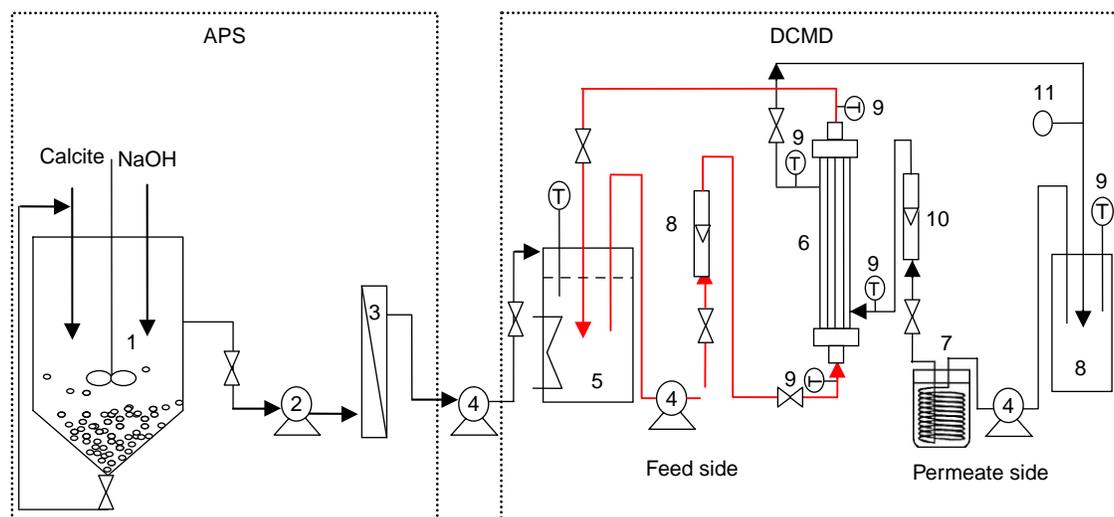
Outside/inside diameters	Porosity	Average pore radius	Thickness	LEP <sub>w</sub>
1 mm/0.6 mm	80%	0.15 μm	0.2 mm	250 kPa

### Experimental apparatus

The experimental apparatus is illustrated in Figure 1. It is consisted of two parts: the APS unit and the DCMD unit. There is a valve to control the connection of the two units.

The DCMD unit consisted of two thermostatic cycles, the feed one and the permeate one. The feed and the permeate flowed co-currently in the experiments, and the feed flowed inside the hollow fiber, whereas the permeate flowed through the intertubular space. Two magnetic pumps were used to provide the flow of the feed preheated in the thermostatic bath and the permeate cooled through the cooling coil. The feed flow rate was 0.60 m/s, whereas the permeate flow rate was 0.10 m/s during the process. There were 4 thermometers equipped on both the inlet and the outlet of the feed and the permeate side.

This APS apparatus consisted of a 10-L crystallization reactor with a conical bottom, and a poleless speed-adjusting agitator. And there was a 2 μm nylon cartridge filter (CLD-P, ChengDeLai, China) for the solid-liquid separation.



**Figure 1** | APS-DCMD process set up: (1) 10 L crystallization reactor; (2) magnetic pump; (3) cartridge filter; (4) magnetic pump; (5) feed reservoir; (6) membrane module; (7) cooling coil; (8) permeate reservoir; (9) thermometer; (10) flow meter; (11) conductivity monitor.

## EXPERIMENTAL METHOD

### DCMD process of PRO concentrate

In the experiments, the inlet temperature of the feed and the permeate were kept at 50°C and 20°C, respectively. The permeate flux was measured by the overflow volume of the permeate reservoir, and the permeate conductivity was measured by an online conductivity monitor during the experimental period. After the experiments, membrane fouling was examined by SEM-EDS analysis.

### Acidification pretreatment

The pH of the PRO concentrate was adjusted to 6.0 and 5.0 by adding different volumes of hydrochloride, respectively. After acidification, DCMD experiments were carried out. Permeate flux and conductivity were monitored during the process and after the experiments, membrane fouling was examined by SEM-EDS analysis.

### APS pretreatment

Based on the results of the small-scale calcium removal tests described in the literature (Qu *et al.* 2009), initial solution pH was adjusted to 10.10, the calcite dosage was 5 g/L, and the agitating rate was 200 r/min. The precipitation reaction time was 1.5 h, after steady-state was reached, the suspended solids were allowed to settle for 1 h, and then

pumped to the cartridge filter for solid–liquid separation. The following DCMD experiments were in accordance with the former DCMD process.

### Analysis methods

The permeate conductivity was measured by an online conductivity monitor. The concentration of  $\text{Ca}^{2+}$  was determined with EDTA titration, and the concentration of  $\text{SO}_4^{2-}$  was measured by the spectrophotometer (DR/4000U, HACH, USA). The analysis for soluble silica was carried out using the molybdosilicate method and the spectrophotometer.

The morphology and component of membrane fouling was investigated using scanning electron microscopy (S-3000N, HITACHI, Japan) coupled with energy dispersion spectrometry (Genesis, EDAX, USA). The membrane samples were made by liquid nitrogen and then dried in the oven at  $50^\circ\text{C}$ . Then the samples were sputter coated with gold for SEM observation. The accelerating voltage was 5 kV.

## RESULTS AND DISCUSSION

### DCMD process of PRO concentrate without any treatment

Figure 2 shows the variation of permeate flux and conductivity during the DCMD process of PRO concentrate without any treatment. An initial permeate flux was observed, just as reported in other works (Barbe *et al.* 2000;

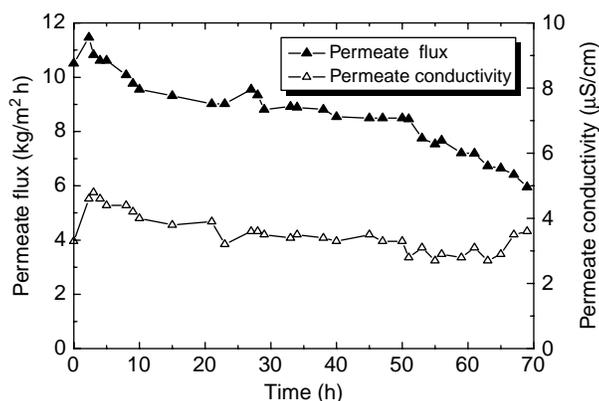


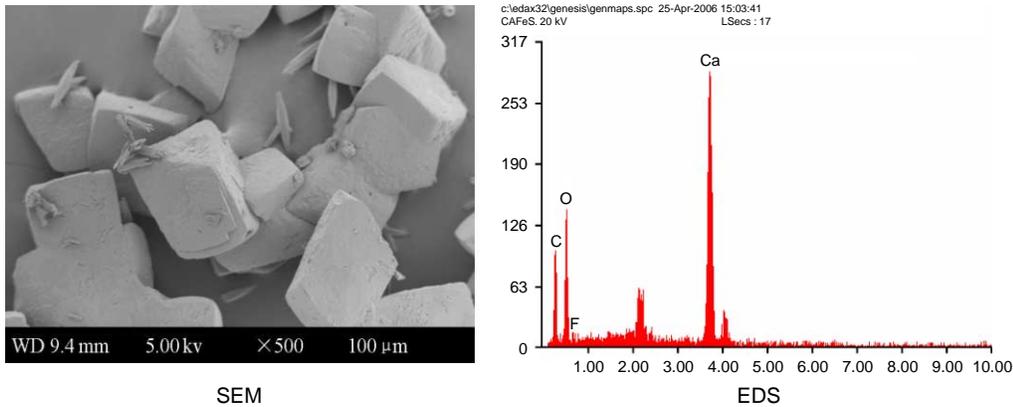
Figure 2 | Variation of the efficiency during the DCMD process.

Gryta 2005). After the initial increase, a continual decline of the permeate flux was found. The feed flow rate decreased from an initial 0.60 m/s to 0.45 m/s when the permeate flux decreased from 10.61 to 7.53 kg/m<sup>2</sup> h after running for 50 h. A large amount of deposit was found at the inlet of the membrane module. So it can be assumed that the feed flow decrease caused by the deposit clogging was the main reason for the decrease of the module efficiency. It is because the feed was pumped with a magnetic pump; therefore, an increase of the feed flow resistance caused a decline of flow rate. The flow rate decrease may cause an unfavorable increase of the temperature polarization and comprise a possible reason for the observed reduction of the module efficiency (Gryta 2005). The permeate conductivity kept declining and stabilized at about 3.5 µS/cm finally, which indicated that the PVDF membrane exhibited a stable hydrophobicity.

The deposit collected from the module inlet was examined by SEM–EDS analysis after the experiments. The results are shown in Figure 3. It can be noted that the deposit was powder-like and had a hexagonal structure. And the EDS analysis showed the deposit consisted of Ca, C and O. Thus, it can be concluded that the deposit was  $\text{CaCO}_3$ . Till the shutdown of the DCMD performance, the formation of  $\text{CaSO}_4$  precipitate was not found.

### Acidification pretreatment

The variation of permeate flux and conductivity during the DCMD process after acidification treatment is shown in Figure 4. Stage I in Figure 4 shows DCMD performance of the PRO concentrate without any treatment, which is in accordance with Figure 2. The results presented in Figure 4 (stage II) were obtained after the solution pH was adjusted to 6.0. There was a sharp increase of the permeate conductivity at the beginning of the process. It resulted from  $\text{CO}_2$ , which was not degassed completely after acidification, crossing the membrane to the permeate side. After the initial increase, the permeate conductivity was stabilized at about 3.0 µS/cm. The problem of  $\text{CaCO}_3$  was alleviated by acidification, so the permeate flux declined only 20% after 200 h running after acidification. Then a sharp flux decline was observed. Up to the permeate flux decline, the PRO retentate was concentrated about



**Figure 3** | SEM-EDS analysis of the deposit collected from at the inlet of the module.

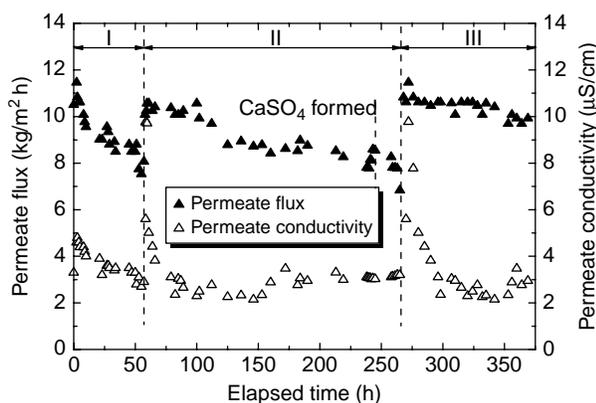
40 times as the initial concentration and the whole water recovery increased up to 98.8%.

Our previous research (Qu *et al.* 2007) proved that, at high levels of water recovery,  $\text{CaSO}_4$  crystallization may take place when  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  on the feed side exceed the solubility limit of  $\text{CaSO}_4$ . In this experiment,  $\text{CaSO}_4$  formed after 200 h running of the DCMD performance. The changes of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  during the process (Figure 5) and the sharp permeate decline could give a description of it.

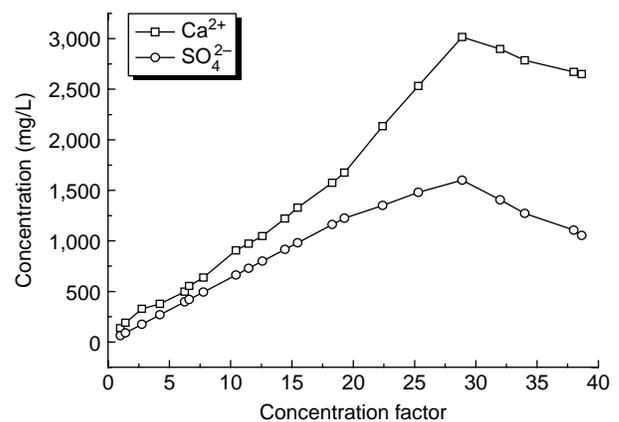
Compared to  $\text{CaCO}_3$  precipitate,  $\text{CaSO}_4$  may cause a sharp decline of the permeate flux. That is because of the different morphology between them.  $\text{CaCO}_3$  had a hexagonal structure, and was more tenacious and compact; while  $\text{CaSO}_4$  had a needle shape and was loosely attached (Sheikholeslami 2003). So in the experiment,  $\text{CaCO}_3$  was found to attach to the feed container and the tubes,

the probability of clogging the membrane module was decreased. While  $\text{CaSO}_4$  was found moving freely in the solution, once it formed, it would lead to a rapid clogging of the module, which would cause a sharp flux decline.

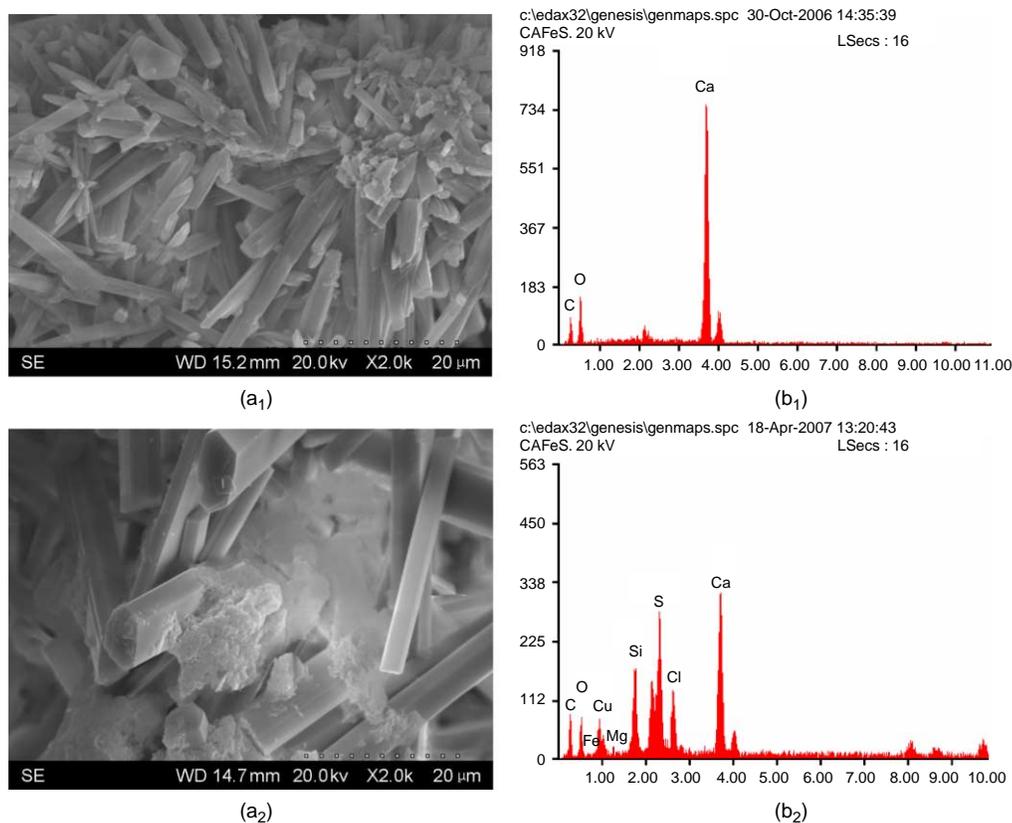
The SEM-EDS analysis of the deposit collected at different experimental times is shown in Figure 6. The thin column-like precipitate shown in Figure 6(a<sub>1</sub>) was the deposit collected before the sharp permeate flux decline. It looked like the needle morphology of the  $\text{CaSO}_4$  precipitate, but the EDS (Figure 6(b<sub>2</sub>)) showed that it mainly consisted of Ca, C and O. It was stated by Sheikholeslami (2003) that the morphology of  $\text{CaCO}_3$  may have a change when there are a high concentrations of  $\text{SO}_4^{2-}$ . Thus, it can be concluded that the deposit was  $\text{CaCO}_3$  precipitate. The deposit found after the sharp decline is shown in Figure 6(a<sub>2</sub>). It can be seen from the image that the deposit was a mixture of various precipitates.



**Figure 4** | Variation of the efficiency during the DCMD process.



**Figure 5** | Changes of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  during DCMD process of PRO concentrate at pH 6.0.



**Figure 6** | SEM-EDS analysis of deposits collected at different times (a<sub>1</sub> SEM of the deposit found before the sharp flux decline; a<sub>2</sub> SEM of the deposit found after the experiment; b<sub>1</sub> EDS of the deposit found before the sharp flux decline; b<sub>2</sub> EDS of the deposit found after the experiment).

The analysis of solution pH showed that, although the solution pH was adjusted to 6.0 at the beginning of the experiment, the solution pH stabilized to about 8.0 finally. At this pH, the formation of  $\text{CaCO}_3$  and silicate was available. The EDS analysis (Figure 6(b<sub>2</sub>)) showed the deposit mainly consisted of Ca, Si, S, Cl, C and O. So it can be concluded that the deposit was a mixture of  $\text{CaSO}_4$ ,  $\text{CaCO}_3$  and silicate.

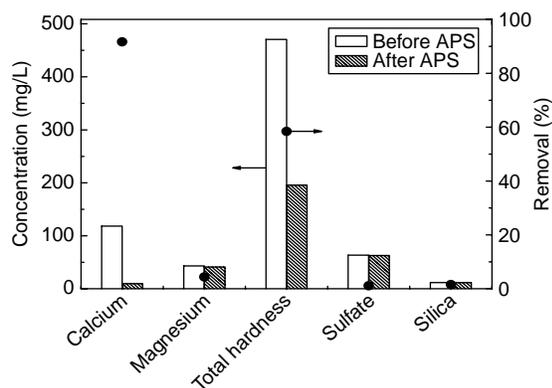
The pH of the feed PRO retentate was adjusted to 4.0 in stage III. Until the end of the process, the problem of scaling was eliminated just as reported in other works (Karakulski & Gryta 2005). All the experiments mentioned above were at a laboratory scale, further research should be carried out.

### APS pretreatment

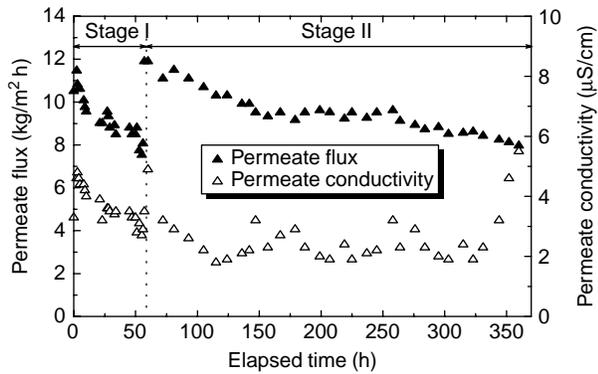
Acidification pretreatment can alleviate and even eliminate  $\text{CaCO}_3$  scaling, however, at high concentration factors,

the formation of  $\text{CaSO}_4$  can still occur in the bulk solution and lead to a sharp permeate decline. Thus, APS treatment was utilized in the experiments for the calcium precipitate fouling control.

Figure 7 shows the elemental analysis of the PRO concentrate before APS and after APS. The results



**Figure 7** | Elemental analysis of the PRO concentrate before and after APS treatment.



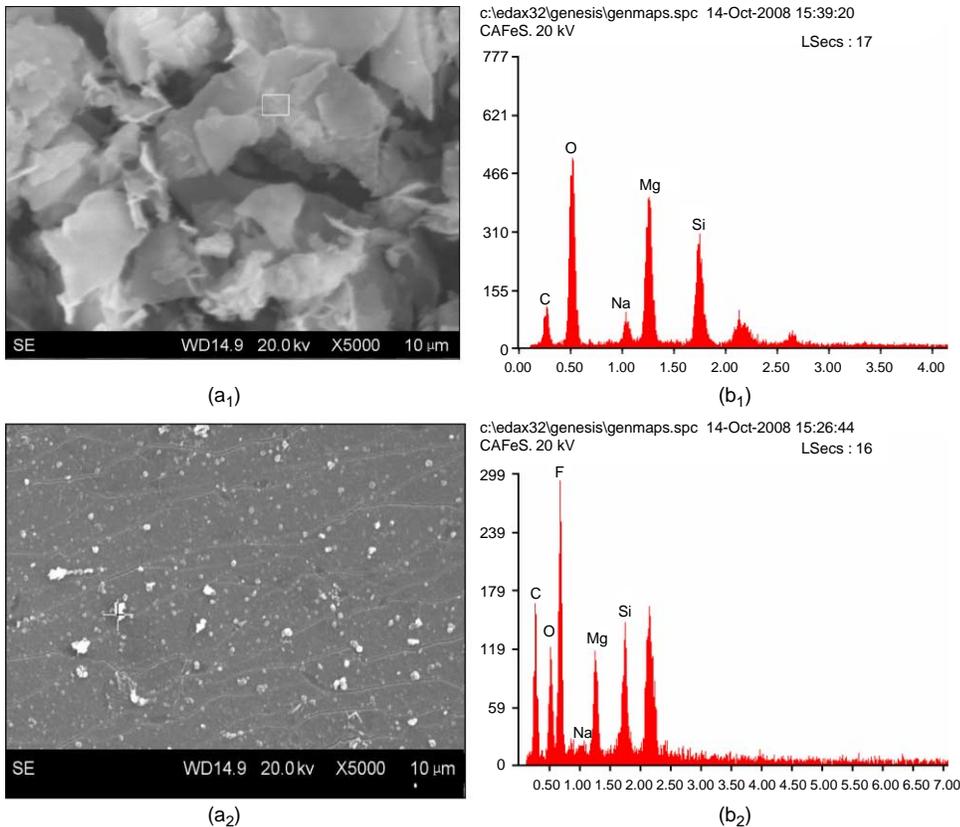
**Figure 8** | Variation of permeate flux and conductivity as a function of elapsed time.

revealed that after APS treatment, calcium decreased from 118.20 to 9.72 mg/L, with the removal efficiency about 92%. In addition, the analysis indicated 4.4% removal of magnesium, 1.1% removal of sulfate and 1.6% removal of silica. There was also a measurable 58.4% removal

of total hardness, which was mainly caused by the calcium depletion.

DCMD desalination performance of the PRO concentrate after APS treatment is illustrated in Figure 8. Stage I in Figure 8 is the DCMD performance of the PRO concentrate without any treatment, which is in accordance with Figure 2. Stage II in Figure 8 presents DCMD performance of the PRO concentrate after APS treatment. The elemental analysis (Figure 7) showed that, after the APS treatment, the calcium concentration had such a significant decrease from 118.8 to 9.5 mg/L that the probability of  $\text{CaCO}_3$  and  $\text{CaSO}_4$  scaling was significantly decreased. Thus permeate flux declined only 20% after 300 h running, then the PRO concentrate was concentrated 40 times and the whole recovery was enhanced to 98.8%.

A little deposit was found both at the module inlet (Figure 9(a<sub>1</sub>)) and at the membrane surface of the module (Figure 9(a<sub>2</sub>)). Since the APS enabled 92% removal of  $\text{Ca}^{2+}$ ,



**Figure 9** | SEM-EDS analysis of deposits collected at the module inlet and the membrane surface after APS (a<sub>1</sub> SEM of the deposit found at the module inlet; a<sub>2</sub> SEM of the deposit found at the membrane inner surface; b<sub>1</sub> EDS of the deposit found at the module inlet; b<sub>2</sub> EDS of the deposit found at the membrane inner surface).

the element and morphology of the deposit had a significant change. The EDS analysis showed that the deposits both consisted of Mg, Si, C and O. So it can be concluded that the deposit was a mixture of  $MgCO_3$  and silicate.

## CONCLUSION

In the present work, direct contact membrane distillation was applied to concentrate the primary reverse osmosis concentrate. Membrane fouling was discussed and two kinds of pretreatment, acidification and accelerated precipitation softening, were used for the calcium scaling control. The main conclusions are as follows:

- (1) During the DCMD desalination process of PRO concentrate, at low concentration factor, the formation of  $CaCO_3$  was the main reason for the permeate flux decrease.
- (2) Acidification pretreatment can alleviate and even eliminate the influence of  $CaCO_3$ , however, at high concentration factors, the formation of  $CaSO_4$  can still occur in the bulk solution and lead to a sharp decline of the module efficiency.
- (3) Accelerated precipitation softening pretreatment enabled 92% removal of  $Ca^{2+}$ , so the influence of calcium precipitation was effectively controlled.
- (4) The experimental results showed that after the proper pretreatment, the PRO concentrate (with the recovery of 50%) can be concentrated 40 times by DCMD and the recovery can be significantly enhanced to 98.8%.

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