

Emergent membrane technologies for mine water purification

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Abstract Membrane technologies were studied to purify neutralising pond water for high water recovery and quality. Reverse osmosis produced good flux until it decreased rapidly at a recovery of 60%. Even 80% recovery could be obtained by forward osmosis, except when ammonium carbamate was used as a draw solution and scaling already occurred at the early-stage of filtration. The flux in membrane distillation was good and stable until scaling occurred. If calcium was removed water recovery could be increased to 93%. The order of metal rejection efficiency of the technologies was membrane distillation > reverse osmosis > forward osmosis.

Keywords Mine water, purification, reverse osmosis, forward osmosis, membrane distillation

Introduction

Given the limited availability of water in many countries, water reuse in industry is increasing. On the other hand, the mining industry can have a strong environmental impact. Wastewater from the mining industry needs to be purified before discharging it to surrounding water faces. The limits for metals and sulphate vary from site to site but there is a trend towards tighter limits in the future. The most used practice at mines is to raise the pH to alkaline to precipitate dissolved metals and sulphate before discharging excess acidic water from mine area. This is usually done by lime or limestone in neutralising ponds (Johnson and Hallberg, 2005). Precipitated particles, such as a metal hydroxides and calcium sulphate (gypsum), settle down and the solution, neutralising pond (NP) water, will overflow. The used pH and other present dissolved substances, such as sodium chloride, have an effect on solubility of precipitates (Li and Duan, 2011), thus also on the metal sulphate contents of overflow.

When additional treatment is required for reuse or discharge, either nanofiltration (NF) or reverse osmosis (RO) membranes may be required. Both, NF and RO, produce good water quality, but due to scaling, productivity of the RO process can be quite low, i.e. a water recovery of 50-60% (Shenvi et al. 2015; Kyllönen et al. 2016). When mine waters contain a lot of sulphate and are treated by lime, there is a great risk of gypsum scaling on the membrane. Scaling occurs on the membrane surface when sparingly soluble salts are concentrated beyond their solubility limit, and leads to significant flux reduction and salt rejection impairment, and limits the water recovery of the desalination process (Zhao et al. 2017). In RO, the use of antiscalants is the widely adopted technique to prevent scaling by calcium carbonate and gypsum. Also pre-treatment of the feed by pH adjustment, ion exchange, NF/UF, and precipitation softening may help in reducing scaling (Shenvi et al. 2015). Precipitation softening through the use of a variety of chemicals, such as sodium carbonate or sodium hydroxide and carbon dioxide together, has been utilised for the removal of calcium and magnesium ions from feed water (Zhao et al. 2016).

Due to the very low hydraulic pressure required, forward osmosis (FO) is considered to have a lower fouling tendency than a pressure driving membrane processes (Zhao et al. 2012). The driving force of the FO process is the osmotic pressure created by a salinity difference between a feed water and draw solution which are separated by a FO membrane. Ammonia-carbon dioxide and ammonium bicarbonate (NH_4HCO_3) are considered as promising draw solutions in the FO desalination process, since the fresh water can be recovered from the diluted draw solution by moderate heating (Li et al. 2015). If waste heat is available, the process can be economical. The scaling in the FO process can be induced by both concentration polarization and reversely diffused ions from draw solutions. For example, if NH_4HCO_3 is used as a draw solution and the feed contains calcium-ions, CaCO_3 scaling can be formed when carbonate from the draw solution and calcium from the feed meet in membrane pores (Li et al. 2015).

In thermally driven desalination technology, MD, the increased water vapour pressure from the higher temperature drives vapour through the pores of the hydrophobic membrane, where it is collected on the cooler permeate side. Because only vapour is allowed to cross through the membrane, MD is more fouling resistant than RO and has a potential 100% rejection of ions and macromolecules (Warsinger et al. 2015). In MD, temperature and concentration have a polarisation effect on scale formation. The scaling can cause wetting and thus result in contamination of the permeate by the feed (Warsinger et al. 2015).

Methods

The feed was sand filtered and microfiltered NP from mine water. Feed water and permeate were characterised by pH, conductivity (λ), suspended solids (SS) and element content measurements (Table 1). The pH and the conductivity were measured using standard hand held meters VWR pH 100 for pH and VWR EC 300 for conductivity. SS was determined using a WHATMAN ME25 (0.45 μm) filter drying the solids at 105°C overnight. Chemical elements were analysed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometry). The procedure was carried out using a standard SFS-EN ISO 11885. Sulphur, sodium and calcium were the dominating elements in NP water (Table 1).

Table 1 pH, conductivity, osmotic pressure, suspended solids and ICP-OES analysis results of the studied NP water. Variations of the analysed results were within 8 %.

| pH | λ mS/cm | π bar | SS mg/L | Ca mg/L | Mg mg/L | Mn mg/L | Na mg/L | K mg/L | S mg/L | Fe mg/L | Al mg/L |
|-----|--------------------|--------------|------------|------------|------------|------------|------------|-----------|-----------|------------|------------|
| 9.7 | 6.9 | 2.0 | <0.3 | 480 | 5 | <0.05 | 1400 | 40 | 1300 | 0.39 | 0.18 |

Reverse osmosis of NP water was carried out using XFRLE (Dow, USA) at 10 and 15 bar pressure. The fluxes calculated based on the permeate flow measurements were all normalised to a temperature of 25°C. Pure water flux for the XFRLE membrane was 68 ± 5 LMH at 10 bar pressure and 25°C temperature. Magnesium sulphate (MgSO_4) rejection for

the membrane was $99.6 \pm 0.4\%$ and sodium chloride (NaCl) rejection $98.0 \pm 0.4\%$. In FO, a Toray FO (Toray, Korea) membrane and either sodium chloride NaCl, MgSO_4 , or ammonium carbamate ($\text{NH}_2\text{COONH}_4$) were used as draw solutions. FO membrane was characterised with pure water using 1 M NaCl as a draw solution. The average flux was $35 \text{ LMH} \pm 8 \text{ LMH}$ when five pieces of membrane were studied. In direct contact membrane distillation, called MD in this study, a PTFE $0.2\mu\text{m}$ membrane (Sterlitech, USA) was used. Pure water was used at the permeate side so the temperature difference was 60°C feed/ 20°C permeate. Pure water flux for MD membrane was 35 LMH .

Osmotic pressures (Table 2) of the draw solutions were analysed using a Vapro 5600XR osmometer from Wescor, Inc. The calibration was done for the osmolality range $100 - 1000 \text{ mmol/kg}$ ($2.4 - 24 \text{ bar}$). The osmotic pressure of NP water was measured 2.0 bar (Table 1).

Table 2. The properties of draw solutions used in FO process.

| | C | pH | Conductivity | Osmotic pressure bar |
|-----------------------------|------------|-----------|---------------------|-----------------------------|
| | g/L | | mS/cm | |
| NaCl (1M) | 57 | 8.0 | 88 | 40 |
| MgSO_4 | 180 | 7.4 | 60 | 43 |
| $\text{NH}_2\text{COONH}_4$ | 98 | 10 | 96 | 41 |

In scaling control studies, calcium was precipitated before membrane filtration by increasing the pH of the NP water up to 12.3 using 5M sodium hydroxide (NaOH) and after that by dispersing carbon dioxide (CO_2) through a ceramic microfilter into the NP water when the pH was 10.2. pH was kept above 10 until the precipitate was filtered using a pore size of $10 \mu\text{m}$. Using this procedure, calcium content for the NP water decreased from 430 mg/L down to 6 mg/L . pH was lowered for filtration and kept below 8.0 during filtration by sulphuric acid in order to prevent calcium carbonate scaling.

Results and discussion

The flux in using XFRLE RO membrane decreased at 10 bar pressure from 45 LMH to 28 LMH when water recovery increased to 50%. The decrease was reasonable taking into account the osmotic pressure increase of the NP water. The gypsum precipitates started to be formed in the concentrate and flux started to decrease more rapidly after water recovery (WR) of 65% (Fig. 1). The flux decrease was seen in a significant increase of permeate conductivity. The flux decrease was clearer when a pressure of 15 bar was used. Then the scaling started to form earlier and the flux decreased dramatically at a WR of 57%. RO filtration could not continue after WR.

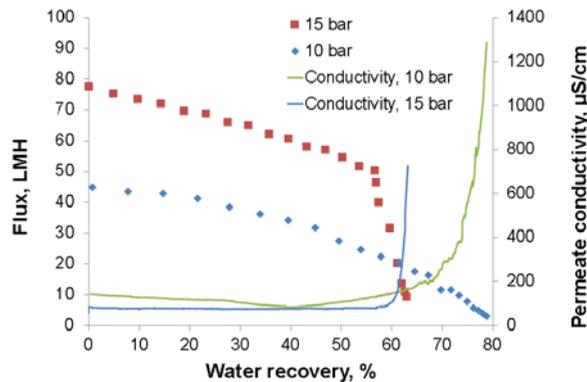


Figure 1. Fluxes and permeate conductivities in RO of NP water at 10 and 15 bar as a function WR.

Good permeate quality and rejections were obtained using a XFRLE membrane for the main components in the NP water, i.e. calcium, sodium, and sulphate. Rejections for them were more than 97% (Table 3).

When the NP water was filtered using ammonium carbonate as a draw solution the flux started to decrease at an early stage of filtration, WR of 10%, due to calcium carbonate scaling. The carbonate ion could transfer from the draw solution side to the feed side. pH adjustment of the feed below 8 did not help in scaling prevention. The flux decrease was not seen when other draw solutions were used or when a pure 1% sodium solution with no calcium was filtered. Similar flux decline was obtained when the NP water was first concentrated up to a WR of 60% using RO and filtered by FO (Fig. 2). The flux started to decrease immediately with ammonium carbamate while other draw solutions, NaCl and $MgSO_4$, produced stable flux and good water recoveries, 79% and 83% respectively. FO could be continued, though gypsum started to precipitate. However, FO membranes were also occasionally broken by scaling. The flux with $MgSO_4$ was very low compared to fluxes in RO and FO using NaCl as a draw solution.

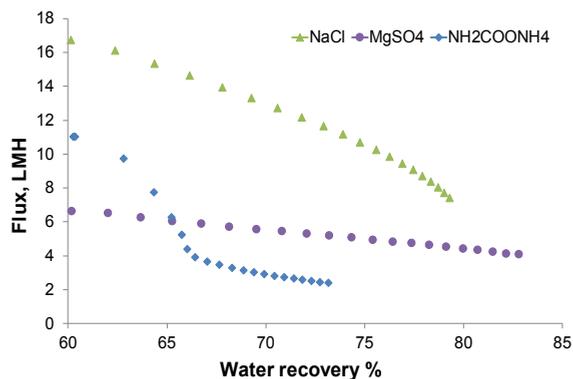


Figure 2. Fluxes of RO concentrate as a function of WR in FO using three different draw solution.

Sulphate rejection for the Toray FO membrane was good, over 97% (Table 3). When the draw solution was MgSO_4 there was back diffusion of salts, $70 \text{ mmol/m}^2\text{h}$, from the draw solution side to the feed side and sulphate rejection was not determined. Back diffusion was clearly seen when using other draw solutions as well. The rejection of calcium was only moderate, 76% or more, for both NP water and RO-concentrate when using the studied draw solutions. In all cases, rejections of monovalents, i.e. sodium and potassium, were very low for the studied membrane.

MD produced very stable flux until at a water recovery of 50% the flux decreased dramatically due to gypsum scaling (Fig. 3). Permeate quality was very good. All the measured components were below detection limit except sodium (Table 3). However, rejection for sodium was also very good, more than 99.9%. The membrane was not wetted during the short lab test and if unbroken it could be used again when rinsing with water.

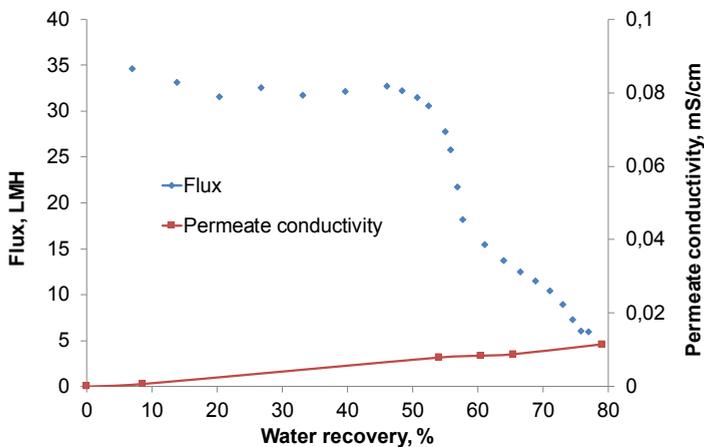


Figure 3. Flux and permeated conductivity in MD of NP water.

Table 3. Measured permeate qualities (mg/L) of NP water in RO and MD. The quality of FO permeates using ammonium carbamate as a draw solution is calculated. <LOD means under limit of detection.

| | Ca | Mg | Na | K | S |
|------------------------------|------|------|------|------|------|
| RO (XFRLE) | 1.1 | 0.2 | 28 | 0.3 | 15 |
| FO (Toray FO) | <LOD | 1.8 | 1400 | 29 | 6.8 |
| MD (PTFE $0.2 \mu\text{m}$) | <LOD | <LOD | 1.1 | <LOD | <LOD |

All the filtration methods studied suffered from scaling caused by either gypsum or calcium carbonate. When used sequentially, the highest WR, 93%, was achieved when calcium was removed and the NP water was concentrated first by RO followed by MD. The concentration

factor in this case was 15 (Fig.4). Fluxes were good and scaling was not seen in either of the concentrates. Osmotic pressure of the feed increased and was finally 18 bar in RO. Thus, the hydraulic pressure at the end of filtration was too low and an even higher pressure than 20 bar should have been used. The flux in MD was stable up to a concentration factor of 15 when the hydrate form of sodium sulphate seemed to precipitate and the flux decreased dramatically. In the filtration of calcium removed NP water permeate qualities were very good in both RO and MD concentrations. Rejection of the main components was over 99%.

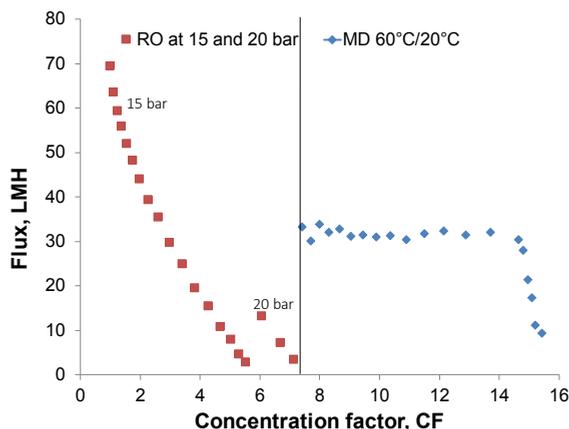


Figure 4. Concentration of calcium removed NP water using RO and MD technologies

Conclusions

Membrane technologies, as well as the emergent technologies of FO and MD, suffer from scaling in mine water purification, which hinders their ability to achieve high WR and concentration factors. The main scalant in NP water is gypsum. FO of NP water also suffers from calcium carbonate scaling when ammonium carbamate is used as a draw solution. High WR and concentration factor can already be obtained by using conventional membrane technology, RO, when the main scalant cause, calcium, is removed. MD produces good fluxes even with a highly concentrated feed. Good quality water can be produced in RO and MD while permeate quality in FO was poor when using the studied membrane.

Acknowledgements

The research was carried out partly in the FO fouling project financed by the Academy of Finland and VTT, and partly in the MinePro project financed by Finnish Funding Agency for Innovation (Tekes), VTT Research Centre of Finland Ltd (VTT) and the companies. The Academy of Finland, Tekes, VTT, Terrafame Group, Aquaminerals, Teollisuuden Vesi, Sansox, Solenis, and Outotec are acknowledged for their support of the MinePro project.

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