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TECHNICAL ARTICLE

Experimental Aspects of Scaling Control in Membrane Filtration of Mine Water

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Abstract This study focused on membrane filtration of neutralized pond water, which may be necessary when good quality water is required for hydrometallurgical processes. Neutralized mine water can still have fairly high metal and sulphate levels, which can hinder discharge and reuse possibilities. Both nanofiltration and reverse osmosis are effective in removing metals and sulphate, but scaling can be a severe problem. Microfiltration as a pre-treatment method, although meant for particle removal, seemed to decrease the amount of scalants, thus delayed scaling on the membrane surface and increasing water recovery for both nanofiltration and reverse osmosis. It is possible that the presence of particles in the feed water promoted crystal growth in the turbulent flow and caused the removal of dissolved constituents. Alternatively, supersaturation could have occurred, allowing microfiltration to remove the scalants as particles. The Liqum sensor indicated that redox values started to increase again just before scaling began due to precipitation in the supersaturated membrane concentrate solution. Thus, the sensor seemed to provide real time, in-situ, early-stage scaling warning.

Keywords Neutralizing pond water · Microfiltration · Nanofiltration · Reverse osmosis · Scaling · Real-time measurements

Introduction

An average mine uses 0.4–1.0 m^3 of water for every ton of ore processed (Gunson et al. 2012). Given the limited availability of water in many countries, water reuse is increasing. However, high quality water is needed, especially for flotation but also for other hydrometallurgical processes, such as leaching and bioleaching (Muzenda 2010). The Tekes Green Mining Program PuMi-project was focused on water treatment concepts that could improve mine water reuse and aid the industry in meeting increasingly stringent environmental regulations. The concepts considered included separation technology, which in this project was membrane filtration, pre-treatment, and reject treatment. Important waters to be managed and/or reused at mines were identified as neutralised pond (NP) water, acid mine drainage (AMD), and circulated flotation process water (Kinnunen et al. 2014; Kyllönen et al. 2014). Since lime/limestone precipitation is the most commonly used water purification technology for AMD (Ackil and Koldas 2006; Johnson and Hallberg 2005), lots of NP water is available for purification and reuse. This research focused on membrane filtration of NP water, which is one of the technologies used when high quality water is required.

Before excess water is discharged from a mine area, the pH is typically made alkaline to precipitate dissolved metals. This is usually done using lime or limestone in neutralizing ponds. Precipitated particles, such as metal hydroxides and calcium sulphate ($CaSO_4$, gypsum), settle, and the treated water is discharged. The selected pH and the presence of other dissolved substances, such as sodium chloride, can affect the precipitation process (Li and Duan 2011), and thus the metal and sulphate content of the effluent. When additional treatment is required, for reuse or discharge, either nanofiltration (NF) or reverse osmosis (RO)

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membranes may be required. When multivalent ions dominate, NF should be sufficient, but if monovalent ions are to be rejected, RO may be required. However, membrane rejection is always dependent on all the ions present in the feed solution.

Scaling is a general problem in NF and RO filtration, but it is especially a problem at metal sulphide mines. 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 a membrane surface when sparingly soluble salts are concentrated beyond their solubility limit (Rahardianto et al. 2006), and can lead to significant flux reduction and salt rejection impairment, i.e. shortening of membrane life. The degree of supersaturation of the scaling can be quantified in terms of the gypsum saturation index (*SIg*), defined as:

$$SIg = \frac{\left(Ca^{2+}\right)\left(SO_4^{2-}\right)}{Ksp} \tag{1}$$

where K_{sp} is the solubility constant for the gypsum.

Briefly, cationic and anionic species collide and produce ion pairs in solution. These pairs then go on to create micro-aggregates or unstable clusters, which become nucleation centres or seed crystals in a process known as homogenous nucleation. Alternatively, heterogeneous nucleation occurs, i.e. the liquid/surface boundary or the presence of particles promotes crystal growth, particularly if there are surface defects and areas of turbulent flow (Heath et al. 2013). As the micro-crystals continue to grow, they fuse to form adherent macro-crystals. Growth then continues via further adsorption of scaling ions to eventually form a uniform coating with subsequent deposition covering the rough-scaled surface (Heath et al. 2013).

Apart from the type and concentration of ions, filtration circumstances, such as temperature and pH, can affect solubility and scaling (Antony et al. 2011). Control of pH has been successful in scaling control but not for the control of gypsum scaling due to the weak pH dependence of gypsum solubility (Rahardianto et al. 2006). Scale inhibitors, i.e. antiscalants, adsorb onto the surface of micro-crystals, thereby delaying further growth and crystal precipitation, and thus scaling (Shenvi et al. 2015; Sweity et al. 2015). There are also other ways to control scaling, such as ion exchange (Antony et al. 2011), ultrafiltration, or nanofiltration before RO (Shenvi et al. 2015), intermediate chemical demineralization (Antony et al. 2011), magnetic treatment methods (Salman et al. 2015), rotation filtration (Lee and Lueptow 2003), and ultrasound (Nasser et al. 2013). Microfiltration (MF) is generally used as a security filter for NF and RO since prevention of membrane erosion and clogging of modules require it. MF has not been reported to influence scaling, but if scalant precipitation can be promoted by turbulent flow (Heath et al. 2013), it should be possible to decrease scaling potential by turbulent MF pre-treatment.

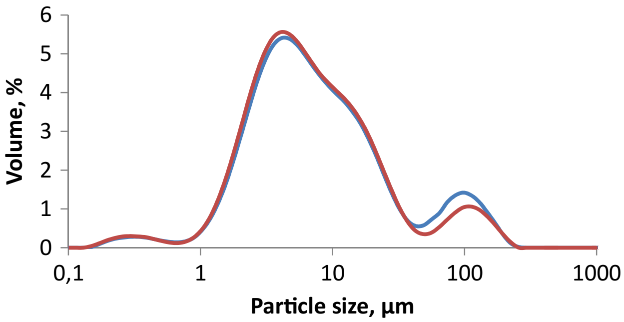

Fig. 1 Two measurements of particle size distribution of NP1

Also, a new sensor technique was tested to identify the occurrence of scaling, which can destroy a membrane. The real-time test sensors consisted of an information collecting unit for use in the aqueous phase. The sensor was connected to a routine for multivariate data processing, which generates an output pattern that represents a synthesis of all the components in the sample when subjected to a sample containing different compounds. The output pattern is based on the selectivity of different individual sensing units and is correlated to a specific taste or quality aspect (Winquist 2008).

Materials and Methods

Feed Water

This study was carried out using NP water from two mines, NP1 and NP2. Feeds, permeates, and concentrates were characterized by pH, conductivity (λ), total dissolved solids (TDS), suspended solids (0.45 µm for NP1 and 1.2 µm for NP2) and element content measurements (Table 1). Chemical element content was analysed by ICP-OES (inductively

Table 1 pH, conductivity and ICP-OES analysis results (mg/L) of the studied NP waters

	pH	λ mS/cm	TDS g/L	SS mg/L	Ca	Mg	Mn	Na	K	S	Ni	Fe	Al
NP1	9.5	4.6	7.1	6.3	410	280	1.6	1500	29	1700	0.1	0.1	0.1
NP2	7.9	10	13	10	460	2300	2.0	240	140	3300	<0.1	<0.1	<0.1

coupled plasma optical emission spectrometry), using a standard SFS-EN ISO 11885. TDS was determined by drying the samples at 105 °C overnight.

In NP1, sulphur, sodium, and calcium were the dominant elements. Sulphate content, 5150 mg/L, was calculated by assuming that the dissolved sulphur was all present as sulphate. In NP2, which was treated at a lower pH, the dominant elements were sulphur, magnesium, and calcium.

The average particle size, 11 µm, of NP1, was determined using a Malvern ZetaSizer (Fig. 1). Precipitation and particle formation continue during storage, so the average particle size is not stable. However, the result can still be used to provide the size range for pore size selection in MF.

Microfiltration

MF was carried out using a Sofi filter (Sofi Filtration Ltd, Finland, Fig. 2) with metallic filter elements having a pore size of 0.2 and 1 µm, using periodic backwash. The filter unit generates a high cross flow velocity using a patented method (Rantala 2012). MF was carried out at room temperature (22 °C). The pressure was 1.0 bar in 0.2 µm MF and 0.2 bar in 1 µm MF. Pure water fluxes were 1500 ± 100 and 29,000 ± 4000 LMH/bar, respectively. Filtration data was collected by on-line measurements including pressure, feed flow rate, and mass of permeate.

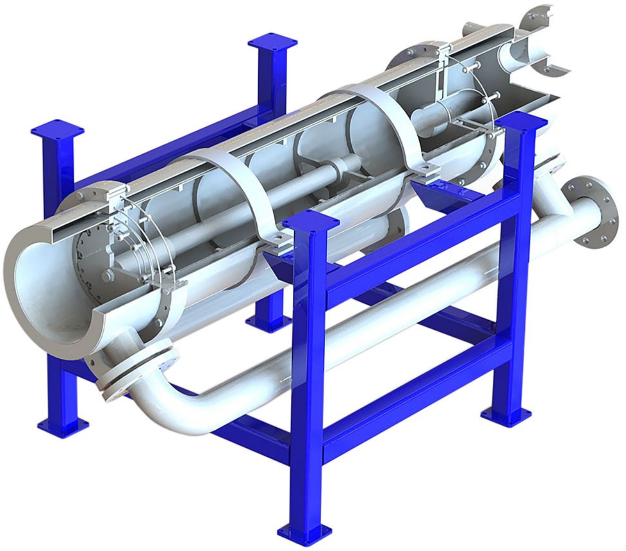

Fig. 2 Schematic picture of the Sofi Filter micro-filtration (MF) equipment

Nanofiltration and Reverse Osmosis

Two different membranes, Filmtec NF270 and NF90, were selected for the NF studies. BW30 (Filmtec) was used for the RO filtration. Filtration tests included membrane characterization, i.e. determination of pure water flux, flux during salt rejection measurement and salt rejection, on-line flux, temperature and pressure measurements, water recovery determinations, and quality analysis of feed, permeate, and concentrate. Reported magnesium sulphate rejection for NF membranes was at least 98 %. The measured values for the membranes were similar to what was reported by the manufacturer (Table 2). The NF90 membrane is typically used in water softening units, having a sodium chloride (NaCl) rejection rate between 90 and 96 %, while the NF270 membrane rejects approximately half of the NaCl (Dow 2015). The NaCl rejection measured by conductivity reduction for the BW30 membrane was slightly less than reported by the manufacturer when analysed by salt rejection.

NF and RO were carried out using a commercial SEPA module with a membrane area of 140 cm^2. The module was assembled to cross flow membrane equipment that provided on-line temperature, pressure, flow, and conductivity measurements. The temperature during the filtration was kept at 25 °C. The operation pressures varied according to membrane used. The effect of an antiscalant (KemGuard 5804, Kemira Oyj, Finland) was tested at 1 ppm concentration in the case of microfiltered NP1. Filtrations were continued until the flux decreased dramatically, which was assumed to happen due to a uniform coating of scaling (Heath et al. 2013).

Table 2 Nanofiltration and reverse osmosis membrane characterisation using pure water and either 2000 ppm magnesium sulphate solution (NF) or 2000 ppm NaCl solution (RO)

Membrane	Pure water testing		Salt testing		
	Pressure (bar)	Permeability (LMH/bar)	Pressure (bar)	Permeability (LMH/bar)	Rejection (%)
NF, NF270	5.0	17.8 ± 1.0	5.0	13.6 ± 0.5	98.0 ± 1.0 ($MgSO_4$)
NF, NF90	10	10.6 ± 0.5	10	7.4 ± 0.2	99.5 ± 0.2 ($MgSO_4$)
RO, BW30	10	6.2 ± 0.2	10	4.2 ± 0.4	96.0 ± 1.0 (NaCl)

Real-Time Scaling Measurement

While other water monitoring and contamination detection systems are designed to look for specific inorganic molecules, the Liqum sensor (Liqum Oy, Finland) takes the opposite approach. The sensor unit allows the operator to set the required definition of purity, and then monitors the water continuously for deviations from that defined purity. The sensor ‘tastes’ any changes as soon as they occur, and reports them instantly in real-time. The tested Liqum sensor has a reference electrode and seven working electrodes. Each electrode is sensitive to many difference ions to varying degrees, and produces a signal based on redox reactions. Depending on the potential applied and type of working electrode, redox active compounds are either oxidized or reduced at the working electrode, giving rise to a current (Krantz-Rülcke 2001). For example, if a red-ox active specie is reduced at the electrode surface, the reaction can be written:

$$\mathrm{Ox} + \mathrm{ne}^{-} \rightarrow \mathrm{Red}^{-} \tag{2}$$

where Ox is the oxidised form and Red is the reduced form of the analyte (Winquist 2008).

The Liqum probe was used in RO (BW30) filtrations of NP2 water. Electrodes signals were collected and compared, first to turbidity and YSI meter measurements, and later to flux data from the different filtrations.

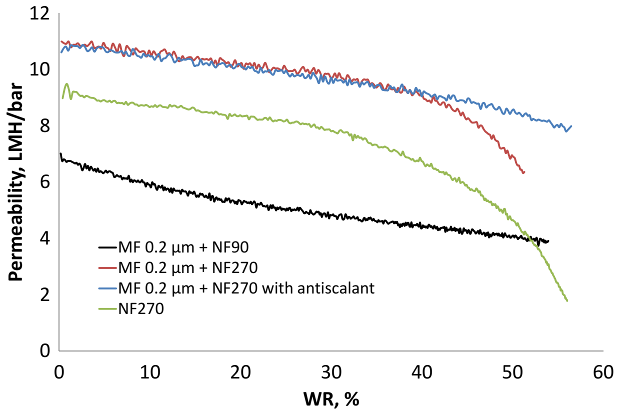

Fig. 3 NF270 and NF90 filtrations of NP1. Permeability as a function of water recovery

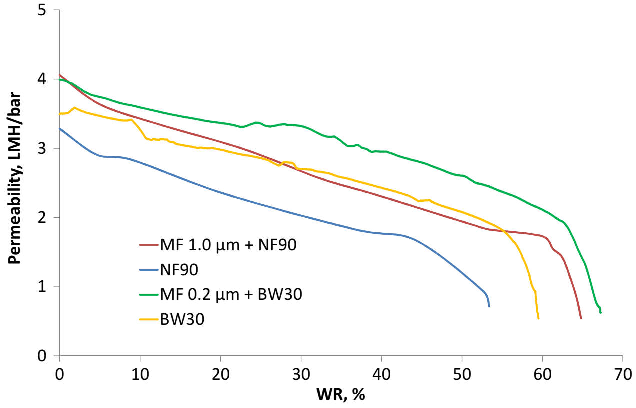

Fig. 4 NF90 and BW30 filtrations of NP2. Permeability as a function of water recovery

Results and Discussion

The flux was 300 ± 30 LMH/bar in 0.2 µm MF of NP1 and water recovery was 96 %. NP2 was only clarification-filtered for NF and RO filtration. Thus, shorter filtrations were carried out for NP2 than for NP1. During the short NP2 filtrations, the flux for the 0.2 µm MF was higher, 800 LMH/bar. For the 1 µm MF, the flux was 25,000 LMH/bar, which was pretty close to pure water (29,000 LMH/bar).

MF should only remove particles. However, ions concentrations in the MF permeate were consistently less than in the feed solution (Table 3). In the presence of particles, scalant precipitation can be promoted in turbulent flow (Heath et al. 2013). The MF technique used in this study seemed to promote gypsum precipitation and subsequent removal by filtration, which decreased gypsum concentrations for NF and RO. Suspended solids in the influents

Table 3 Analysis of the results of feeds and permeates of MF

	Ca	Mg	Mn	S
NP1 feed	410 ± 10	280 ± 10	1.6 ± 0.2	1700 ± 100
NP1 0.2 µm permeate	410	290	0.3	1600
NP2 feed	460 ± 20	2100 ± 200	2.0 ± 0.5	3300 ± 100
NP2 0.2 µm permeate	420	1800	0.9	2900
NP2 1 µm permeate	390	2000	1.8	2900

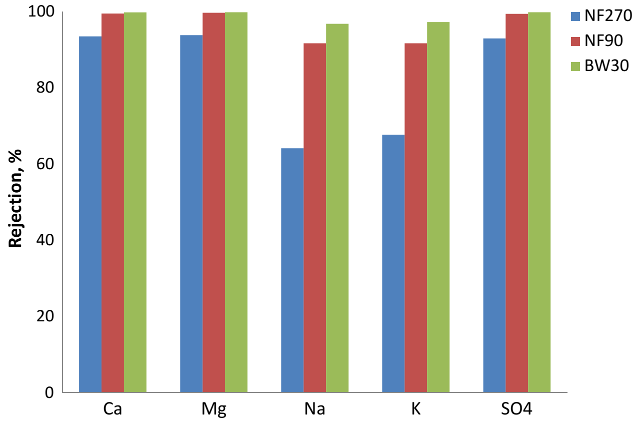

Fig. 5 Rejections of some components during NF and RO

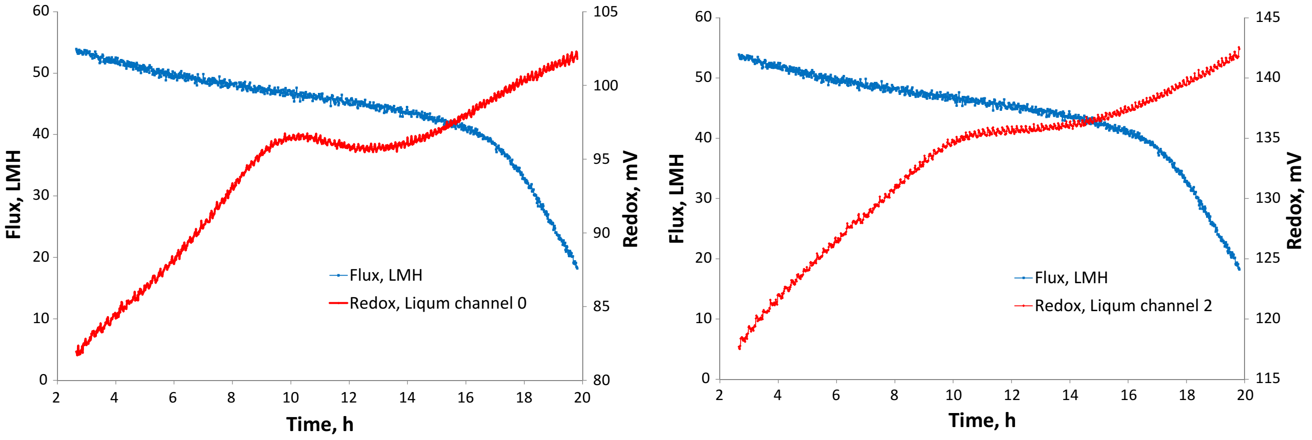

Fig. 6 The Liqum electrode signal 0 (*left*) and 2 (*right*) and flux as a function of time when filtering NP2 by RO

were only 6.3 mg/L (NP1) and 10 mg/L (NP2), but this was apparently sufficient for induced scalant precipitation. Alternatively, the feed solutions were supersaturated and precipitated scalants were removed by the MF pre-filtration.

MF pre-filtration increased the flux in all NF and RO filtrations, which could have been due to the decreased concentration of particles in the feed and less particle fouling. The NF flux of NP1 was 20 % higher for 0.2 µm pre-filtered than with no pre-filtration (Fig. 3). Also rapid flux decrease, i.e. precipitation of sparingly soluble ions on the membrane surface, scaling, seemed to start significantly later with MF than without, at water recoveries of 40 and 34 %, respectively. When an antiscalant was used for a MF pre-filtered sample, the effect was even greater and minor scaling was seen, with up to 55 % water recovery when filtration was stopped.

The effect of MF was similar when NP2 was filtered using NF or RO (Fig. 4), with either the 0.2 or 1 µm MF. MF pre-filtration increased the flux by 25 % when NP2 was filtered by NF90. An increase was also seen when NP2 was pre-filtered at 0.2 µm for both the NF270 or BW30 filtrations. Water recovery obtained in NF90 was 43 % with no pre-treatment and up to 60 % with pre-treatment by 1 µm MF. It was 54 % for BW30 without and 63 % with pre-treatment by 0.2 µm MF. It is noteworthy than fluxes at 1 bar of pressure during 1 µm MF were manifold, 25,000 LMH, compared to fluxes during 0.2 µm MF at 800 LMH. Thus, a pore size of 1 µm is preferable, if it is effective.

Lower water recoveries were obtained using NF270 than when using tighter membranes. BW30 worked best in that sense. Rejections were as expected, with the highest for BW30 and the lowest for NF270 (Fig. 5), and higher for multivalent ions than for monovalent ions.

The working electrodes of the Liqum sensor produced different type of redox curves with different electrode materials during concentration filtrations. With electrodes 0 and 2, RO filtration of NP2 water produced hours of distinctly steady state redox values. The redox values started to increase again just before the flux collapsed (Fig. 6), i.e. scaling occurred. The flatter period in Fig. 6 reflects the time needed to implement corrective actions, such as add some antiscalant to the feed solution. Thus, it appears that the Liqum sensor could be used to provide an early-stage warning of scaling.

Conclusions

Lime/limestone precipitation is the most commonly used water treatment technology at mines, but NP water can still have high metals and sulphate concentrations, which hinders its discharge and reuse. Both NF and RO are workable technologies to remove metals and sulphate, depending on the target water quality. However, scaling is an issue with both NF and RO and antiscaling agents are typically required. Microfiltration as a pre-treatment method for NF and RO, although meant for particle removal, seems to decrease the concentration of scalant ions, thus decreasing scaling on the membrane surface and increasing water recovery. It is possible that heterogeneous nucleation occurs during microfiltration, i.e. the liquid/surface boundary or the presence of particles promotes crystal growth, particularly if there are surface defects and areas of turbulent flow. Alternatively, when supersaturated precipitation occurs, the microfiltration removes the scalant particles. Finally, the Liqum probe that we tested could possibly be used to provide an early-stage warning of scaling, which would assist in minimizing chemical usage and maximizing water recovery in membrane filtration.

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