Factors influencing nanofiltration of acid mine drainage

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Abstract Membrane technology is an established strategy to treat acid mine drainage (AMD). Nanofiltration offers economical advantages over reverse osmosis, and allows for concentrating and recovering valuable metals from AMD waters. Understanding the relationship between AMD pH and membrane charge is required to ensure compliance with stringent discharge criteria, and to maximize metal recovery for profit. The membrane iso-electric point (IEP) is a significant parameter in the rejection of ions. Maximum metal recovery was observed when the pH was lower than IEP. Ongoing research is exploring the opportunity to customize the position of the IEP by membrane surface modification.

Keywords Acid Mine Drainage, Nanofiltration, Feed pH, Iso-electric point, Ion rejection

Introduction

Acid mine drainage (AMD) is a typical by-product of the mining industry and it is well known for its impact on environmental sustainability and water security (Evangelou 1998). Johnson and Hallberg (2005) highlight two key points in the choice of suitable technologies to treat AMD: i) it is fundamental to consider AMD remediation as a resource, thus encouraging recovery and recycle of the products of AMD treatment (Nodwell and Kratochvil 2012); ii) legislation defines discharge criteria that may determine the choice of a system to effectively remove sulfate as well as metals and acidity from mine waters.

Membrane treatment by reverse osmosis (RO) and nanofiltration (NF) is an established strategy for heavy metal removal as it is capable of achieving strict discharge criteria while providing high efficiency, easy operation and space saving (Fu and Wang 2011). Recent studies successfully applied membrane separation to treat AMD (Zhong *et al.* 2007; Rieger *et al.* 2009; Al-Zoubi *et al.* 2010; Mortazavi and Chaulk 2012). RO and NF provided similar rejection performance for polluting metals, however NF was suggested as the preferable treatment due to lower operating costs, *e.g.* higher fluxes at lower pressure, and its ability to selectively concentrate and recover metals and sulfuric acid.

The separation mechanism of NF membranes involves membrane surface charge, *i.e.* electrorepulsion, and sieving effects (Qin *et al.* 2004). Feed pH determines both the membrane charge density and charge polarity by establishing the zeta-potential of the membrane surface. Many studies focusing on the relationship between feed pH, membrane charge, and ion rejection, agree on the significant effect of feed pH, and minimum rejections are usually obtained at the isoelectric point (IEP) (Artug 2007; Qin *et al.* 2004). Since the IEP of commercially available NF membranes ranges between pH 3 to 5 (Childress and Elimelech 1996; Tanninen *et al.* 2004; Artug 2007), thus bracketing the pH range of most AMD streams, understanding the rejection behavior for a particular membrane-AMD problem is critical for evaluation of a NF treatment strategy.

The objective of this study was to test a commercially available NF membrane on an AMD solution to further understand the relationship between rejection performance and feed pH. The pH of the original solution was modified to create feeds ranging between 1.5 and 4.5. The IEP of the membrane was first empirically estimated by a $NaCl$-Na_2SO_4 synthetic solution characterized by sulfate concentrations in the range of typical AMD solutions (Al-Zoubi *et al.* 2010).

Methods

AMD solution was provided by Aditya Birla Nifty Copper mine (Western Australia). The AMD composition at the original pH of 4.5 is shown in Table 1. AMD discharge criteria are site-specific and have to comply with increasingly stringent environmental targets. The criteria for sulfate and metals range between drinking and general purposes water guidelines (Table 1).

Parameter	Unit	Concentration	Discharge Criteria
pH	-	4.5	6-8.5
Ca^{2+}	mg L^{-1}	480	50
Cu^{2+}	mg L^{-1}	410	1-50
K^{+}	mg L^{-1}	310	-
Mg^{2+}	mg L^{-1}	770	50
Mn^{3+}	mg L^{-1}	440	0.005-0.5
Na^{+}	mg L^{-1}	2000	-
Cl^{-}	mg L^{-1}	2300	-
SO_4^{2-}	mg L^{-1}	6900	250-1000

Table 1 *Composition of AMD solution provided by Aditya Birla Nifty Copper mine. Discharge criteria as defined in Rieger et al. (2009) and ANZECC (2000).*

A synthetic solution of about 600 mg L^{-1} sodium chloride and 18 g L^{-1} sulfate ($NaCl$ and Na_2SO_4) was produced to empirically determine the position of the IEP as the rejection minima is observed at the IEP. The sulfate concentration used was representative of sulfate levels of typical AMD solutions (Al-Zoubi *et al.* 2010). Artug (2007) acknowledged that filtration using $NaCl$-Na_2SO_4 ion system is important to characterize the membrane in terms of the position of IEP and surface charge polarity.

The schematic diagram of the cross-flow flat sheet membrane test unit is shown in Fig. 1. A Dow NF270 polyamide nanofiltration membrane (0.0138 m^2) was used because of the availability of published work describing its zeta potential and IEP. Filtration experiments were carried out at operating pressures of 5 to 8 bar and permeate flux of 25 to 35 L m^{-2} h^{-1}. The feed flow rate and temperature were constant at 200 L h^{-1} and 24 ± 1 °C, respectively. The experiments were carried out in full re-circulation mode (both permeate and retentate were re-circulated to the feed tank).

The experiments with $NaCl$-Na_2SO_4 solution were carried out with feeds ranging from pH 4 to pH 2.6 at 0.2 pH decrements using HCl. The aim of these experiments was to estimate the position of the IEP by observing rejection

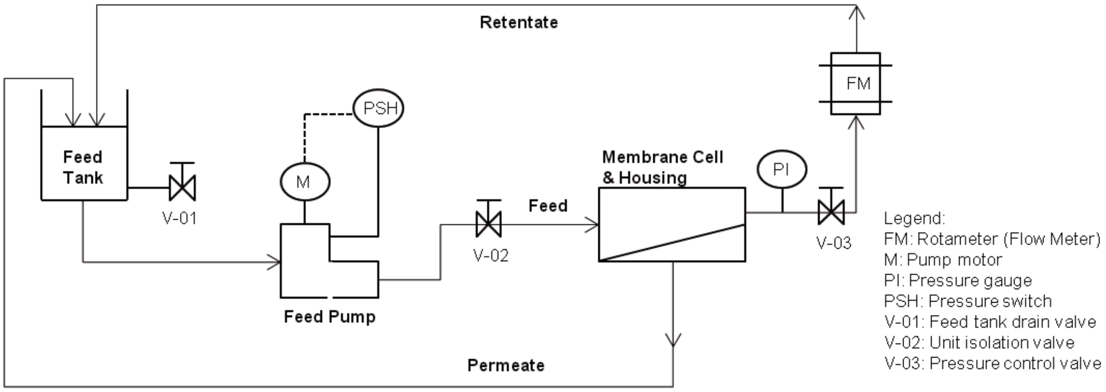

Fig. 1 *Schematic diagram of lab-scale NF unit test.*

minima (Artug 2007). The published NF270 IEP range is between pH 2.5 and 4 (Tanninen *et al.* 2004; Artug 2007; Al-Rashdi *et al.* 2012).

The experiments with the AMD solution (Table 1) were carried out similar to the NaCl-Na_2SO_4 tests with the pH ranging from 4.5 to 1.5 in 0.2 unit decrements by adding HNO_3. A total of 5 L of AMD solution was available and a 2 L feed tank was used in each test. The collection of permeate and feed samples started after 15 min of filtration at each pH value (120 mL per sample). Samples were sent to an external laboratory for analysis. Membrane rejection performance was calculated for each ion as the concentration ratio between the permeate and the feed sample. At each sampling point a total volume of 240 mL was removed for sampling purposes, and an equivalent volume of replacement feed was added to the 2 L feed tank. These additions caused a 2 to 5 % increase in ion concentration relative to the original feed (Table 1).

Results and Discussion

Fig. 2 shows ion rejection *vs.* pH for the NaCl-Na_2SO_4 solution. Minimum rejections of Cl^-, Na^+ and SO_4^{2-} were obtained at pH equal to 3.04 (Fig. 2a and b), suggesting the IEP being at the vicinity of pH 3. This is consistent with previous studies (Tanninen *et al.* 2004; Artug 2007; Al-Rashdi *et al.* 2012). Minimum rejection at IEP is explained by the fact that sieving effect is the only active separation mechanism, as membrane charge is zero at the IEP (Qin *et al.* 2004). The membrane is positively charged for pH values lower than 3 and negatively charged at pH values higher than 3. Rejections of Na^+ and SO_4^{2-} followed the same trend (Fig. 2a), as the retention of Na^+ ions depended on the rejection of SO_4^{2-} due to electroneutrality condition (Artug *et al.* 2007). Decreasing rejection of Na^+ at pH < 2.8 (Fig. 2a) was also observed by Tanninen and Nystrom (2002) and was attributed to a decreased positive surface charge due to an increased concentration of H^+ ions. Negative Cl^- rejections (Fig. 2b) indicated Donnan effects (Tanninen *et al.* 2004): the concentration of Cl^- increased in the permeate while SO_4^{2-} was rejected in order to maintain electroneutrality (Artug *et al.* 2007).

Results of the experiments on the AMD solution are shown in Fig. 3 and 4. Rejections

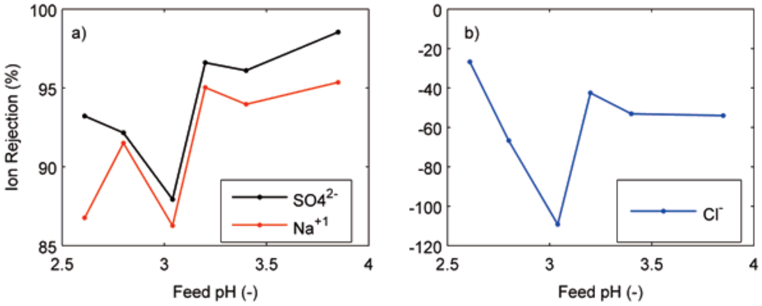

Fig. 2 *Ion rejection at varying pH for the NaCl-Na_2SO_4 solution. a) Rejection of sulfate and sodium ions. b) Rejection of chloride ions.*

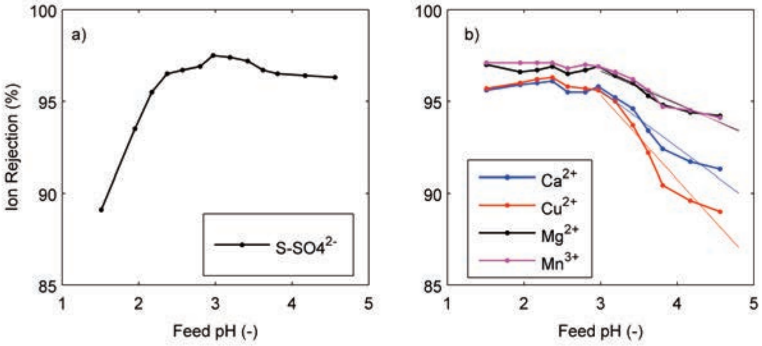

Fig. 3 *Ion rejection at varying pH for the AMD solution provided by Aditya Birla Nifty Copper mine. a) Rejection of sulfate. b) Rejection of calcium, copper, magnesium, and manganese ions. Significant decreasing trends of cations rejections are observed for pH higher than 3 (p-value < 0.05).*

above 95 % were achieved for all cations at feed pH lower than 3, however significant decreasing rejections were observed at increasing pH (Fig. 3b, p-value < 0.05) (as also found by Zhong *et al.* 2007 and Al-Rashdi *et al.* 2012). Cations were highly rejected when membrane was positively charged (pH < 3), but the rejection decreased as the membrane became increasingly negative (at pH > 3).

A different trend was observed for sulfur whose rejection increased at feed pH > 3 (Fig. 3a), in accordance with an increasingly negatively charged membrane (Szoke *et al.* 2002; Al-Zoubi *et al.* 2010). Note that at pH values lower than 2, sulfur ion was mostly present as bisulfate ion (Tanninen *et al.* 2004), which readily transmitted. Lower rejections were also due to the positively charged membrane at pH < 3.

The concentration of sulfate and metals in the permeate was compared with discharge criteria as defined in Table 1 (Fig. 4). At pH values higher than the IEP, sulfate concentrations were well below the upper guideline of 1000 mg L^{-1} and reached the sulfate limit as required by drinking water criteria (Fig. 4d). On the contrary, metal concentrations, and particularly calcium, copper and magnesium, approached the upper bound of the discharge criteria at feed pH higher than the IEP (Fig. 4a and b). The concentration of manganese in the permeate did not meet the discharge criteria at all pH values (Fig. 4c).

Our results confirmed the findings of previous studies on the importance of membrane charge to determine ion rejections in NF-AMD problems (Zhong *et al.* 2007; Al-Zoubi *et al.* 2010; Al-Rashdi *et al.* 2012). NF is a suitable technique to treat mine water as it allows concentrating and recovering valuable metals, while meeting discharge criteria. However, understanding the interaction between membrane IEP and AMD pH is important to maximize the rejection and recovery of metals. For this particular system, at a 50 % volume recovery, the Cu^{2+} concentration in the permeate could approach 180 mg L^{-1} at pH > IEP, while 100 mg L^{-1} can be approached at pH < IEP (we acknowledge other membranes are available that would provide superior rejections). Due to this phenomenon the discharge criteria may be exceeded if the membrane charge is not well understood. In addition, higher concentrations of Cu^{2+} in the permeate at pH > IEP may represent a significant loss of metal that could otherwise be recovered.

To achieve the highest recovery of metals, the membrane IEP needs to be higher than the AMD pH. Test work conducted on different

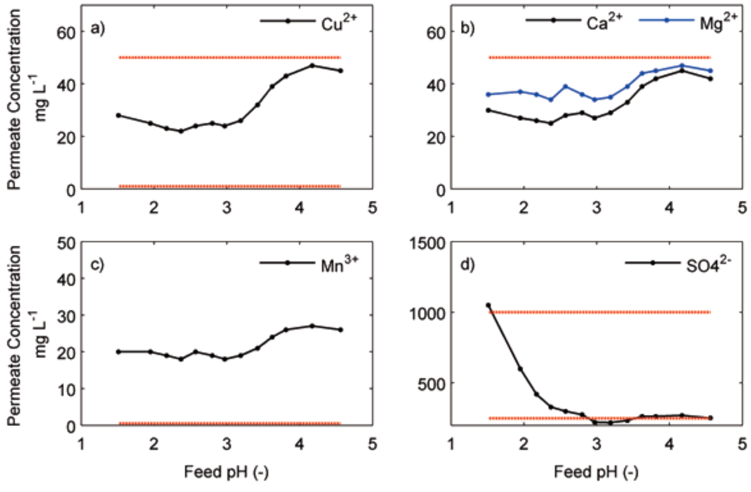

Fig. 4 *Ion concentrations in permeate samples at varying pH for the AMD solution provided by Aditya Birla Nifty Copper mine. Concentration of a) copper, b) calcium and magnesium, c) manganese, d) sulfate with relative discharge criteria as defined in Table 1.*

membranes will ensure membranes characterized by a suitable IEP relative to the AMD pH are selected. Alternatively, surface membrane modification to customize the position of the IEP relative to the AMD pH can be considered (Kim *et al.* 2002; Mukherjee *et al.* 2005). This represents a potentially novel technology application to maximize metal recovery.

Contrary to our expectations, minimum rejections of sulfate ion at the IEP were not detected when testing the AMD solution. On the other hand, minimum sulfate rejection was obtained in the tests conducted on the NaCl-Na_2SO_4 solution, which is in accordance with the literature (Artug 2007). To the best of our knowledge, there is no published work showing minimum rejections at the IEP for AMD solutions as most of the studies focus on simple single or binary ion systems (Artug 2007; Qin *et al.* 2004). This aspect is currently the objective of further investigations.

An indicative cost analysis comparing NF to RO was performed using an economic model. The model was based on known fabrication costs for similar scale projects conducted by the authors. The key variables were the product flow rate, volume recovery and number of membrane stages. The model also takes into consideration the material of construction, level of control and automation, and the potential complexity of CIP/cleaning arrangements. The operating parameters input to the model were as described in Al-Zoubi *et al.* (2010) and listed in Table 2. Capital investment was calculated on the basis of feed and permeate flow rates, and volumetric recovery. At a constant pressure of 15 bar the permeate flow rate for the two NF membranes was about double that for RO (Table 2). The capital cost for NF was about 10 % less than for RO. In term of operational costs, to obtain a permeate flux of 20 $L\ m^{-2}\ h^{-1}$, an operational pressure of 10 and 14 bar was needed for NF and RO, respectively (Table 2). This pressure difference translated in about 30 % savings of operational costs associated with energy requirements.

Conclusions

The importance of pH of an AMD solution and IEP of the NF membrane in determining ion rejection was demonstrated in this study. Optimum metal rejection occurred when the solution pH was below the IEP and diminished significantly as the solution pH deviated above the IEP. Anion rejection followed the opposite trend. Understanding these phenomena is important to comply with discharge criteria and maximize metal recovery. Novel approaches are needed to ensure that appropriate membranes and operating parameters are chosen

Parameter	Unit	Nanofiltration GE-Osmonics DK	Nanofiltration NF99	Reverse Osmosis RO HR98PP
		Capital Cost Estimate		
Feed Pressure	bar	15	15	15
Permeate Flux	$L\ m^{-2}\ h^{-1}$	38	43	22
Estimated Cost	AUD $m	2.75	2.7	3.02
Cost Difference relative to RO	%	-9	-11	-
		Operational Cost Estimate		
Permeate Flux	$L\ m^{-2}\ h^{-1}$	20	20	20
Feed Pressure	bar	10	10	14
Estimated Cost	AUD $ pa	750.9	750.9	1051.2
Cost Difference relative to RO	%	-29	-29	-

Table 2 *Capital and operational cost comparison between two nanofiltration and one reverse osmosis applications to AMD treatment. Data are taken from Al-Zoubi et al. (2010), where tests were conducted at: feed flow rate = 600 $L\ h^{-1}$; volumetric recovery = 75 %; temperature = 20 °C; pH = 2.4.*

to suit the specific AMD problem. Ongoing research aims at exploring the opportunity of customizing the position of the IEP by surface membrane modification.

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