Membrane technology applied to acid mine drainage from copper mining
K. Ambiado, C. Bustos, A. Schwarz and R. Bórquez

ABSTRACT
The objective of this study is to evaluate the treatment of high-strength acid mine drainage (AMD) from copper mining by nanofiltration (NF) and reverse osmosis (RO) at pilot scale. The performances of two commercial spiral-wound membranes – NF99 and RO98pHt, both from Alfa Laval – were compared. The effects of pressure and feed flow on ion rejection and permeate flux were evaluated. The results showed high ion removal under optimum pressure conditions, which reached 92% for the NF99 membrane and 98% for the RO98pHt membrane. Sulfate removal reached 97% and 99% for NF99 and RO98pHt, respectively. In the case of copper, aluminum, iron and manganese, the removal percentage surpassed 95% in both membranes. Although concentration polarization limited NF performance at higher pressures, permeate fluxes observed in NF were five times greater than those obtained by RO, with only slightly lower divalent ion rejection rates, making it a promising option for the treatment of AMD.

Key words | acid mine drainage, concentration polarization, nanofiltration, pilot study, reverse osmosis

INTRODUCTION
Acid mine drainage (AMD) is a common byproduct of the mining industry, which results from the oxidation of sulfide mineral waste in the presence of water, oxygen and microorganisms (Nordstrom et al. 2000). On occasion, this problem persists after mineral extraction has concluded due to poorly managed or non-existent closure of dumps and tailings dams (Morin et al. 1991; Adiansyah et al. 2015). When this toxic mixture flows into groundwater, streams and rivers, it gives rise to various environmental problems. AMD is toxic to aquatic organisms, destroys ecosystems, corrodes infrastructure and contaminates water in regions in which freshwater is scarce (Simate & Ndlovu 2014).

The formation of AMD is governed by various chemical reactions (Akci? & Koldas 2006). In the case of pyrite, one of the primary minerals associated with the generation of AMD, the oxidation process involves three main stages (Dold 2010): (i) sulfur oxidation (Equation (1)), (ii) ferrous ion oxidation (Equation (2)) and (iii) hydrolysis and precipitation of ferric ion as iron hydroxide (Equation (3)).

\[
\text{FeS}_2(s) + \frac{7}{4} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2\text{H}^+ \quad (1)
\]
\[
\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2} \text{H}_2\text{O} \quad (2)
\]
\[
\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 3\text{H}^+ \quad (3)
\]

At pH < 4, the kinetics of ferrous ion oxidation are strongly increased by microbiological activity (Akci? & Koldas 2006). Ferric ion that does not precipitate as hydroxide is converted into the main oxidant of pyrite by means of Equation (4), which at the same time results in a greater decrease in pH (Simate & Ndlovu 2014):

\[
\text{FeS}_2(s) + 14\text{Fe}^{3+} + 8\text{H}_2\text{O} \rightarrow 15\text{Fe}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad (4)
\]

The complete reaction of pyrite oxidation is summarized below:

\[
\text{FeS}_2(s) + \frac{15}{4} \text{O}_2 + \frac{7}{2} \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (5)
\]

These reactions result in the production of mine drainages with low pH and high concentrations of sulfate and dissolved metals (Tsukamoto et al. 2004). Therefore, AMD
must be treated before it is discharged into receiving bodies of water in order to mitigate its environmental impact.

AMD generated by the copper industry usually contains elevated concentrations of copper which, in the case of Chile, result from oxidation of the principal mineral of copper, chalcopyrite, a reaction that can be written as (Dold 2010):

\[
2\text{CuFeS}_2(s) + \frac{17}{2} \text{O}_2 + 5 \text{H}_2\text{O} \rightarrow 2\text{Cu}^{2+} + 2\text{Fe(OH)}_3(s) + 4\text{SO}_4^{2-} + 4\text{H}^+ 
\]

As the environmental impacts of AMD became more evident and acknowledged, the amount of studies dedicated to research into and treatment of AMD also increased (Simate & Ndlovu 2014). Various treatments have been applied to AMD, but two have stood out due to their low costs. The first of these is aeration followed by the addition of an alkaline agent (lime, limestone, caustic soda or ashes), causing the precipitation of metal hydroxides and mineral phases (Rieger et al. 2009). The second treatment option consists of biological processes such as wetlands (aerobic and anaerobic) and biochemical reactors based on sulfate-reducing communities (Benner et al. 1999; Kaksonen & Puhakka 2007; Neculita et al. 2007; Sheoran et al. 2010; ITRC 2013).

Chemical treatment via the addition of alkaline substances to raise the pH and precipitate metals as carbonates and hydroxides is very effective, but it can be costly and problematic. A single pH value may not be effective for all regulated metals in AMD, the generated sludge is voluminous and difficult to dewater, and, after disposal, is sensitive to pH variations (Zinck 2006; Nalco 2009; Sánchez-Andrea et al. 2014). A more sustainable option for the treatment of AMD must be based on the recovery and reuse of heavy metals (Simate & Ndlovu 2014), and applying selective extraction in this treatment is very difficult. The same is true of biological treatments, which offer advantages such as high removal of metals at a low pH, stable sludge and very low operating costs (Neculita et al. 2007). However, their disadvantages are that they normally need pre- and post-treatment and their efficiency is limited by the space available for their implementation (ITRC 2013). In addition, both treatments present low sulfate ion removal due to the not sufficiently low solubility of calcium sulfate (in the case of treatment by addition of lime or limestone) and the low thermodynamic efficiency of the biological reduction of sulfate (in the case of biological treatments), making it difficult to reach the discharge criteria (Hedin et al. 1994; Da Silveira et al. 2009). Therefore, the removal of sulfate ions is a very relevant factor when choosing a suitable treatment for AMD (Akcil & Koldas 2006).

Filtration processes using membranes, such as nanofiltration (NF) and reverse osmosis (RO), have emerged as cost-effective alternatives for the treatment and recovery of water and minerals from AMD due to their selectivity, operating costs, high treatment flows and status as an environmentally friendly technology (Al-Zoubi et al. 2010a, 2010b). Recent studies on the treatment of AMD using semipermeable membranes can be found in the literature (Al-Zoubi et al. 2010a, 2010b; Ramos et al. 2013; Mullett et al. 2014; Aguiar et al. 2015).

NF offers a good alternative for the treatment of mining wastewater due to its high rejection of polyvalent ions. Copper retention reaches 96–98%, even in an acidic environment (Cséfalvay et al. 2009). Meanwhile, RO membranes, with a pore diameter smaller than that of NF membranes, remove microcontaminants and are capable of retaining up to 99.7% of salinity; they are therefore used in desalination. As pore diameter decreases, the fluid pressure must increase in order to reach the same permeate flux; RO membranes therefore operate at high pressures (from 10 to 80 bar), which ultimately translates into greater operating costs (Bórquez & Ferrer 2016).

In previous studies, Härtel et al. (2007) studied the applicability of NF and RO in the treatment of AMD at laboratory scale. A highly concentrated acid drainage (14.1 g/L of \( \text{SO}_4^{2-} \) ions and 2.8 g/L of copper) of low pH (pH = 2.7) was treated by NF (NF99) and RO (DSS-HR98PP), resulting in total ion rejection between 84% and 87% for NF99 and between 90% and 95% for the DSS-HR98PP membrane between 10 and 40 bar. Following the same line of investigation, Rieger et al. (2009) evaluated, at laboratory scale, the treatment of an AMD that was also highly concentrated and of low pH, using the same membranes. The results showed that, with a transmembrane pressure between 10 and 40 bar, total ion rejection rates between 81% and 87% for NF99 and 91% and 95% for the RO98PP membrane were obtained. These researchers concluded that the most promising option was NF, considering that it delivers high metal and sulfate rejection at a lower energy cost in comparison with RO (Rieger et al. 2009).

Ion separation by membranes occurs mainly due to steric hindrance and Donnan exclusion (Luo & Wan 2013; Aguiar et al. 2016). In NF, the second mechanism is key and can be quite complex, as it depends on the acid-base behavior of the membrane selective layer, and solution pH and ionic composition. The membrane develops a surface
charge as the result of pH-dependent protonation and deprotonation of surface functional groups (Chaudhari & Murthy 2010; Fornarelli et al. 2013; Mullett et al. 2014; Aguiar et al. 2015). At a certain pH of the solution, known as the isoelectric point (IEP), the net charge of the membrane is zero. If the pH of the solution is above the IEP, the membrane presents a negative charge; when the pH is below the IEP, the membrane presents a positive charge (Mullett et al. 2014). Reported IEP values vary over a wide range depending on solution composition. For example, IEP values are between 4.8–5.7 and 2.7–3.3 for NF90 and NF270 membranes, respectively (Aguiar et al. 2016). The Donnan exclusion mechanism involves the electrostatic repulsion of ions with the same charge as the membrane (termed co-ions), and the subsequent rejection of counter-ions by the membrane in order to maintain the electric balance of the solution. Electrostatic repulsion is stronger for multivalent ions, and, hence, they are more retained than monovalent ions. For symmetric electrolytes (e.g. NaCl and CaSO4) rejection is symmetric (V-shaped curve), having a minimum at the IEP (Luo & Wan 2013). However, for asymmetric electrolytes (e.g. Na2SO4), rejection is asymmetric around the IEP (S-shaped curve), being much higher when the membrane co-ion is the divalent one. In multi-electrolyte solutions such as AMD, with SO4\(^2\), Ca\(^{2+}\), and Mg\(^{2+}\) being the predominant ions, a minimum SO4\(^2\) rejection was indeed obtained at pH 5 and pH 3.5 for NF90 and NF270 membranes, respectively, close to their reported average IEPs (Aguiar et al. 2016). Similarly, the main cations experienced rejection minima at the IEP, but only for NF270. On the other hand, with NF270 membrane and AMD containing also significant quantities of monovalent ions, asymmetric rejection behavior was detected as no rejection minima were evident and divalent cations were significantly more rejected below IEP, and sulfate, above IEP (Mullett et al. 2014).

This study evaluated the applicability of NF and RO to the treatment of AMD using commercial membranes – NF99 and RO98pHt – with the removal of sulfate ions as the main objective. AMD is not presently regulated locally and hence no specific standards exist, which is why treatment results are compared to the most stringent local industrial discharge criteria. As previously reviewed, these membranes have already been researched at laboratory scale (Al-Zoubi et al. 2010a, 2010b), but in this study we aim to evaluate them at pilot scale using a unit designed to work with spiral membranes, while at the same time broadening the studied transmembrane pressure interval, bringing it close to the operating pressure limit of each membrane. Thus, it will be possible to obtain an approximation of the results that would be obtained at real scale, enabling future evaluation of the design of a treatment plant that considers the variability of the composition of the studied AMD (from copper mining operations) and its volumetric flow rate.

**MATERIALS AND METHODS**

**Membranes**

In this study, two commercial membranes from Alfa Laval were investigated. For NF, the NF99 membrane was used, while for RO, the RO98pHt membrane was used; both are spiral-wound. The NF99 membrane is composed of a thin-film composite membrane on polyester support material, while the RO98pHt membrane is composed of a thin polyamide layer on polypropylene support material. In Table 1, the characteristics and maximum allowable pressure, pH and temperature values for both the operating and cleaning process of each membrane are presented. In addition, the maximum rejection of each membrane as reported by the manufacturer is presented.

**AMD composition**

The acid drainage samples used in this study were provided by a copper mining operation currently active in Chile. In order to remove any suspended or precipitated solid or biological contamination that could be present in the samples, they were first microfiltered using a Rhodia Orelis unit equipped with an inorganic membrane of titanium/zirconium alloy supported on ceramic material (Kerasep) with a nominal cut-off of 0.45 μm. The composition of the membrane. Thus, it will be possible to obtain an approximation of the results that would be obtained at real scale, enabling future evaluation of the design of a treatment plant that considers the variability of the composition of the studied AMD (from copper mining operations) and its volumetric flow rate.

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<table>
<thead>
<tr>
<th>Membrane</th>
<th>NF99</th>
<th>RO98pHt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rejection-size</td>
<td>&gt;98% MgSO₄</td>
<td>&gt;97% NaCl</td>
</tr>
<tr>
<td>Membrane area (m²)</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Operating</td>
<td>Max. pressure (bar)</td>
<td>42</td>
</tr>
<tr>
<td>pH</td>
<td>3–10</td>
<td>2–10</td>
</tr>
<tr>
<td>Max. temperature (°C)</td>
<td>50</td>
<td>60</td>
</tr>
<tr>
<td>Cleaning</td>
<td>Max. pressure (bar)</td>
<td>5</td>
</tr>
<tr>
<td>pH</td>
<td>1–11.5</td>
<td>1–12.5</td>
</tr>
<tr>
<td>Max. temperature (°C)</td>
<td>50</td>
<td>60</td>
</tr>
</tbody>
</table>
obtained drainage is detailed in Table 2, along with the average monthly extreme concentration and volumetric flow values observed at the deposit from which the sample was taken, for a period of 2 years.

It can be deduced from Table 2 that this AMD presents a pronounced seasonality, where the lowest flow rates are associated with greater ion concentrations and vice versa. This seasonality is due to the snowmelt and rainfall that occur in the area, which affect the dilution level of the generated AMD.

**Experimental set-up**

The filtration experiments were carried out using an Alfa Laval Pilot Unit 2.5 RO/NF, which uses spiral membranes with a membrane area of up to 2 m². In addition, a Poly Science cryostat with a 50% ethylene glycol/water solution connected to the heat exchanger of the Alfa Laval unit was used in order to maintain a constant temperature during the experiment. In Figure 1, a schematic diagram of the experimental unit is presented.

The AMD sample is deposited in the tank, from which it is pumped into the filtration unit, separating the concentrate and the permeate. Both flows are recirculated to the feed tank. The experiments were carried out at different feed velocities (with concentrate flows from 700 to 1,150 L/h) and in a range of transmembrane pressure between 4 and 50 bar for the RO98 pHt membrane and 4 and 40 bar for the NF99 membrane, with both operating at 25 ± 1 °C. The unit was operated at the same feed flow and varying pressures within the studied range, with the experiment carried out continuously and permeate flux measured at regular intervals, and filtering for 1 hour at each studied transmembrane pressure. Pressure, temperature, energy consumption and concentrate flow were recorded by observing the values provided by the unit. Conductivity and pH were determined at room temperature using a YSI 3200 conductivity instrument and a Hanna Instruments HI 9126 pH meter, respectively. Sulfate ion concentration was determined using the spectrophotometric method (SulfaVer® 4 kit), while metal concentration was determined using the Perkin Elmer AAAnalyst 400 atomic absorption spectrometer. Permeate flux was calculated by manually measuring the amount of liquid collected in a certain time period. Permeate flux density \( J_p \) (L/(m²·h)) was obtained using Equation (7) (Al-Zoubi et al. 2010a):

\[
J_p = \frac{V}{t \cdot A} \tag{7}
\]

where \( V \) (L) is the permeate volume collected, \( t \) is time (h) and \( A \) is the membrane area (m²).

Ion rejection \( R \) was calculated using the following expression (Al-Zoubi et al. 2010a):

\[
R = 1 - \frac{C_p}{C_i} \tag{8}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Sample concentration</th>
<th>Concentrations (2012 and 2013)</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>mg/L</td>
<td>36</td>
<td>Concentrations</td>
<td>17</td>
<td>95</td>
</tr>
<tr>
<td>As</td>
<td>mg/L</td>
<td>0.0</td>
<td></td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Cu</td>
<td>mg/L</td>
<td>372</td>
<td></td>
<td>61</td>
<td>528</td>
</tr>
<tr>
<td>Fe</td>
<td>mg/L</td>
<td>0.39</td>
<td></td>
<td>0.5</td>
<td>28</td>
</tr>
<tr>
<td>Mn</td>
<td>mg/L</td>
<td>124</td>
<td></td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Zn</td>
<td>mg/L</td>
<td>78</td>
<td></td>
<td>7</td>
<td>85</td>
</tr>
<tr>
<td>Sulfate</td>
<td>mg/L</td>
<td>2,300</td>
<td></td>
<td>721</td>
<td>4,106</td>
</tr>
<tr>
<td>Chlorides</td>
<td>mg/L</td>
<td>160</td>
<td></td>
<td>18.6</td>
<td>201</td>
</tr>
<tr>
<td>pH</td>
<td>–</td>
<td>4.0</td>
<td></td>
<td>4.0</td>
<td>4.6</td>
</tr>
<tr>
<td>Conductivity</td>
<td>mS/cm</td>
<td>4.4</td>
<td></td>
<td>1.03</td>
<td>4.65</td>
</tr>
<tr>
<td>Flow rate</td>
<td>L/s</td>
<td>–</td>
<td></td>
<td>380</td>
<td>9.8</td>
</tr>
</tbody>
</table>
where \( C_f \) is the conductivity or concentration of ions in the feed liquid (\( \mu \text{S/cm or mg/L} \)) and \( C_p \) is the conductivity or concentration of ions in the permeate (\( \mu \text{S/cm or mg/L} \)).

An important parameter when considering the energy performance of the system is given by the electrical energy consumed by the pump per unit of permeate flux, referred to as energy consumption (\( C_e \), kWh/m³).

\[
C_e = \frac{P}{V_p}
\]  

(9)

where \( P \) is the electrical power demanded by the pump (kW) and \( V_p \) is the permeate flux obtained (m³/h).

RESULTS AND DISCUSSION

Permeate flux dependence on pressure and flow rate

Initially, hydraulic permeability was determined experimentally with deionized water for the studied membranes. Values of 6.5 L/(m²·bar·h) for the NF99 membrane and 1.25 L/(m²·bar·h) for the RO98pHt membrane were obtained, which are partially consistent with previous studies (Rieger et al. 2013; Al-Zoubi et al. 2013b). Rieger et al. (2009) obtained permeability values of 6.30 L/(m²·bar·h) and 2.92 L/(m²·bar·h) for the NF99 and RO98pHt membranes, respectively. Al-Zoubi et al. (2010b) also obtained a permeability value of 6.3 L/(m²·bar·h) for the NF99 membrane.

The permeability of the membranes when treating AMD was evaluated, comparing it with the permeability of the membranes when filtering deionized water; the results are illustrated in Figure 2.

Perfect linearity is observed between the pressures and permeate fluxes for deionized water. This linear relation responds to the equations of diffusion through the membrane, which are well known (Coulson & Richardson 2002). In addition, it is observed that the permeate fluxes obtained for AMD are quite high, in agreement with previous studies at laboratory scale (Rieger et al. 2009; Al-Zoubi et al. 2010b), and close to the values obtained with deionized water, which could be due to the relatively low ion content of the treated AMD.

In the case of the NF membrane (Figure 2(a)), it is also observed that the difference between permeate fluxes obtained at different concentrate flows increases at greater pressures, making it clear that a greater permeate flux is obtained at a greater concentrate flow velocity, closer to the flow obtained with deionized water. When the circulation velocity of the fluid in the system is lower, the phenomenon known as concentration polarization is observed, which occurs when a greater quantity of ions remains trapped on the surface of the membrane, causing its rejection and permeability to decrease because the osmotic pressure on the feed side increases. Operating at a greater

![Figure 2](https://iwaponline.com/wst/article-pdf/75/3/705/455740/wst075030705.pdf)
concentrate volumetric flow rate helps to sweep away the contaminants trapped on the surface of the membrane, thus decreasing concentration polarization and making the permeate flux values obtained closer to those obtained with deionized water (Hilal et al. 2004). In agreement with De Morais Coutinho et al. (2009), an increase in tangential velocity increases the permeate flux rate by provoking greater turbulence, causing a dispersion of the solute molecules concentrated on the surface of the membrane, reducing the thickness of the boundary layer.

In Figure 2(a), greater concentration polarization is observed for the NF99 membrane since the linear relationship between pressure and density is not maintained at high pressures. Rieger et al. (2009) also observed a decrease in permeability when filtering AMD with this membrane, but because they used a different membrane configuration, they obtained a trend of increased flux with pressure that was linear, with no flattening of the permeate curve at high pressures.

This phenomenon is less evident in the case of the RO membrane (Figure 2(b)), where major differences are not observed when increasing the feed flow to the system due to the lower permeate fluxes and the consequent lesser accumulation of ions on the concentrate side. However, for equivalent permeate fluxes, the effect on both membranes was similar. In fact, with a permeate flux of 50 L/(m²·h), the difference between the permeate flux obtained with deionized water and AMD is 16% and 12% for the NF99 and RO98pHt membranes, respectively.

That the phenomenon of concentration polarization was observed in this study for the NF99 membrane and was not documented in previous studies in which flat membrane configurations or samples were used with this membrane (Rieger et al. 2009; Al-Zoubi et al. 2010b) is due to the fact that when the geometry of the membrane (flat or spiral) is modified, its performance can change (Arunkumar et al. 2016).

Rejection dependence on pressure and flow rate

Figure 3 shows total ion rejection, determined by the relationship between conductivity in the feed and conductivity in the obtained permeate. Due to recirculation of both concentrate and permeate, the conductivity in the feed remains constant, while the conductivity in the permeate varies with the relative amounts of water and ion fluxes across the membrane. In turn, the permeate flux depends mainly on pressure, and the ion fluxes on concentration gradients.

In Figure 3, it is observed that RO rejection increases with pressure, because of the water flux increase (Figure 2), while ion passage remains constant, and hence a more diluted permeate is generated. In the case of NF, this trend is reversed at higher pressures as concentration polarization generates a larger driving force for ion fluxes across the membrane.

An optimum ion removal is obtained at 15 bar in the case of the NF99 membrane, reaching 92% removal with a concentrate flow of 1,150 L/h. At pressures over 15 bar, a decrease in the rejection obtained by NF is observed, which, in agreement with Al-Rashdi et al. (2015), occurs because increasing the pressure increases concentration polarization as explained earlier, which is consistent with what is observed in Figure 2(a).

In the case of the RO membrane, ion rejection increase with transmembrane pressure is not significant. Starting with a total ion removal of 95%, it reaches a removal of 98% at 50 bar. In addition, the RO98pHt membrane is not affected by concentrate volumetric flow rate due to the comparatively low permeate flow rates and associated low concentration polarization, and always obtains ion retention greater than 95%. On the other hand, in the case of the NF membrane, a significant concentrate flow rate effect on the total ion removal is observed, which is explained by concentration polarization.

Effect of pressure and flow rate on rejection of main components

In Figure 4, removal of aluminum, copper, manganese, zinc and sulfate ions is presented for both membranes. For RO, it
is observed that there are no differences with respect to the applied concentrate flow, as is the case in Figure 3. In the case of NF, there are evident differences at different concentrate flows, where, at a lower flow, the concentration polarization effect has a consequent decrease in rejection.

It is observed in Figure 4 that both membranes present high levels of metal removal, especially in the cases of...
copper and manganese, of which RO removes over 98%, as in previous studies (Rieger et al. 2009). With respect to the NF99 membrane, lower rejections than those obtained with the RO membrane are observed, with this difference more evident when operating at lower concentrate flows. With NF, at a concentrate volumetric flow rate of 1,150 L/h (where the effect of concentration polarization decreases notably), metal and sulfate rejections greater than 90% are obtained. In addition, at the optimal operating pressure (15 bar), metal rejections greater than 95% (except zinc) are obtained; these rejections are very close to those obtained with the RO membrane and consistent with those observed in previous studies (Rieger et al. 2009; Al-Zoubi et al. 2010b).

As can be observed in Figure 4(e), as with total ion removal, the RO98pHt presents greater sulfate removal than NF99 membrane, managing to remove practically all the sulfate originally present in the AMD. In addition, no concentrate flow effect is observed. Meanwhile, the NF99 membrane presents significant differences for both studied concentrate flow rates. As the AMD pH continues to drop with time, the rejection of NF99 membrane could decrease if its IEP is below present AMD pH (Aguir et al. 2016).

In Table 3, an analysis of the permeate obtained for each membrane at 15 bar is presented, and the obtained concentrations are compared with local discharge standards and international drinking water standards.

The permeate obtained at 15 bar by both NF and RO does not comply, for some analyzed parameters, with the international drinking water standards, exceeding the permitted maximum limits. This situation necessitates the creation of a second filtration stage in order to meet the criteria of the drinking water standards and obtain quality water for reuse in human consumption.

It is observed that the rejection of the metals is, in most cases, greater at a greater concentrate flow or tangential velocity over the membrane. In the case of sulfate, the obtained values are within the proposed standards for both the NF and RO membranes, with a significant difference noted in the NF99 membrane between different concentrate flow rates. With respect to sulfate removal, it becomes more evident that it is important to treat AMD at a greater tangential velocity in order to thin the boundary layer over the membrane and thus increase the rejection rate and permeate fluxes, decreasing the effect of concentration polarization.

As previously mentioned, sulfate removal becomes a very relevant factor when choosing an AMD treatment system. In this case, it is observed that with both membranes, very favorable results are obtained in that regard. However, a comparison of the volume of AMD treated systems shows that NF is a better alternative than RO. Due to the high permeate fluxes that it generates, it has greater applicability at the industrial level compared to the RO membrane.

### Evolution of the pH of the permeate

In Figure 5, it is observed that the permeate pH was always less than the feed pH, meaning that the hydrogen ion was negatively rejected. This situation appears to be common for both RO and NF membrane processes when membranes are negatively charged at feed pH above IEP (Qin et al. 2004, 2005; Zhu et al. 2007), because the small positive hydrogen ion more easily penetrates negatively charged membranes compared to other cations. Negative rejection has been also observed for monovalent ions in mixtures with polyvalent ions, influenced by Donnan equilibrium (Luo & Wan 2015). Furthermore, Figure 5 shows that when increasing the operating pressure during the experiments, the pH of the permeate did not remain stable. The different permeate pH trends for RO and NF membranes follow the trends observed for total (Figure 3) and individual (Figure 4) ion rejection. As total and individual ions are more rejected, the hydrogen ion is less negatively rejected and vice versa.

### Table 3  Composition of feed flow of AMD and permeate obtained at 15 bar with membranes NF99 and RO98pHt, at (25 ± 1) °C, and local discharge standards, and EU (1998) and USEPA (2016) drinking water standards

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Cu (mg/L)</th>
<th>Zn (mg/L)</th>
<th>Mn (mg/L)</th>
<th>Fe (mg/L)</th>
<th>SO₄²⁻ (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed flow</td>
<td>372.15</td>
<td>77.80</td>
<td>124.55</td>
<td>0.39</td>
<td>2,300.00</td>
</tr>
<tr>
<td>NF99 with concentrate flow of 700 L/h</td>
<td>23.90</td>
<td>4.45</td>
<td>6.05</td>
<td>–</td>
<td>122.00</td>
</tr>
<tr>
<td>NF99 with concentrate flow of 1,150 L/h</td>
<td>11.70</td>
<td>3.50</td>
<td>2.00</td>
<td>–</td>
<td>10.20</td>
</tr>
<tr>
<td>RO98pHt with concentrate flow of 700 L/h</td>
<td>1.44</td>
<td>0.11</td>
<td>0.38</td>
<td>0.02</td>
<td>5.88</td>
</tr>
<tr>
<td>RO98pHt with concentrate flow of 1,150 L/h</td>
<td>1.18</td>
<td>0.13</td>
<td>0.35</td>
<td>0.00</td>
<td>6.00</td>
</tr>
<tr>
<td>USEPA</td>
<td>1.30ᵃ</td>
<td>5.00ᵇ</td>
<td>0.05ᵇ</td>
<td>0.30ᵇ</td>
<td>250.00ᵇ</td>
</tr>
<tr>
<td>EU</td>
<td>2.00</td>
<td>–</td>
<td>0.05</td>
<td>0.20</td>
<td>250.00</td>
</tr>
<tr>
<td>Most stringent local discharge standard</td>
<td>1.00</td>
<td>3.00</td>
<td>0.30</td>
<td>5.00</td>
<td>1,000.00</td>
</tr>
</tbody>
</table>

ᵃPrimary drinking water standard (USEPA 2016).
ᵇSecondary drinking water standard (USEPA 2016).
For a better comparison of the two membranes, Figure 6 presents the relationship between permeate flux and energy consumption obtained for the RO98pHt and NF99 membranes.

The permeate flux obtained by NF is up to six times greater than that obtained by RO. This relationship decreases when transmembrane pressure increases, and when the concentrate flux or tangential velocity over the membrane decreases, a situation associated with the phenomenon of concentration polarization that NF99 exhibits.

A comparison of the energy consumption of the two membranes shows a trend the same as that of permeate flux. It can be clearly observed that the energy consumption of the RO membrane is much greater than that of the NF membrane, reaching levels four or five times as high. This is because energy consumption is inversely related to the obtained permeate flux; a lower permeate flux is therefore related to greater energy consumption, which results in a less efficient process in terms of the volume of water treated.

In agreement with Fornarelli et al. (2013), the capital costs of a treatment employing NF membranes are 10% lower than those of a treatment employing RO, based on an economic model for projects developed by the authors. The greatest cost difference between the two technologies is operating costs, which are associated mainly with differences in energy consumption (Figure 6). Therefore, NF is a more attractive process for remediating AMD, in spite of the lower level of treatment, due to its low operating costs (reflected in lower energy consumption), in comparison to RO. In particular, NF appears to be a better option for sulfate ion removal in comparison with other less effective methods, such as precipitation with lime.

CONCLUSIONS

AMD, in particular that which results from copper mining in mountainous areas, presents significant variations in its flows and chemical characteristics due to climatological and geological factors.

It is demonstrated in this study that NF and RO are suitable treatments for AMD due to the high rejection of toxic metals and ions that they achieve. Ion removal reached 92% for NF and 98% for RO, while sulfate removal was 97% and 99.7% for NF and RO, respectively, operating under optimal pressure conditions.

It was also observed that, at pilot scale, tangential velocity (concentrate flow) proves to be an important factor in the performance of the NF99 NF membrane, since with a greater flow it was able to significantly reduce the concentration polarization effect, obtaining greater permeate fluxes and increasing ion rejection. The optimum was determined to be at 15 bar, with a total ion removal of 92% and a permeate flux five times greater than that obtained with the RO membrane.

In summary, NF presents acceptable rejection rates and lower operating costs, making it an attractive option from an...
industrial point of view. When considering the use of these technologies at industrial scale, it is first necessary to carry out studies such as this one at pilot scale, in which a better approximation of the performance of the membrane at real scale is obtained since its geometric configuration, for example, is considered. In the case of the NF99 membrane, this characteristic proved very relevant in its performance, which demonstrates the necessity of completing studies at pilot scale, operating the system continuously for more prolonged periods, in order to verify the behavior of the membranes in the presence of fouling and concentration polarization.

It can be concluded that for the studied AMD, the NF treatment at 15 bar is a promising treatment option due to the high sulfate removal that it achieves, with high permeate fluxes and low energy costs in comparison to the RO membrane. However, in cases in which the AMD presents a marked seasonality, it could be necessary to work temporarily under much greater pressures.

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