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Nanofiltration of acid mine drainage

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ABSTRACT

Acid mine drainage (AMD) is recognized as one of the more critical environmental problems in the mining industry, with the potential of severe contamination of surface and groundwater, as well as soils. Different conventional methods are used to treat AMD such as lime neutralization, in which lime is added to AMD to raise pH and then precipitate the dissolved toxic heavy metals. In addition to a high concentration of sulphate, the sludge produced by this process has no economic value and has to be disposed of in large areas of land. Nanofiltration (NF) membranes are a new alternative method employed to treat AMD in this work. First, neutralization of AMD collected from the copper mine in Chile using both sodium hydroxide and lime will be investigated to find the optimum formed sludge. Then, three commercial NF membranes (NF99, DK, GE) have been used to filter AMD at two different pressures of 20 and 30 bar and at two different concentrations. The results showed that NF membranes successfully treated AMD with a very high rejection (>98%) of heavy metals. This indicates their suitability in treating this type of wastewater in a more environmentally friendly process. The DK membrane had the highest rejection even at low studied pressure (20 bar) and high AMD concentration. Meanwhile, NF99 had the highest flux, yet its rejection was slightly lower than the DK membrane, especially at the latter condition. Finally, the GE membrane had the lowest rejection and flux at all studied conditions. Further study is required to address the scaling effects on the membrane surface.

Keywords: Acid mine drainage; Nanofiltration; Membrane; Lime; Neutralization; Scaling

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1. Introduction

Acid mine drainage (AMD) is an extensive environmental problem associated with both working and abandoned mining operations. It results from the natural oxidation of sulphide minerals, such as pyrite (FeS_2), mackinawite (FeS) and chalcocite (Cu_2S), when exposed to the combined action of water and oxygen. Sources of AMD [1] are underground and open pit mining works, overburden and waste rock dumps, flotation tailing dams and concentrate stockpiles. Most of these sources remain active for decades or even centuries after mine closure. AMD is characterised by high acidity (pH 2–4), high sulphate concentration (1–20 g/L) and high concentrations of metals and other toxic elements such as Fe, Mn, Al, Cu, Ca, Pb, Mg, Na and Ni [2,3]. This causes a severe contamination of surface and groundwater as well as soils. The chemical equation of AMD production from pyrite is shown in the following equations [4]:

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$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (1)$$

The dissolved Fe^{2+}, $SO_4{}^{2-}$ and H^+ represent an increase in the total dissolved solids and acidity of the water. After the sequence has been initiated, a self-accelerating cycle is established in which Fe^{2+} is oxidized by oxygen, equation 2, to Fe^{3+}, which is subsequently reduced by pyrite [5].

$$Fe^{2+} + 1/4O_2 \rightarrow Fe^{3+} + 1/2H_2O \quad (2)$$

At pH values between 2.3 and 3.5, ferric iron precipitates, such as $Fe(OH)_3$, leave little Fe^{3+} in solution, which subsequently oxidizes additional pyrite while simultaneously lowering pH [4].

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 2H^+ \quad (3)$$

A combination of Eqs. (1)–(3) gives Eq. (4) which represents the eventual precipitation of $Fe(OH)_3$ and production of sulphate ion in an acid solution.

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 4H^+ \quad (4)$$

The accumulation of such ferric hydroxide represents an unavoidable by-product of the mining and mineral industries and one of the significant contributors to water pollution.

Different conventional methods were used in treating AMD. Lime ($Ca(OH)_2$) or limestone ($CaCO_3$) neutralization is a traditional approach used by many investigators [6–10], in which lime or limestone is added to precipitate the sulphate as gypsum and the metals as hydroxides followed by gravity separation of the solid product thereby raising the pH. This process generates large amounts of gypsum sludge contaminated with metals, and is also expensive and labour intensive. In South Australia, the cost of this treatment was estimated at $250,000/year in 1988 [11]. Moreover, the remaining sulphate content is still about 600 mg/l, which exceeds or would exceed the environmental requirements for such water going to the receiving bodies.

The two–step neutralization ferrite formation process is a modified neutralization method used to treat AMD [12,13]. In this process, magnesium oxide or calcium carbonate are used during the first neutralization step to raise the pH to around 4.8 to produce low solubility heavy metals hydroxide sludge, which can easily be removed. In the second neutralization step, sodium hydroxide is applied to reach a pH of 8.5 to produce ferrite sludge by precipitating ferrous and ferric hydroxides together with the remaining heavy metals. The author [13] concluded that this process was effective in sludge production and for removing toxic heavy metals from the AMD. In another study, blast furnace slag [14] was investigated instead of limestone, and it was concluded that this process has the potential to absorb metal ions with increased pH to neutral. On the other hand, Petrik et al. [15] showed that it was possible to use fly ash or fly ash leachate as an alternative agent in neutralization of AMD without the addition of liming agent. Recently, Rios et al. [16] investigated coal fly ash, natural clinker and synthetic zeolites in batch experiments as low-cost sorbents for treatment of AMD, giving good results in adsorption of metals from AMD. Gitari et al. [17] utilized the solid residue (SR) generated from active treatment of AMD using fly ash to blend it with varying amounts of fly ash and 6% ordinary Portland cement and fresh fly ash to assess the neutralisation and contaminants attenuation in AMD with time, but this work needs more research to explore the leachability of the toxic trace elements in the long-term. Limestone, dolomite, and fly ash have also been used to treat AMD as individual adsorbents or a combination of these [18]. In another study, Cheong et al. [19] tried a simple anaerobic reactor to remove high heavy metals from AMD and to increase pH value. The reactor was filled with a mixture of rice stalk, cow manure and limestone. The main disadvantages of this process were low permeability in the reactor and clogging of the conveyance system. Another researcher [20] suggested using organic covers to prevent diffusion of oxygen into reactive sulphide wastes and subsequently to eliminate sulphide compounds oxidation and generation of acidic waters. This method, which was considered a low cost solution for the prevention of AMD generation, did not affect the environment as it consisted of using industrial waste rather than natural materials.

Biological treatment is another alternative method for treatment of AMD in which sulphate-reducing bacteria (SRB) were used to remove metals and raise pH value. These reactors commonly use a variety of carbon substances (i.e. manure, wood chips) to reduce sulphate to sulphide, which forms metal sulphide precipitates [21–25]. This process for some typical organic materials generates hydrogen sulphide, which elevates pH. Therefore, AMD was usually neutralized before any biological treatment [25]. The effectiveness of these methods decreases as carbon substances are consumed in the SRB reactor. Therefore, Barnes et al. [26] suggested using lactate and methanol as a carbon source in a similar sulphate-reducing bioreactor process, while Tsukamoto and Miller [27] studied the addition of both latter chemicals to manure substrate as a method to reactivate SRB reactors. Organic waste materials have been tested as alternative substances to SRB reactors [28]. These materials were oak chips, spent oak from shiitake farms, spent mushroom compost, sludge from a wastepaper recycling plant and organic-rich soil. The results showed that the removal of sulphate and metal ions was slower in the reactor with raw oak than in reactors packed with other waste materials at the beginning of the operation, but all reactors showed similar performance at later stages [28]. Cation exchange process is another potential method used to treat AMD [29]. Not only would ion exchangers remove potentially toxic metals from mine runoff, there was also the possibility of making a profit from the recovered metals. However, the cost of ion exchange materials compared to the relatively small returns, as well as the inability of current technology to efficiently deal with the vast amounts of mine discharge, renders this solution unrealistic at present.

A promising new alternative method to treat AMD uses state-of-the-art nanofiltration (NF) membranes. A NF membrane is a type of pressure driven membrane with properties in between reverse osmosis (RO) and ultrafiltration (UF) membrane. NF offers several advantages, such as low operation pressure, high flux, high retention of multivalent anion salt and organic molecules above 300 Da, relatively low investment, low operation and maintenance cost, and is environment friendly [30]. Furthermore, NF can either be used to treat all kinds of water including ground-, surface-, and wastewater or used as pre-treatment for desalination process [31–33]. Jacangelo et al. [32] reported that NF is used for removal of natural organic matter (NOM). To date, NF has been employed primarily for groundwater containing relatively low total dissolved solids, but with high total hardness, colour, and disinfection byproduct (DBP) precursors. Escobar et al. [33] found that the rejection of assimilable organic carbon was greater than 90% at pH 7.5 using a TFC-S NF membrane. A comprehensive review on the use of NF membranes in water treatment has been presented elsewhere [30]. Because of these advantages, the applications of NF worldwide have increased [34].

Few researchers studied the application of NF in treating mining waste water. A low sulphated (3,000 ppm), hard (2,000 mg $CaCO_3$/L) water from a flooded iron mine was treated by Jarny NF plant for the production of drinking water (125 m^3/h) in France [35]. The plant was working for two years. The results showed that NF70 (Dow company) can reject sulphate and reduce the hardness up to 98%. The water produced by plant has always met the drinking water standards, even though raw water concentrations exceeded largely the design values. In South Africa, Visser et al. [36] tried to treat gold and coal mine water contains, again, low concentration of sulphate (3,000 ppm) using different types of commercial NF membranes. All experiments were carried out in a dead-end membrane set-up at pressures between 3 and 20 bar and at different pH values. The results showed that both NF70 and NF90 membranes can reject sulphate ion in the range of 95–99% at a neutral pH. At lower pH, the performance decreases due to the presence of a higher fraction of monovalent HSO_4^- ions and as well as a possible change in the membrane charge from negative to positive. In another study, the recovery of heavy metals by precipitation using sulphide addition and/or pH increase and NF membrane has been investigated [37]. The results showed that the rejection of metals is almost constant at pH 7 and 1.5. However, the higher the concentration or the lower pressure used, the lower the rejection.

The objective of this study is to investigate the application of NF membranes for treatment of AMD using cross-flow system. First, the AMD will be neutralized with lime to show the optimum formed sludge. Second, three commercial NF membranes (NF99, DK, GE) will be investigated to treat AMD at 20 and 30 bar and at two different concentration levels. For each condition, the permeate flux will measured over time up to 160 h, in order to check the scaling effect on the surface of the membranes.

2. Experimental

2.1. Membranes

Three commercial NF membranes were used in this study, of which two were manufactured by GE-Osmonics (USA). These two membranes are GE and DK, which are made from Composite polyamide and thin film (TF) type, respectively. Although, the manufacturer classified GE membrane as a UF membrane, we considered it a NF membrane according to its manufacturing data. The third membrane, NF 99, was obtained from Alfa Laval Company (Sweden), which was made of TF composite on polyester. The data of all investigated membranes given by the manufacturers in addition to some values taken from the literature are shown in Table 1. All membranes were immersed at least one hour before being used in any experimental work.

2.2. Permeation experiments and set-up

The permeation experiments were carried out in a laboratory scale test cell. A schematic diagram of the experimental set-up is shown in Fig. 1. It mainly consists of a 30 litre feed tank, a high performance piston pump, two parallel test modules, water bath and a

Table 1
Chemical and physical characteristics of NF membranes taken from literature or supplied by the manufacturers

Membrane	NF 99	GE	DK
Manufacturer	Alfalaval	GE-Osmonics	GE-Osmonics
Surface material	TF composite on polyester	Composite polyamide	TF
Temperature resistance (°C)	50	N/A*	90
pH range (25°C)	2-10	2–11	2–11
Permeability (L/(m^2 h bar)) (25°C)	N/A	N/A	5.0, (20°C)
Rejection-Size	>98%-$MgSO_4$	500 Dalton	98%-$MgSO_4$

N/A: Not available.

control unit. In order to remove large particles from the original AMD solution, it was filtered through a paper filter (Filtrak 388; Spezialpapierfabrik, Niederschlag, Germany). Twenty litres of the AMD feed was pumped in total recycle mode using a Cat 1051 plunger pump into a junction which distributes the flow equally to the two membrane modules. Each module consists of a sinter plate to support a circular area membrane sample with an effective membrane area of 63.6 cm^2. The AMD solution was fed to the centre of the membrane sheet from the top, where both concentrate line exited as a radial flow through a gap along the perimeter of the membrane and the permeate line exited through the sinter plate. The control unit in the set-up tracked the parameters such as pressure, flow and temperature at required values (Fig. 1). Two experiments, therefore, were carried out in a cross-flow NF membrane process at the same time using either the same or different types of membranes.

The pressure of the membrane cell was set at 20 and 30 bar for the original and concentrated AMD. The concentrated AMD was obtained from reverse osmosis of the original AMD until 50% of permeate (pure) water were removed and the total ion content was accordingly raised by a factor of 2. For simplicity, the concentrations of the original and concentrated AMD are assumed to have the symbols of 1x and 2x, respectively. In order to determine the flux decline and thus the scaling tendency of the membranes, the flux was first measured over time for all studied conditions up to 160 h for most cases. The experiments were carried out at feed rate of 650 L/h and temperature at 35°C, adjusted through the water bath, in total re-circulation mode, i.e. both the concentrate and the permeate streams were re-circulated into the feed tank, so that the feed concentration was kept approximately constant. Water losses by evaporation were compensated by adding deionised water to the feed tank when

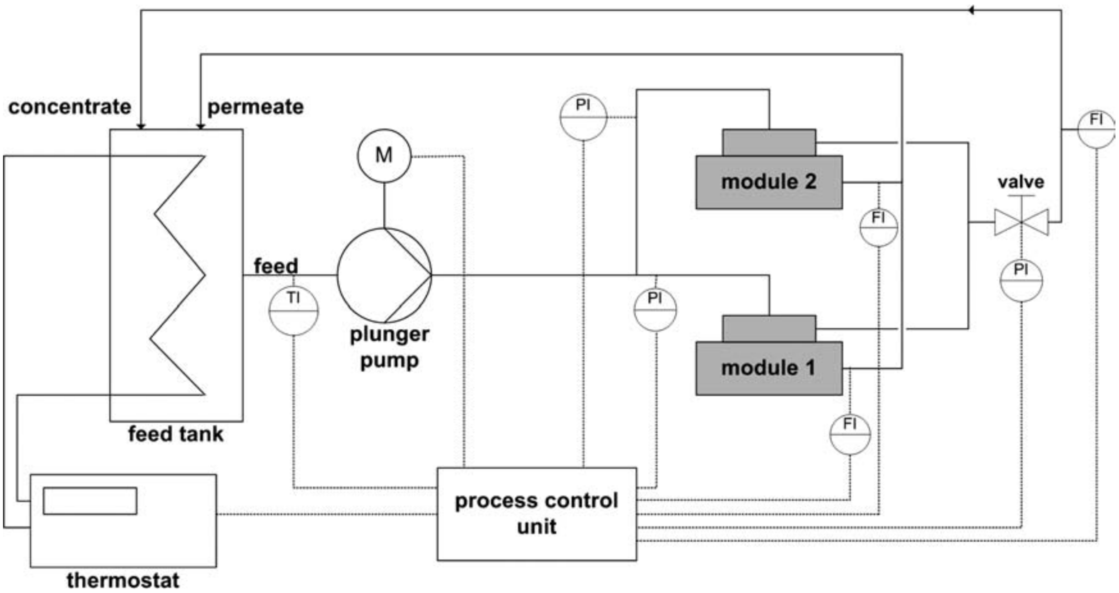


Fig. 1. Apparatus set-up.

the conductivity of the feed increased. The flux, the conductivity, and the ion concentration of the permeate flow were measured manually for each experiment. For simplicity, the polarization concentration was neglected in this study; therefore, the rejection (R) was calculated either for AMD solution or for cations using the following equation:

$$R = 1 - \left(C_p/C_f\right), \tag{5}$$

where C_p and C_f are permeate and feed concentrations (ppm), respectively. The flux (L.h^{-1}.m^{-2}) was calculated as:

$$\text{Flux} = V_p/(tA), \tag{6}$$

where V_P is the volume of the collected permeate (L), t is time (h), and A is effective membrane area (m^2).

2.3. Sampling and analytical methods

The AMD sample was provided by our cooperation partner, Siemens company (Erlangen-Germany), which was taken from copper mine industries in Chile. These industries used a flotation process to separate large particles from an original AMD sample. The provided AMD sample will be analysed in detail and the results are shown in the next section. In order to determine the general rejection of AMD for each investigated NF membrane, the conductivity for the feed and permeate solutions was measured at ambient temperature by a conductivity Hand-Held Meter LF 330/340 (WTW-Germany) with auto-correction temperature (i.e. the temperature is corrected to 35°C), while pH values were measured using a pH 340 meter (WTW-Germany). All ions, except sulphate anion, concentration were determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) with OPTIMA 3000 (Perkin-Elmer-USA). The sulphate concentrations were measured by an optical method using both test kits LCK 153 and LCK 353 (HACH LANGE-Germany) to measure sulphate ions over the ranges 40–150 and 150–900 mg/l, respectively.

3. Results and discussions

3.1. Characteristics of AMD

3.1.1. AMD sample

As mentioned above, AMD was sampled from the drainage water of a Chilean copper mine. The properties of the investigated AMD solution, which was analysed in this work, are summarised in Table 2. It is clear that the latter solution is strongly acidic (pH<2.5) and metal-rich due to the oxidation of sulphide minerals, and its orange-brown colour is due to the very high concentrations of ferric iron in solution. Further, this AMD contains high concentrations of sulphate, copper and aluminum, a medium concentration of other divalent cations (Ca, Mn, Mg), and very low concentration of monovalent cations (Na, K) as shown in Table 2. Moreover, the investigated AMD is considered as very hard water as the concentration of calcium and magnesium is higher than 120 ppm.

Table 2
Analysing of the original AMD and the standard concentration for potable water according to World Health Organizing (WHO)

Metal	Concentration (ppm) In AMD solution	Standard Concentration for potable water (ppm)
Aluminum(Al)	1139.0	0.20
Sulphate (SO_4)	14337	250
Calcium (Ca)	325.9	40
Copper (Cu)	2298.0	2.0
Iron (Fe)	627.5	0.200
Manganese (Mn)	224.5	0.050
Magnesium (Mg)	630.60	20
Sodium (Na)	6.89	200
Potassium (K)	4.31	12

3.1.2. Neutralization of AMD

Sodium hydroxide (NaOH) and hydrated lime ($Ca(OH)_2$) were added to the investigated AMD in order to study their neutralization effects and the precipitations formed. Figs. 2 and 3 show experimental and modelled neutralization curves for titration with 1 M NaOH solution and 1 M $Ca(OH)_2$ suspension. Both figures show the dependence of pH value and pH gradient to added volume of alkaline agent. The concentration of both hydroxides have been chosen to be high (i.e. 1 M) in order to cover a wide range of pH values and, therefore, cause the precipitation of heavy metals to occur. Additionally in the titration test with 1 M $Ca(OH)_2$ the precipitation of gypsum occurs. This will not be discussed here in details since there is unknown relation between gypsum precipitation and pH values. It is clear that both figures have the same trend in the precipitation of metals, but the main differences between both hydroxide compounds are their solubility in water and their cost. NaOH is completely soluble in water, but is more expensive, while $Ca(OH)_2$ has low solubility, and could reach over saturation at high pH values.

Figs. 3 and 4 show the function of pH to the added alkaline agent. Additionally the pH-gradient is plotted

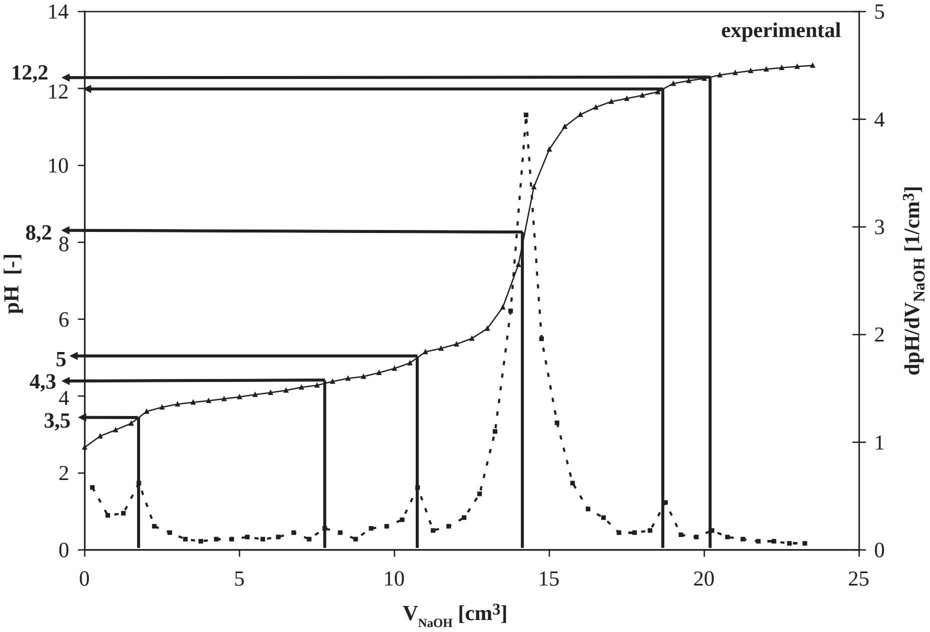


Fig. 2. Experimental neutralization pH and pH-gradient curves for mine water with 1M NaOH solution.

to identify pH-buffering equilibriums. pH-''hot spots'' are found in experimental neutralizations curves at pH values in ranges of 3.5 to 5.5/6.5 and 8 to 12. Merely, some of the buffering zones in the experimental results show more peaks in the gradient function, which is due to lesser accuracy. The consumption of 1 M $Ca(OH)_2$ is about a half of the experimental results for 1 M $Ca(OH)_2$ and 1M NaOH (experimental), respectively.

Five buffering zones have been identified experimentally and are shown in Table 3. The experimental results show a good agreement with values taken from literature [39–41]. At a pH of 2.7, the untreated mine water is close to the first buffering zone of manganese oxyhydoxide, which explains the steep initial slope in the experimental curve [41]. According to Uhlmann et al. [39], the first buffering zone overlaps with the

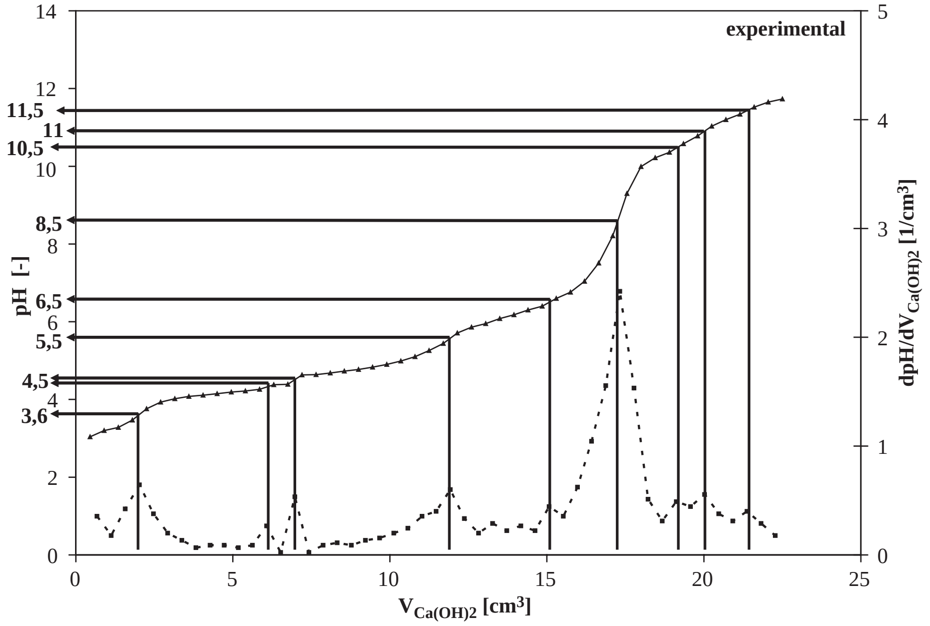


Fig. 3. Experimental and simulated neutralization pH and pH-gradient curves for mine water with 1M $Ca(OH)_2$ suspension.

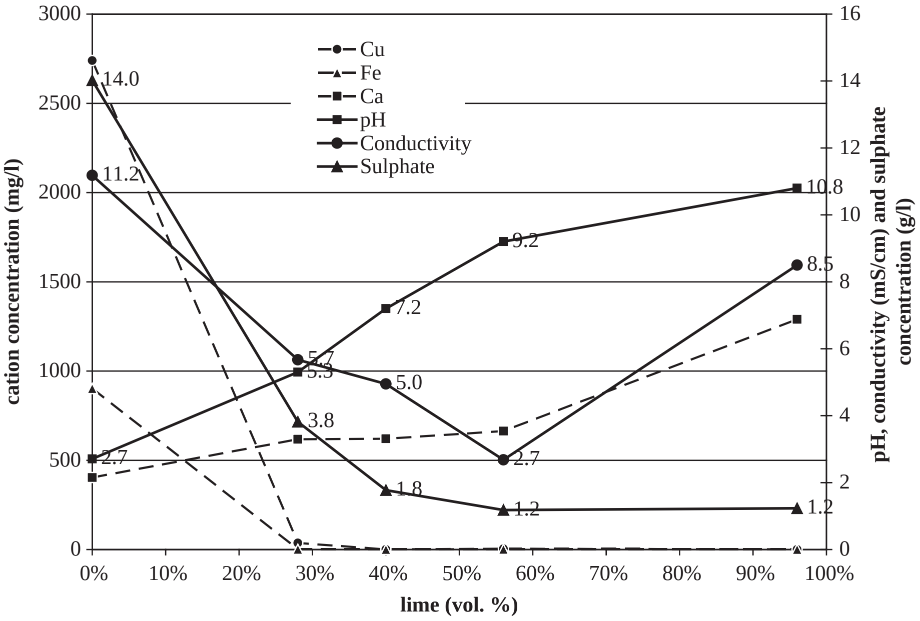


Fig. 4. The concentration of Cu^{2+}, Fe^{3+}, Ca^{2+}, SO_4^{2-}, pH, and conductivity after the addition of lime to AMD solution.

second zone, which is characterized by Fe and Al, which is bound to sulphate in the pH range of 2.9 to 4.3 for Fe and 4.3 to 5.5 for Al. Furthermore, the latter authors were able to identify the Al:S ratio and identified the precipitated Al-SO_4-compound as aluminium hydroxysulphates [e.g. basaluminite]. Additionally, the hydrolysis reaction for ferric iron with a pKa about 3 leads to precipitation of FeOOH and $Fe(OH)_3$ in the buffering zone II, respectively. According to Cheng et al. [40], the fourth identified buffering zone corresponds to the formation of several copper hydroxy-complexes and $Cu(OH)_2$, that precipitates with pH in the range of 12. The last buffering zone (V) overlaps with the 4th buffering zone and corresponds to the formation of $Al(OH)_3$ (amorphous, gibbsite, hydrolysis of Al^{3+}) [39,40].

In a more detailed study, the hydrated lime (1 M) was added again to AMD at five different volumes. These volumes, which were calculated as a percentage volume ratio of added lime to the total volume of original AMD, are 0%, 30%, 40%, 56%, and 96%. The supernatant was separated from the precipitant and analysed for each case by measuring the concentration of typical metal cations and the sulphate ion (Na^+, Cu^{2+}, Fe^{3+}, Ca^{2+}, SO_4^{2-}), pH, and the conductivity. Fig. 4 shows the result of lime additions, where the concentration of the studied cations is shown on the left *y*-axis, while the concentration of sulphate, pH, and conductivity is shown on the right *y*-axis. The hydrated lime dissolves in the solution and provides the hydroxide and calcium ions, which cause the increase of pH value and the concentration of calcium ions as shown in Fig. 4.

Table 3
pH-buffering of metal species in acid mine waters [39–41]

Buffering zone	pH	Reaction/buffering compounds	Reference
I	~2.7	$Mn^{2+} + 0.25\ O_2 + 1.5\ H_2O = MnOOH + 2H^+$	[41]
II	3.5 … 5	$Fe^{3+} + 3\ H_2O = Fe(OH)_3$ (s) $+3H^+$	[39,41]
	4 …5.5	Al-Hydroxysulphate	[39]
III	6 … 8	Cu^{2+}, $Cu(OH)^+$	[39,40]
	4.3 … 8.2	*carbonic acid buffering*	[39]
IV	8 …12	Cu^{2+}, $Cu_2(OH)_2^{2+}$, $Cu(OH)_2$ - buffering	[39,40]
V	8 … 11	$Al(OH)_3$ (amorphous), gibbsite buffering: $Al^{3+} + 3H_2O = Al(OH)_3$ (s) $+ 3H^+$	[39,41]

As a result, the concentration of both Cu^{2+}, Fe^{3+} decreases due to their reaction with the hydroxide ions and precipitations of these cations start to form in the range of pH value 5.7 and 7.2 (neutral case). Moreover, the conductivity of the solution is also decreased until the precipitations of investigated heavy metals were formed. However, after that, it increased as a result of the addition of hydroxide ions to the AMD solution. However, the concentration of sodium was not plotted in Fig. 4 because its concentration was very low and was not affected by any addition of lime, as its solubility was very high at the studied conditions [42]. Sulphate ion concentration decreases with increasing concentration of calcium ions up to pH 9.2, where the precipitations of hydroxides are completely formed and the sulphate ions concentration becomes constant with any addition of lime as shown in Fig. 4. This stagnation of sulphate concentration results from the solubility product of gypsum, which is about 2,000 mg/l of $CaSO_4 \cdot 2H_2O$ corresponding to a sulphate concentration of about 1,200 mg/l. Therefore, the optimum conditions for the neutralization of the investigated AMD with 1 M lime solution should be using lime at a half volume of original AMD solution in a pH range from 7.2 to 9.2. On the other hand, at pH 9.2 the concentration of sulphate is relatively high (1,200 ppm) and is not acceptable under environmental requirements. Another main shortcoming of the lime method is the high amount of formed sludge (50% of the original AMD), which needs special expensive methods to separate it, taking into account the regional discharge criteria. Therefore, it is necessary to find methods like NF membranes as either a single or a hybrid unit with lime addition to overcome the problems mentioned.

3.2. NF membrane results

3.2.1. Permeate flux with time

The permeate flux of AMD solution as a function of time at investigated pressures and concentration using the three investigated membranes will be considered in this section. The flux data, which was measured regularly with time up to around 160 h is shown in Fig. 5. It was seen from the experiments that the flux remained constant after the mentioned time for some cases, while in other cases it reached steady state early. It is evident from Fig. 5 that the flux increases with increasing pressure and decreasing concentration for all investigated membranes. Moreover, the flux for all investigated membranes, at all studied conditions, decreased with time due to scaling over the surface of the membranes, which will be discussed later.

The highest flux was obtained using NF99 membrane as shown in Fig. 5(a), which was initially 110 L $m^{-2}.h^{-1}$ at 30 bar and concentration of 1x, however the flux decreased down to 80 L $m^{-2}.h^{-1}$ after 100 h. The effect of pressure on the flux was obviously shown in Fig. 5(a) where its value decreased down by 32% when the pressure changed from 30 to 20 bar at concentration of 1x and 25% at concentration of 2x. On the other hand, Fig. 5(b) shows that the DK membrane has a moderate permeate flux (in the range of 95–69 L $m^{-2}.h^{-1}$) for time levels from 0 to 140 h at concentration of 1x and 30 bar and almost constant flux (in the range of 72–60 L $m^{-2}.h^{-1}$) at concentration of 2x for the same range of time and pressure. However, the effect of pressure on the flux is clearly shown in Fig. 5(b) for the latter membrane, where the flux dropped down to around 40% at 20 bar for both concentrations 1x and 2x. It is worth mentioning that both NF99 and DK membranes gave relatively high rejection ($R \sim 88\%$) of undesired components such as heavy metal cations and sulphate, from AMD solution as shown in Figs. 5(a) and (b). It is evident from these figures that rejection, which was measured via conductivity, was not significantly affected by the pressure and concentration, which means that both membranes can be used even at low pressure (20 bar) and high concentration (2x) with high quality. More details about the rejection of metals will be addressed in the next section. The GE membrane, as compared to the other two membranes, gave the lowest rejection and flux as well as an irregular trend of flux at different concentrations as shown in Fig. 5(c), indicating inappropriateness of the GE membrane in treating AMD solution.

3.2.2. Rejection of metal cations and sulphate

In this section, the rejection of metal cations found in AMD solution using three investigated membranes will be studied at concentrations of 1x and 2x and pressures of 20 and 30 bar. The studied constituents are Cu, Fe, Mn, Ca, Mg, Al, and SO_4, as well as the monovalent cation of Na. Tables 3–6 show pH values for AMD solutions before and after filtration processes, the analysis of dissolved constituents concentration in the feed and permeate sides, and the rejection of the constituents. It can be seen that all investigated NF membranes have high performance in treating the AMD solution except for the GE membrane at some operating conditions. At a concentration of 1x and 20 bar, NF99 and DK membranes were able to produce cleaned water at a very acceptable concentration of cations and sulphate (i.e. high rejection >99%) as shown in Table 4. Such concentrations are very comparable to the concentration of similar ions found in potable water according to the World Health Organization (WHO) as shown in the third column of Table 2. The high obtained rejection

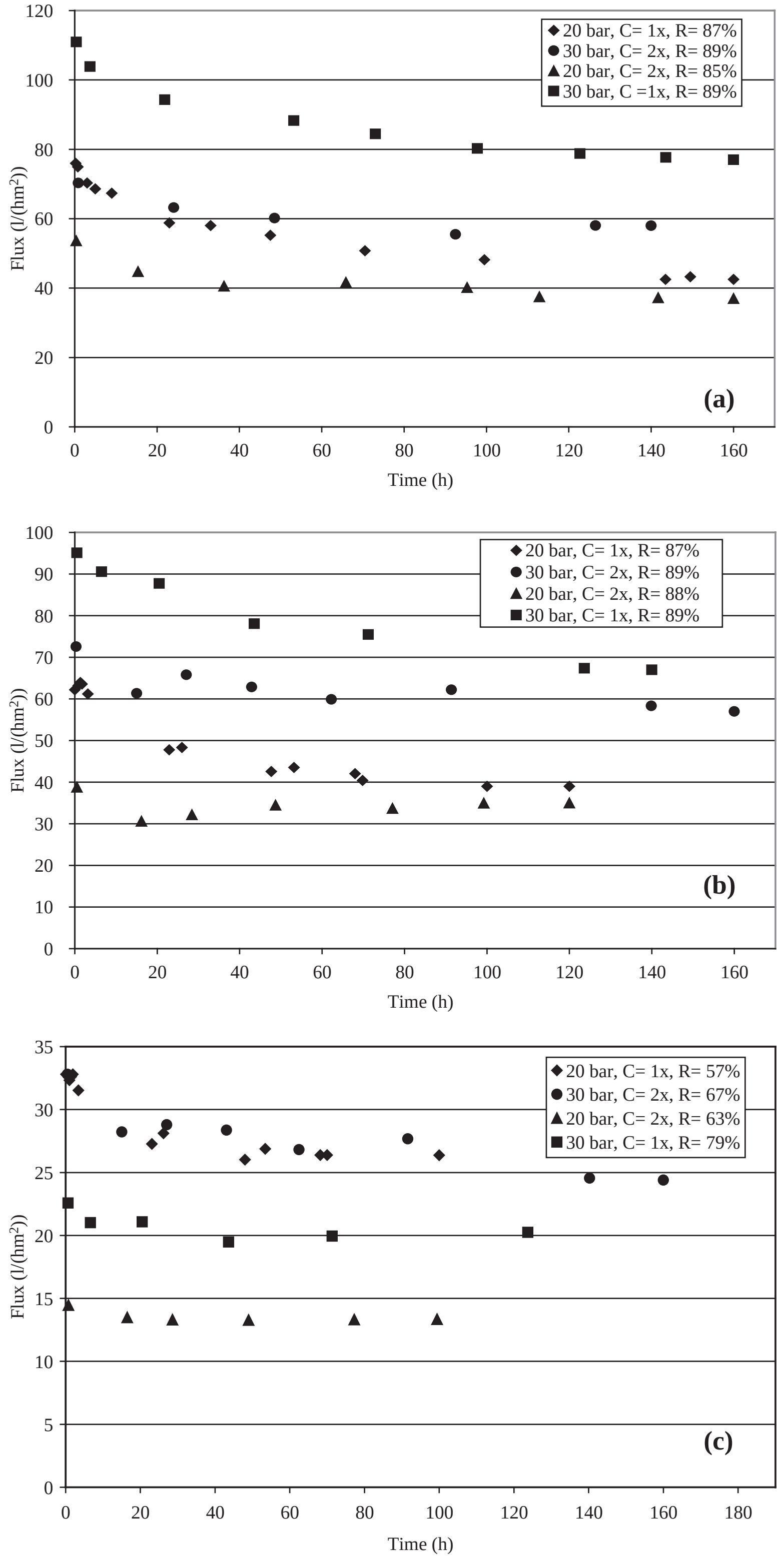


Fig. 5. Permeate Flux of the AMD with time at investigated pressures and concentrations using: (a) NF99, (b) DK, and (c) GE.

Table 4
Rejection of metals and sulphate using all investigated NF membranes at 20 bar and original AMD solution

C=1x, 20 bar	pH	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	Al (mg/l)	SO4 (mg/l)
Feed	2.7	2,040	620	185	303	559	12.3	1030	13,360
Permeate (NF99)	2.6	2.68	0.76	0.18	0.42	0.44	1.55	0.51	158
R% (NF99)		99.9%	99.9%	99.9%	99.9%	99.9%	87.4%	99.9%	98.8%
Permeate (DK)	2.5	12.24	1.86	0.92	1.82	2.80	1.27	3.09	213.76
R% (DK)		99.4%	99.7%	99.5%	99.4%	99.5%	89.7%	99.7%	98.4%
Permeate (GE)	2.8	828.2	101.1	72.7	120.6	218.6	8.18	202.9	3621
R% (GE)		59.4%	83.7%	60.7%	60.2%	60.9%	33.5%	80.3%	72.9%

values, which are promising for use in the treating of AMD solution, could be explained on the basis of steric hindrance mechanism due to the fact that NF membranes have relatively small pore size [43] while the size of cations are relatively large. As a result, the rejection of sodium anion for all investigated membranes is relatively low as its size is relatively small. Again, GE membrane had low rejections for all investigated anions at all studied conditions of concentrations and pressures as shown in Tables 4–7. The effect of pressure on the rejection of heavy metals has been studied at AMD concentration of 1x and 30 bar and the results are shown in Table 5. It is clear rejection was not affected by increasing the pressure for NF99 and DK membranes; while for GE membrane the rejection was slightly improved. This means that there was no need to carry out experiments above 20 bar at any AMD solution concentration levels. Table 5 shows the feed and permeate analysis of AMD and its rejection using three investigated membranes at 2x concentration and 20 bar. In a comparison with data obtained at 1x and 20 bar (Table 4), it can be seen that the concentration was only influential on the rejection data of DK membrane, which was decreased slightly with increasing concentration. The other two membranes showed similar performance in treating AMD at high concentrations. Again, the pressure effect has been studied for the concentration of 2x as shown in Table 7, which has the same trend in the effect of pressure as the case of 1x concentration (Table 5), where pressure only affected the rejection for GE membrane. It is worth mentioning that DK membrane has the highest rejection of undesired heavy metal cations and ions among the investigated membranes even at high concentration of AMD solution and low pressure. On the contrary, as mentioned earlier, NF99 has relatively high flux as shown in Fig. 5(a) compared to the flux obtained using DK membrane as shown in Fig. 5(b). Thus, an optimization study is indispensable for the proper choice of NF membrane in treating AMD.

3.2.3. Scaling effect

The precipitation and deposition of insoluble mineral salts onto the membrane surfaces or into internal structure of the membrane (scaling) is one of the major problems for all investigated NF membranes, which may block the membrane pores preventing the solvent from transporting through the membrane [44]. This will cause a decline of the permeate flux with time as shown previously in Fig. 5. Moreover, scaling not only shortens NF membrane service life, but incurs high operating cost. Fig. 6 shows the scaling effect on the surface of DK membrane—as an example—for all investigated conditions (i.e. 20 bar (1×, and 2×), and 30 bar (1×, 2×)). These photos were obtained by

Table 5
Rejection of metals and sulphate using all investigated NF membranes at 30 bar and original AMD solution.

C = 1x, 30 bar	pH	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	Al (mg/l)	SO4 (mg/l)
Feed	2.5	2,650	743	245	335	721	16.6	1,240	15,500
Permeate (NF99)	2.5	9.23	1.89	0.75	2.05	2.01	1.97	2.24	243
R% (NF99)		99.7%	99.7%	99.7%	99.4%	99.7%	88.1%	99.8%	98.4%
Permeate (DK)	2.6	21.2	5.20	1.72	2.68	5.05	0.930	7.44	36.4
R% (DK)		99.2%	99.3%	99.3%	99.2%	99.3%	94.4%	99.4%	98.7%
Permeate (GE)	2.3	479.7	56.5	44.6	60.0	133.4	7.24	125.2	355.6
R% (GE)		81.9%	92.4%	81.8%	82.1%	81.5%	56.4%	89.9%	87.3%

Table 6
Rejection of metals and sulphate using all investigated NF membranes at 20 bar and about two-fold concentrated AMD solution

C = 2x, 20 bar	pH	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	Al (mg/l)	SO4 (mg/l)
Feed	2.4	4,260	1,340	390	527	1,210	30.8	2,020	31,900
Permeate (NF99)	2.2	114	18.8	9.81	13.6	29.8	4.47	29.3	819
R% (NF99)		97.3%	98.6%	97.5%	97.4%	97.5%	85.5%	98.5%	97.4%
Permeate (DK)	2.3	42.6	9.28	3.51	4.74	10.9	4.03	12.1	510.4
R% (DK)		99.0%	99.3%	99.1%	99.1%	99.1%	86.9%	99.4%	98.4%
Permeate (GE)	2.6	1465.4	158.1	127.9	178.65	395.7	20.14	266.6	6699
R% (GE)		65.6%	88.2%	67.2%	66.1%	67.3%	34.6%	86.8%	79.0%

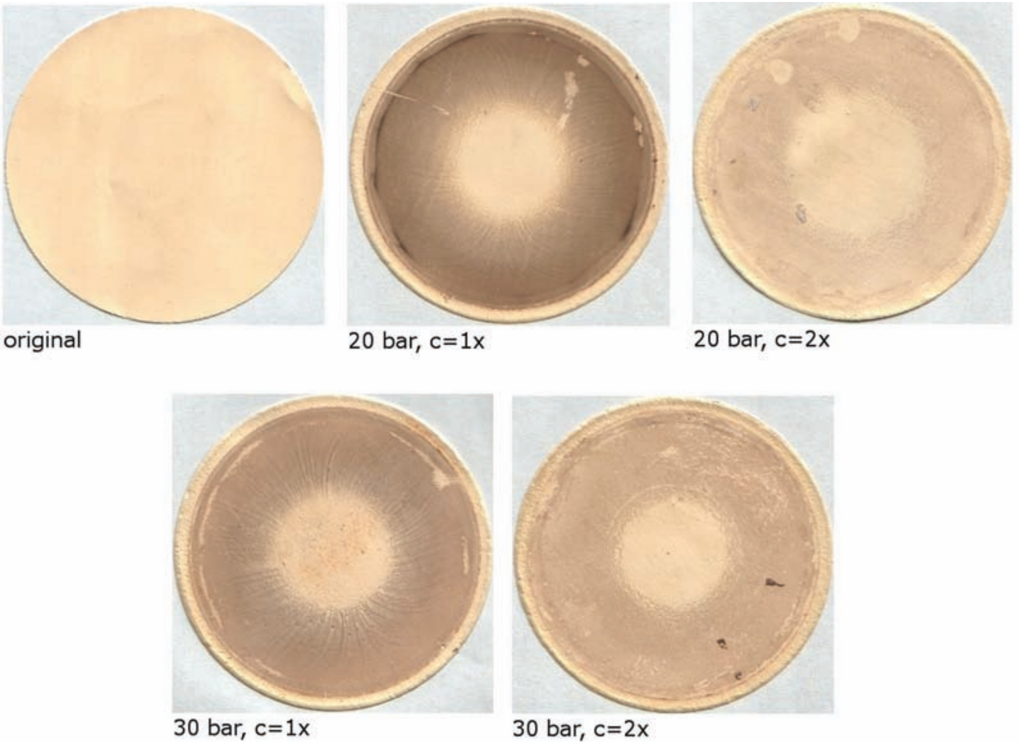
scanning of the membranes using a normal scanner MD9693 (Medion company) after 160 h operating time. It is evident from the figure that at low concentration of AMD (1x) the darkish colloid layer, which can be swept away easily, was formed. On the contrary, a white crusty layer has been seen over the membrane surface at high concentration (2x) for both investigated pressures 20 and 30 bar. It is expected that this layer was formed due to the precipitations of calcium sulphate (gypsum) [38]. Further studies are required to analyze the formed scaling layer and to find a suitable anti-scaling solution in order to clean this layer from the membrane surface, and extend the life time of the membrane.

3.3. Economic consideration

Although high quality requirement for NF feed water, membrane fouling, high energy consumption, large volume of water lost as retentate are the main barriers that arise when considering NF for improving conventional ground water treatment, the capital and operating costs are still the major factors in implementing NF technology for production of drinking water [45]. It is difficult to analyse and to compare the capital costs of different NF plants which are based on the operating conditions (production capacity, recovery rate, amortization period ...) and the quality of product water. Concerning the operating cost, the estimated one in this case is comparable to many other costs evaluated for production of drinking water by NF. Elazhar et al. [45] investigated the economical evaluation for a plant of fluoride removal by NF having a capacity of 2400 m^3/d. The design of this plant was at a recovery rate of 84%, a fluoride rejection of 97.8% and a pressure pump of 10 bar. The results showed that the capital cost was 748,003 € and the calculated operating cost to 0.212 €/m^3. For another NF plant in Florida with a capacity of 53,000 m^3/d for groundwater, Bergman [46] gave a total treatment cost of 0.23 €/m^3. In Belgium, Bruggen et al. [47] discussed the economical side of the implementation of NF for treatment of 48,000 m^3/d ground water for drinking water production. The capital cost was mainly calculated based on civil investments, mechanical engineering, electrotechnical investments, and membrane investments, while the operating cost was found based on depreciation costs, consumption costs, energy costs, and maintenance costs. The capital cost found at an optimal pressure of 8 bar and at investigated capacity was 12.5×10^6 €, while the operating cost is approximately 0.13 €/m^3. In another study, the capital cost was calculated for NF plant used to remove heavy metals (iron and manganese) from effluent in a totally

Table 7
Rejection of metals and sulphate using all investigated NF membranes at 30 bar and about two-fold concentrated AMD solution

C = 2x, 30 bar	pH	Cu (mg/l)	Fe (mg/l)	Mn (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	Al (mg/l)	SO4 (mg/l)
Feed	2.3	5,290	1,550	501	615	1,430	34.7	2,510	34,600
Permeate (NF99)	2.3	110	24.8	9.82	10.3	28.4	3.22	38.8	804
R% (NF99)		97.9%	98.4%	98.0%	98.3%	98.0%	90.7%	98.5%	97.7%
Permeate (DK)	2.3	5.29	6.2	4.51	5.54	12.9	3.47	12.6	484.4
R% (DK)		99.0%	99.6%	99.1%	99.1%	99.1%	90.0%	99.5%	98.6%
Permeate (GE)	2.5	1565.8	150.4	139.8	175.9	396.1	21.4	276.1	6193.4
R% (GE)		70.4%	90.3%	72.1%	71.4%	72.3%	38.2%	89.0%	82.1%



original 20 bar, c=1x 20 bar, c=2x

30 bar, c=1x 30 bar, c=2x

Fig. 6. Scanning of DK membrane surface before and after experiments after 160 operation time at all studied conditions.

chlorine-free (TCF) bleaching plant [48]. For a TCF plant with a capacity of 300,000 ton air-dried pulp (AD)/year, the effluent that must be treated is 300 m^3/h. based on this capacity, 90% recovery, and membrane area of 2,400 m^2, the capital cost which was calculated for permeate stream free of metals was 5.3×10^6 € and a total cost (including capital and operating costs) of 6 € /ton of pulp. It is clear that all of above NF plants cost are reliable and comparable to other waste water treatment plants. Therefore, the cost of any proposed NF plant for treatment of AMD will be in the above ranges which is more economic that other treatment processes such as neutralization method alone.

4. Conclusion

Traditionally, AMD is neutralized by treatment with lime, resulting in large precipitation of iron, aluminum and other metal hydroxides, as well as sulphate, at high concentration levels. Therefore, this study presents NF membranes as a new alternative method for treatment of AMD produced by mining industries. Three commercial NF (NF99, DK, and GE) membranes have been employed in a laboratory-scale study to investigate their performance in handling AMD collected from copper mining in Chile. It was found that the optimum neutralization of the investigated AMD with 1 M lime solution is using a half volume of AMD in the pH range from 7.2 to 9.2. Moreover, the results showed that NF membranes are capable of reducing the heavy metals concentration found in AMD to low levels, that are accepted by many international organizations especially for industrial and agricultural use. Both DK and NF99 rejected all divalent cations and anions at high levels (>98%) for both investigated pressures of 20 and 30 bar, which confirms that the maximum applied pressure on the NF membrane cell should not exceed 20 bar. The results also showed that the DK membrane is preferable for high concentration of AMD, while NF99 is used, when high permeate flux is required. GE has the lowest rejection and permeate flux at all investigated conditions indicating inappropriateness in treating AMD solution. The only shortcoming of the NF method is scaling, especially for large membrane units. As a result, our future plan is to carry out further experiments to either use a suitable anti-scaling solution to minimize the scaling layer, or use different hybrid methods such as lime neutralization with NF membrane.

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