Abstract

Acidic Mine Waters (AMWs) are characterised by high acidity (pH<3) as H_2SO_4 and elevated contents of metals (Al, Fe, Cu, Zn), including rare earth elements (REEs). Due to the exhaustion of minable REE containing-minerals, AMWs are increasingly regarded as an alternative source of REEs. Among the different alternatives for the pre-concentration of AMWs required to make the REE extraction possible, nanofiltration (NF) membranes emerge as a promising technology because they not only successfully reject multivalent ions (metals), allowing its concentration in the retentate stream, but also permit the transport of monovalent ones, such as H^+ and HSO_4^-, allowing the recovery of sulphuric acid in the permeate. Despite this potential of NF, there is still a lack of modelling tools for predicting the performance of NF membranes because of its dependence on solution composition, membrane properties and interaction between both. In this study, a prediction tool based on the Solution-Electro-Diffusion model (including the effect of solution composition) was developed and experimentally validated for the application of two polyamide-based NF membranes (NF270 and Desal DL) for the recovery of REEs and H_2SO_4 from three different synthetic solutions mimicking AMWs (pH 1.0, 60 mg/L REEs and, 25-600 mg/L Al, Cu, Ca and Zn) differing in their Fe concentration (0-2125 mg/L). Metals were effectively rejected (>98%), whereas H_2SO_4 was transported across the membrane (H+ rejections <30%). The mathematical model was able to predict the performance of both membranes as well as the potential scaling events associated with Fe and Al hydroxides and hydroxy-sulphates.

Keywords: resource recovery; acidic mine waters; NF270; Desal DL; nanofiltration

1. Introduction

The European Union has identified a list of critical materials based on their high importance to its economy and the high risk associated with their supply. This list includes phosphorous, magnesium, tungsten, vanadium and rare earth elements (REEs), which comprise in turn lanthanides, scandium and yttrium, to name a few (European Commission, 2018). Because of their chemical and physical properties, REEs are widely used in electronic, optical, magnetic and nuclear applications, among others (MacLennan, 1989; Wu et al., 2018). Due to the scarcity of these critical elements, circular economy schemes are currently being proposed for their recovery from alternative sources and re-uses.

REEs are found in nature in sedimentary and igneous rocks as oxides. However, the exhaustion of these minerals has made that secondary resources such as permanent magnets, fluorescent lamps, nickel-metal hydride batteries and cathode-ray tubes from television or computer monitors are being evaluated as alternative REE sources (Binnemans et al., 2013). These solid wastes are usually leached with acids, and REE in the generated leachates can then be recovered by solvent extraction, yielding high purity REE-compounds (Jha et al., 2016; Xie et al., 2014).

Other wastes, such as acidic mine waters (AMWs), can be regarded also as REE sources, especially in Europe, which faces a shortage of REEs primary resources. Acidic mine waters (AMWs) are a by-product of the mining industry that occur when sulphide minerals, such as pyrite (FeS_2), are oxidised when entering in contact with water and oxygen. The oxidation of sulphide minerals leads to sulphuric acid production, which can dissolve the surrounding soil minerals. Then, a sulphuric-based stream containing a high content of iron, aluminium, zinc and copper, and a minor presence of REEs is released to the environment (Olías et al., 2004; Sánchez-Andrea et al., 2014; Simate and Ndlovu, 2014). One of the most known cases of AMW generation is allocated in the Iberian Pyrite Belt (South of Spain), where AMWs are

characterised by a pH ranging between 1 and 3.2 and a considerable amount of metals: Al, Fe, Zn, Cu, and Ni, among others. Harmful elements are also present, such as As(<100 mg/L), Cd (<2 mg/L), Cr (<2 ppm) and Pb (<4 ppm) and As (<10 mg/L), while REE at concentrations from 0.3 to 11.7 mg/L of REE (Ayora et al., 2016; Cánovas et al., 2007; Olías et al., 2016). Due to their composition, AMWs can cause acute and chronic diseases in both animals and plants. In animals heavy metals can accumulate in tissues and organs, disrupting their metabolic functions and inhibiting the absorption of vital minerals. In plants, the presence of heavy metals can cause oxidative stress that leads to cellular damage and disturbs the cellular ionic homeostasis, disrupting the physiology and morphology of plants. Moreover, low pH values typical of AMWs (<4.5) can also have adverse effects on many acid-sensitive aquatic organisms thant cannot tolerate these levels of acidity (Simate and Ndlovu, 2014). Such composition makes it necessary to treat AMWs properly in order to avoid environmental issues.

As stated above, AMWs can be considered as an alternative source for REEs recovery. However, due to the low concentration of REE in AMWs (in comparison with leachates from REE-containing minerals) it is desirable to concentrate them before acid neutralisation and solvent extraction steps are carried out for REE recovery. This concentration can be accomplished by membrane technologies (e.g. reverse osmosis (Zhong et al., 2007), forward osmosis (Qiu and He, 2019), nanofiltration (NF) (Ricci et al., 2015) or electrodialysis (Reig et al., 2018)). Among these, NF membranes are gaining importance and are increasingly applied for the treatment of a wide range of waters, including: brackish water (Su et al., 2017), surface water (Foureaux et al., 2019) and landfill leachates (Luo et al., 2020), among others. NF membranes have demonstrated to offer two-fold benefits when treating AMWs: on the one hand, they can concentrate multi-charged ions (and hence REEs) in the retentate side while, on the other hand, and thanks to their ability to allow permeation of mono-charged ions they can concentrate, under high acidity conditions typical of AMWs, H^+ and HSO_4^- (i.e. H_2SO_4) in the permeate side. This sulphuric acid stream can even be recycled and reused in leaching steps if

needed (Kose Mutlu et al., 2018; Mullett et al., 2014). Moreover, since one of the main issues when treating AMW is its large volume needed to be treated, NF membranes can arise as an effective means to reduce it by a factor from 2 to 3.

Nevertheless, and contrarily to reverse osmosis processes, there is still a lack of mathematical models to scale and predict the behaviour of NF membranes for treating AMWs. Mathematical models such as the so-called Solution-Electro-Diffusion (SED) one can describe the transport of species across NF membranes using membrane permeances. This model is based on two assumptions: (i) the separation is achieved due to differences in species diffusivities; and (ii) membranes do not present fixed pores but have a free volume instead (Yaroshchuk et al., 2011). In general, most of the efforts have so far been centred in the description of solutions containing strong electrolytes where the formation of chemical species between ions in solutions is not expected. However, such a scenario is only a too simple representation of real AMWs, where each element may give rise to multiple species in equilibrium with each other. Recent studies have included reactive transport (i.e. chemical association between species) to provide a more accurate approximation (López et al., 2018b; Niewersch et al., 2014). Despite these improvements in transport modelling through NF membranes, organic membrane fouling and scaling events have not been taken into consideration so far on the basis of the low contents of organic matter (below 5 mg/L measured as Total Organic Content), carbonate and phosphate (below 1 mg/L) is relatively low. Nevertheless, special attention must be directed towards the precipitation of sulphate-based minerals, especially Fe and Al hydroxy-sulphates (schwertmannite ($Fe_8O_8(OH)_6SO_4(s)$) and basaluminite ($Al_4SO_4(OH)_{10}\cdot 5H_2O$)), which can co-extract REEs in solution (Lozano et al., 2020, 2019). Therefore, the potential of scaling should be considered by any modelling algorithm aimed at describing transport through NF membranes.

This work addresses the lack of modelling tools for predicting the performance of NF membranes. A mathematical approach (based on SED model) is presented to predict the

behaviour of NF membranes when treating AMWs. Besides, the effect of solution composition on membrane performance was included in the mathematical approach by empirically adjusting the dependence of membrane permeances toward species on the concentration of main components in solution. In order to validate the results and the model, experiments were performed with two different NF membranes (NF270 and Desal DL).

2. Experimental

2.1. Membranes and solutions

Two commercial NF membranes were tested, namely NF270 (from Dow Chemical) and Desal DL (from GE Osmonics), both with a top layer based on a semi-aromatic poly-(piperazine amide). According to the manufacturers, Desal DL incorporates an additional proprietary second layer made of a material comparable to a polyamide, which impacts on membrane properties, such as surface roughness, hydrophilicity and acid-base properties. Both membranes have ionisable amine ($R–NH_2$/$R–NH_3^+$) and carboxylic ($R–COOH$/$R–COO^-$) groups, which are responsible for the membrane charge. The isoelectric points (IEPs) are 2.5 and 4.0 for NF270 and Desal DL, respectively (Kallioinen et al., 2016). The main properties of these membranes are collected in **Table S1 (Supplementary information)**.

The presence of Fe (as a mixture of Fe(II) and Fe(III)) in the AMW to be treated can limit the recovery options of REEs. For this reason, Fe(II) is sometimes pre-oxidized to Fe(III), which is then removed by precipitation with a low-cost alkali reagent (e.g. CaO or $CaCO_3$).

Three synthetic solutions mimicking an AMW from La Poderosa Mine at the Iberian Pyrite Belt (Huelva, Spain), having undergone different degrees of pre-oxidation for Fe removal, were treated. All these solutions contained a sulphuric media (pH around 1.0 ± 0.1) and Al(III) (600 mg/L), Ca(II) and Zn(II) (40 mg/L each), Cu (25 mg/L) and REE such as La, Dy, Nd, Pr, Sm and Yb (10 mg/L each one), but differed in their concentration of Fe(III), which was 0, 500 and 2125

mg/L. All metals (Al, Ca, Zn and Cu) were added as metal-sulphate salts, while REEs were added as chlorides, nitrates, sulphates or oxides. For two solutions, iron was added to the solution as Fe(II) in the form of $FeSO_4$, and was then oxidised with an excess of H_2O_2 (the double than the stoichiometric) to convert Fe(II) into Fe(III). The following solutions and salts were used: H_2SO_4 (96 wt%, Sigma-Aldrich); $Al_2(SO_4)_3 \cdot 18\ H_2O$ (55%, Panreac); $CaSO_4 \cdot 2H_2O$ (100%, Scharlau); $ZnSO_4 \cdot 7H_2O$ (100%, Panreac); $CuSO_4$ (100%, Panreac); $FeSO_4 \cdot 7H_2O$ (98%, Sigma-Aldrich); $La_2(SO_4)_3 \cdot 9H_2O$ (99.9%, Alfa Aesar); $Pr(NO_3)_3 \cdot 6H_2O$ (100% Fluka AG); $NdCl_3 \cdot 6H_2O$ (100%, Fluka AG); $SmCl_3$ (100%, Fluka AG); Dy_2O_3 (99.9%, Fluka AG) and Yb_2O_3 (99.9% Fluka AG), H_2O_2 (30%, Sigma-Aldrich).

A speciation analysis was performed before starting the experiments with the Hydra/Medusa and PHREEQC code (Puigdomenech, 2001; U.S. Geological Survey, 2017). According to it, metals can be present as a free ion (e.g. Al^{3+}, Ca^{2+}) or forming complexes with sulphate, giving negatively or positively charged ions (e.g. $AlSO_4^+$, $Al(SO_4)_2^-$, $CaHSO_4^+$) or even non-charged species (e.g. $CaSO_4$). Complexes with other anions were found at negligible concentrations. **Table S2 (Supplementary information)** collects the chemical equilibrium constants for metal – sulphate complexes, which were used in mathematical modelling.

Figure S1 (Supplementary information) represents the sulphate fraction for a solution mimicking the AMW at pH 1 as a function of Fe(III) concentration. It can be seen that the increase of Fe(III) concentration leads to an increase of iron-sulphate complexes (i.e. $FeHSO_4^{2+}$, $FeSO_4^+$ and $Fe(SO_4)^{2-}$), whereas the fraction of hydrogen–sulphate (HSO_4^-) and sulphate (SO_4^{2-}) decrease. The other metals, as shown in **Table S2**, also form complexes with sulphate, but their concentration in terms of sulphate fraction is lower than 1%, and therefore their profiles are not depicted in **Figure S1.**

2.2. *Membrane cross-flow experimental set-up*

Experiments were carried out with a membrane cross-flow cell (GE SEPA^{TM} CF II) using a flat-sheet membrane (0.014 m^2). A thermostated 30 L tank was used to keep the synthetic solution to be treated at a constant temperature (25 ± 2 °C). Then, a high-pressure diaphragm pump (Hydra-Cell, USA) was used to pump the solution into the membrane cell at a prefixed flow rate and pressure. The set-up was provided with a needle and a by-pass valve to vary the cross-flow velocity (cfv) and the trans-membrane pressure (ΔP). The first one was located at the retentate stream, just at the exit from the membrane test cell, whereas the other valve was placed before the entrance of the solution into the module. At the feed and concentrate lines, two manometers were placed to monitor the pressure. Just before the discharge of the retentate to the tank, a flow-meter and a pre-filter cartridge (100 µm, polypropylene) were placed. Pipes were made of stainless steel to avoid corrosion issues. A scheme of the experimental set-up is shown in **Figure 1**.

Membranes were placed overnight in Milli-Q water to remove their conservation products. After that, deionised water flows across the test cell at 22 bar and cfv of 1 m/s (5 L/min) for 2h to compact the membrane. Samples of 30 mL of permeate were collected for measurements of the permeate flux (and,, with it, of the hydraulic permeability of the membrane) as well as the conductivity to determine when the membrane was compacted.

Before running an experiment, the membrane was compacted with the AMW at the same ΔP and cfv for 2 h. At this stage, both retentate and permeate were recycled back to the feed tank to keep the same conditions along with the membrane compaction. As in the previous case, permeate samples of 30 mL were taken and its conductivity was measured to ensure that the membrane was pressurised.

Experiments were run at a pre-fixed cfv of 0.7 m/s (3.46 L/min), and the ΔP was kept constant at 20 bar. During a filtration experiment, only retentate was recirculated back to the feed tank,

while permeate was continuously removed from the system. In previous studies, the effect of ΔP on rejections was suited, and it was observed that at 20 bar metal rejections were high (>98%), while the transport of H_2SO_4 was not impeded across the membrane (López et al., 2019a). Moreover, at that ΔP concentration polarization was not observed. After collecting 500 mL of permeate and onwards, samples of the solution in the feed tank and permeate (30 mL each one) were analysed and data were represented as a function of permeate recovery, defined as follows (**Eq. 1**) (Schäfer et al., 2005):

$$\%\ permeate\ recovery = \frac{V_{t=0} - V_t}{V_{t=0}}\ x\ 100 \qquad (1)$$

Where $V_{t=0}$ (27 L) and V_t are the volumes of the feed tank solutions at the beginning of the experiment and at time t, respectively.

The concentration factor for a given species was defined as the ratio between the concentration of that species in the feed tank at time t and its initial concentration (C_t/C_0).

Experiments were finished when 30% of permeate recovery was achieved. Then the set-up was cleaned with deionised water for 1h and 30 min at 22 bar and cfv of 1 m/s to remove any impurity that might be left inside the cell.

All the experiments were carried out in duplicate. Samples from the feed tank and permeate were analysed during the experiments with a pH-meter and a conductivity-meter as a preliminary analysis to monitor the membrane performance.

2.3. Analytical methods

2.3.1. Measurement of the concentration of the elements in solution

In order to determine the concentration of the solution elements, samples were analysed using Inductively Coupled Plasma Mass (7800 ICP-MS from Agilent Technologies) and Optical Emission Spectrometer (5100 ICP-OES from Agilent Technologies). Before ICP analysis, samples

were previously filtered (0.2 µm) and acidified with 2% HNO_3. Samples were analysed by an external laboratory.

2.3.2. Measurement of the acidity of the samples

Concerning the determination of the concentration of H^+ with a pH-meter, it must be highlighted that the analysable pH range with glass electrodes was, according to the manufacturer, from 2 to 12, which implied that any measurement of pH in the range of 1 to 2 might have associated a high error and should be regarded as an approximation. Acidity measurements by acid-base titration could not be done due to the precipitation of Fe and Al as hydroxides along with the titration. Therefore, the acidity of the samples was determined with a pH-meter (Crison® GLP21).

3. Numerical tool for prediction of the membrane performance

The equations presented in what follows were applied to the membrane itself (red box in **Fig. 2**), the membrane test cell (green box in **Fig. 2**) and the tank (orange box in **Fig. 2**) to predict the behaviour of the experimental system.

The transport of ions across the NF membranes was described on the basis of the SED model, which was coupled with reactive transport taking into account the chemical speciation in solution. The transport of species across a NF membrane is defined as a combination of diffusion and electromigration, whereas it is assumed there is no coupling between species and solvent (i.e. no convective flux occurs). The model uses "virtual concentrations", which are defined as those in thermodynamic equilibrium with an infinitely small volume inside the membrane. Thus, species flux is described according to **Equation 2** (Niewersch et al., 2014):

$$j_i = -P_i \cdot \left(\frac{dc_i}{dx} + c_i \cdot \frac{d(\ln \gamma_i)}{dx} + z_i \cdot c_i \cdot \frac{d\varphi}{dx} \right) \quad (2)$$

where j_i, P_i, c_i, γ_i and z_i are the flux across the membrane, the membrane permeance, the concentration, the activity coefficient and the valence charge of species i, respectively. x is the dimensionless position in the membrane, and φ is the dimensionless virtual electrostatic potential in the membrane.

The transport of any species i across the membrane must satisfy: i) chemical equilibrium reactions between species, which once identified allow their flux to be solved (**Eq. 2**) for each element that composes the species (e.g. equation referred to Al is a sum of the flux of Al^{3+}, $AlSO_4^+$ and $Al(SO_4)_2^-$) and ii) electroneutrality condition, defined as follows (**Eq. 3**) :

$$\sum_{i=1}^{n}(z_i \cdot c_i) = 0 \qquad (3)$$

The membrane permeance to a given species i (P_i), which indicates the easiness of this species to be transported across the membrane, is acknowledged to depend on the membrane, the species properties and the composition of the solution (e.g. concentration of H^+ or Fe(III)). Partition coefficients and possible changes in the chemical equilibrium constants are included within the membrane permeances to ions (Yaroshchuk et al., 2011).

The SED model has proven to successfully describe rather complex experimental trends in NF of electrolyte mixtures containing various dominant salts and trace ions. In previous studies, the permeance of membranes NF270 and Desal DL towards the same solutes as the ones investigated in the present study (Al, Ca, Zn, Cu, REE, SO_4) were determined under a variety of pH values and Fe(III) concentrations at constant feed composition from 4 to 22 bar (these values are collected in **Tables S3 and S4 Supplementary Information**). However, determined membrane permeances were not constant and depended on solution composition.

In this work, since the permeate was continuously removed from the system while only retentate was recirculated back to the feed tank, it was expected that the feed solution composition changed with time and, with it, the membrane permeances towards the different

ions. One objective of this study was to fit permeances as a function of pH and Fe concentration from values obtained in previous studies through an expression like **Equation 4**, as proposed by Bason et al. (Bason et al., 2010) and Yaroschuck (Yaroshchuk, 2002):

$$P_i = a_o + a_1 \cdot X^{a_2} \quad (4)$$

where a_0, a_1 and a_2 are fitting parameters and X is the concentration of H^+ or the one of Fe(III), so that membrane permeances in this study could be predicted at any time as feed composition changed with time

The flux of solvent across the membrane was described with the following equation (**Eq. 5**) (Schäfer et al., 2005):

$$J_v = k_w \cdot (\Delta P - \Delta\pi) \quad (5)$$

where J_v is the solvent flux across the membrane, k_w is the hydraulic permeability of the membrane, ΔP and $\Delta\pi$ are the differences of pressure and osmotic pressure between feed and permeate. Osmotic pressure is calculated according to the van't Hoff equation.

In the membrane test cell, global and component mass balances were solved to determine the concentration and flow of the retentate stream (**Eqs. 6.a** and **6.b**):

$$Q_f = Q_r + Q_p \quad (6.a)$$

$$c_f \cdot Q_f = c_r \cdot Q_r + c_p \cdot Q_p \quad (6.b)$$

where Q and c are the flow and concentration, respectively. Subscripts f, r and p refer to the feed, retentate and permeate, respectively.

Finally, an unsteady state mass balance is solved in the feed tank to determine how the volume of the solution varied and how the different compounds were concentrated along with the time (**Eqs. 7.a** and **7.b**).

$$\frac{dV}{dt} = Q_r - Q_f \tag{7.a}$$

$$\frac{d(c_{f,i} \cdot V)}{dt} = Q_r \cdot c_{r,i} - Q_f \cdot c_{f,i} \tag{7.b}$$

where V is the tank volume and t is the running time of the experiment.

After solving **Equations 7.a** and **7.b**, a speciation analysis must be performed to determine the composition of the different species in the feed, and then solve **Equation 2**.

The numerical code was implemented in Matlab to predict the performance of the system (**Figure 2**).

Although the implemented SED model does not contemplate concentration polarisation phenomenon due to the mathematical complexity of the system, the saturation indexes (SI) of the potentially expected mineral phases were evaluated (**Eq. 8**) (Schäfer et al., 2005).

$$SI = \log\left(\frac{IAP}{K_{so}}\right) \tag{8}$$

Where K_{so} is the solubility constant and IAP is the ionic activity product of a given potential mineral involved in a scaling or inorganic fouling event. For example, for the precipitation of jurbanite (i.e. $AlOHSO_4$ (s)) (**Eq. 9**):

$$AlSO_4OH(s) + H^+ \Leftrightarrow Al^{3+} + SO_4^{2-} + H_2O \tag{9.a}$$

$$SI = \log\left(\frac{IAP}{K_{so}}\right) = \log\left(\frac{[Al^{3+}][SO_4^{2-}][OH^-]}{K_{so}}\right) \tag{9.b}$$

Table S5 (Supplementary information) shows a summary of the main mineral phases expected to be formed in the feed solution. The commonly used software designing tools for RO applications (e.g. Wave (Dow-Chem), Hydranautics, Wind-Flow (Suez)) predicts saturation conditions and therefore scaling on the membranes. For such calculus, they consider

concentration polarisation factors. In this case, a factor of 10 was considered to assess the potential fouling at the membrane.

4. Results and discussion

4.1. Dependence of membrane permeances of solution composition

Three different synthetic AMWs containing different concentrations of Fe (0, 500 and 2125 mg/L) were filtered with the NF270 and Desal DL membranes. To address the influence of acidity and Fe(III) concentration on membrane permeances to each species (P_i) experimental data on P_i calculated in previous studies and collected in **Supplementary information (Tables S3 and S4)** were fitted to **Eq. 4**. P_i in the experiments without Fe(III) was expressed as a function of H^+ concentration, while P_i in those containing Fe(III) was fitted as a function only of Fe concentration (pH was around 1.0 ± 0.1, and its effect on P_i was expected irrelevant because membrane charge will not be modified). As an example, **Figure 3** shows the fitting of NF270 membrane permeance values as a function of Fe(III) concentration. For Desal DL the fitting (not shown here) was as good as the one for NF270 permeances.

4.2. Prediction capabilities of the solution-electro-diffusion model in acidic waters and validation with experimental data

4.2.1. Comparison of NF270 and Desal DL membranes for Fe(III) free acidic waters at pH 1.0

Figure 4 shows the concentration variation of the different species in the feed tank and the permeate streams when filtrating a synthetic AMW without Fe(III) at pH 1.0 for the NF270 (**Figs. 4.a and 4.b**) and Desal DL (**Figs. 4.c and 4.d**) membranes.

The results for both membranes with the solution without Fe(III) showed the potential treatment capacity of AMWs with NF. Within the percentage of permeate recovery range

studied (0-30%), both membranes rejected metals from the feed stream at percentages higher than 98% and yielded a permeate rich in sulphuric acid (6 g/L for N270 and 5 g/L for Desal DL, sulphate rejections of 55% for NF270 and 69% for Desal DL) with a minor presence of metallic impurities (below 5 mg/L for both membranes) (**Figure 4**). A ratio 1:1 between H^+ and S (mainly as HSO_4^-) in the permeate was observed for both membranes, which indicated that permeate was mainly composed of purified sulphuric acid. In addition, such rejection of metals (>98%) made feasible concentrating REEs by a 50% at 30% of permeate recovery. This similar behaviour between these two membranes could be related to the resemblance of the composition of their active layers (both membranes are polyamide-based). In terms of water flux across the membrane, NF270 had higher membrane permeability due to its lower polyamide layer thickness (Tang et al., 2009), exhibiting then greater permeate fluxes, which is in agreement with the membrane properties shown in **Table S1**. As in the previous studies, NF270 and Desal DL were able to reject the metal species effectively (e.g. >98%) while they allowed acid to permeate easily across the. Moreover, as in the present case, NF270 was prone to transport better the acid than Desal DL.

These results can be explained on the basis of the main exclusion phenomena taking place in NF membranes: the Donnan and dielectric exclusion. At pH 1.0, both NF270 and Desal DL membranes (whose IEPs are 2.5 4.0, respectively, and thus above the pH of the feed solution) are expected to be positively charged due to the partial and fully protonation of amine (R–NH_3^+) and carboxylic groups (R–COOH), respectively. This fact originates electrostatic repulsions between the charged membrane surface and the metallic cations (e.g. Al^{3+}, Ca^{2+}, Cu^{2+}), which explains why these metallic cations were effectively rejected (Donnan exclusion) (Yaroshchuk, 2001). Conversely, the transport of anions (e.g. HSO_4^-) would be favoured because of the electrostatic attractions between them and the positively charged membrane surface. This phenomenon explained why both membranes permitted easy transport of sulphate (HSO_4^-/SO_4^{2-}) through them. Nevertheless, a stoichiometric number of cations must

permeate to achieve electroneutrality conditions in the permeate side. Then, the H^+ was transported across the membrane because of its higher diffusivity, lower size and lower absolute charge than the rest of cations (Robinson and Stokes, 2002).

On the other hand, the dielectric exclusion must also be considered to explain the transport of ions across the membrane. The cause of this phenomenon is found in the interactions that arise between the ions and bound electric charges induced in the membrane at the interface solution/membrane with different dielectric constants (i.e. polymeric matrix/bulk solution). The effect of dielectric exclusion is more pronounced than the one of Donnan exclusion because the ion-exclusion free energy is dependent on the square of the ion charge, while the Donnan exclusion's is linear with it (Kim et al., 2005; Yaroshchuk, 2000). Dielectric exclusion explained why the transport of multivalent metallic impurities (i.e. Al^{3+}, Ca^{2+} and Cu^{2+}) was more impeded than that of H^+.

Donnan and dielectric exclusion phenomena are responsible for the high selectivity of both membranes for sulphate over metal ions.

In **Figure 4** the predicted concentration values (solid lines) were calculated by using the permeances to species from **Supplementary Information (Tables S3 and S4)**. As can be seen, the calculated concentration values matched the experimental values consistently in the feed tank for both membranes and both dominant and minor species in solution. With regard to the permeate stream, a good matching was generally obtained, although significant discrepancies were observed for H^+ and Al for the NF270 membrane. The discrepancy in acidity values could be due to the fact that their activity values (a_{H^+}) were determined with a pH glass electrode.

4.2.2. Comparison of NF270 and Desal DL membranes for acidic waters containing Fe(III) at pH 1.0: influence of the Fe(III) concentration

The influence of the Fe(III) concentration in the metal concentration and H_2SO_4 recovery factors was studied at two different levels 500 mg/L and 2125 mg/L. **Figure 5** shows the

evolution of the concentration of the different studied solutes in the feed tank and the permeate in the presence of 500 mg/L Fe(III) in the initial solution for NF270 (**Figs. 5.a and 5.b**) and Desal DL (**Figs. 5.c and 5.d**) membranes, respectively.

The presence of Fe(III) resulted in higher rejection percentages of sulphate across the membrane (67% for NF270 and 75% for Desal DL in front of 55 % and 69% in the absence of Fe). The reason for such increase lies on sulphate speciation. In fact, the increase of Fe(III) concentration implied an increase of the positively-charged species $FeSO_4^+$ and $FeHSO_4^{2+}$ molar fractions, while a decrease of the negatively-charged species HSO_4^- and SO_4^{2-} (see **Figure S1**), resulting in enhanced overall transport of sulphate across the membrane due to Donnan and dielectric exclusion phenomena (Kim et al., 2005; Yaroshchuk, 2000). Moreover, the lower presence of HSO_4^- and SO_4^{2-} led also to a lower concentration of sulphate in the permeate (see **Figure S1**).

Fe(III) exhibited a similar behaviour than Al(III) (see **Figures 5.a and 5.c**). Both membranes effectively rejected Fe(III) (>98%), and the content of metallic impurities in the permeate were below 7 mg/L for NF270 and 4 mg/L for Desal DL for each metal (see **Figures 5.b and 5.d**). Moreover, the fact that Fe(III) was present in solution did not modify the concentration factor for REEs (1.5 at 30% of permeate recovery). Similarly to the previous case in the absence of Fe(III), NF270 provided a permeate stream richer in sulphuric acid than Desal DL (4.5 g/L and 3.6 g/L H_2SO_4, respectively), as it can be seen in **Figures 5.a and 5.c**. The higher concentration of HSO_4^- in solution favoured the passage of H^+ across the membrane.

The prediction capacity of the numerical code showed similar levels of accuracy than for the solution without Fe(III). The better predictions for NF270 than for Desal DL, despite their similar chemical properties from the point of view of the active layer, could be associated to the fact that the data set of membrane permeances for the former has been more studied than that of the latter.

The membranes performance in filtrating acidic water with high Fe(III) contents (2125 mg/L) is shown in **Figure 6. Fig. 6.a and 6.c** represent the concentration profile in the feed tank while **Fig. 6.b and 6.c** show the concentration in the permeate, respectively.

The increase of Fe(III) up to 2125 mg/L led to even higher sulphate rejections (73% for NF270 and 84% for DL) (see **Figure 5 and 6**) for the same speciation reasons discussed above (see **Figure S1**). The main impurity in the permeate was Fe(III), reaching concentrations up to 68 mg/L for NF270 and 25 mg/L for Desal DL, while the other metals (i.e. Al, Ca, Cu, Zn and REEs) remained below 10 mg/L for both membranes. Again NF270 yielded a richer stream in H_2SO_4 (4.2 g/L) than Desal DL (3.5 g/L), while both membranes achieved similar metal concentration factors. The prediction provided by the SED model described this increase of Fe(III) in the permeate up to 20-30 mg/L Fe(III) for Desal DL while predicted values for NF270 where much lower than those measured experimentally (up to 70 mg/L).

Table 1 collects the permeate composition at 25% recovery for the experiments performed. As can be seen, the presence of Fe(III) resulted in a hindered transport of sulphuric acid across the membrane and therefore in a lower concentration of sulphuric acid in the permeate, which presented increased concentration of metal impurities if compared in the absence of Fe(III). On the other hand, heavy metals were effectively removed from solution (removal percentages mostly >98%) as it occurred in the absence of Fe(III). While these streams may exhibit some toxicity to aquatic organisms due to their high contents of metals (for the retentate) or low pH (for the permeate) (Simate and Ndlovu, 2014), they are not planned to be discharged into waterbodies but to be treated instead for the recovery of metals an sulphuric acid, respectively.

Both membranes (NF270 and Desal DL) have been studied previously in the literature for wastewaters treatment. Niewersch et al. (2010) studied the selectivity of Desal DL for cations (Al, Fe, Cr, Cu) and phosphoric acid when filtering sewage ash eluates and observeda high

passage of phosphorous, while metals such as Cu were effectively rejected (>93%) at ΔP higher than 17 bar for permeate recoveries ranging from 17 to 90%. This selectivity was found to be dependent on effective pressure and composition of feed solution. Wadekar and Vidic (2018) compared the performance of a TiO_2 ceramic (from Cerahelix) and a polymeric (NF270) NF membranes for treating mine drainage from a coal mine (pH 7.8). Ranging from permeate recoveries between 0 to 75% at ΔP of 35 bar, they found that NF270 rejected effectively (>96%) divalent and trivalent metal ions (e.g. Al(III), Ca(II) and Mg(II), among others), whereas Cl and As exhibited the lowest rejections (<10% and 20% for Cl and As, respectively). At the same time, NF270 was able to recover purified water as permeate at pH 7.8. The ceramic membrane showed metal rejections between 55 and 67%, with lower rejections of Cl and As (<20%).

The conventional ex-situ treatment of AMWs relies on acid neutralisation and metal precipitation by the addition of an alkali. The drawback of this treatment is the generation of a voluminous sludge rich in water, with a solid content of only 2-4%, which makes necessary further solid-liquid separation units (Johnson and Hallberg, 2005; Santos et al., 2004). Nevertheless, in such a treatment no valorisation of the acidic stream is considered, since acid is neutralised and metals are precipitated all together and not recovered. Valorisation of AMWs using membrane technologies other than NF ones has also been researched. For example, Martí-Calatayud et al. (2014) treated an AMW (pH 1.68, 0.02 M $Fe_2(SO_4)_3$, 0.01 M Na_2SO_4) with electrodialysis and obtained a stream with a high concentration of H_2SO_4, while Fe(III) precipitated as $Fe(OH)_3$, which caused an increase in the specific energy consumption from 6 to 15 kWh/kg. Amaya-Vías et al. (2019) evaluated membrane distillation with PTFE membranes for the treatment of an AMW (pH 2.1, 10.5 g/L SO_4, 0.81 g/L Mg and 0.73 g/L Fe) at different temperatures (50-80 °C), obtaining high permeate fluxes (up to 16.80 L/m^2h) with high metal rejections (99%). Despite the good performance of these techniques from the point of view of solutes recovery, it must be taken into account that the high energy requirements

for electrodialysis (electrical) and membrane distillation (thermal) turn both technologies unsuitable for the valorisation of AMWs, making NF a very cost-effective alternative.

From the experimental results, it has been seen that the presence of Fe hinders the recovery of purified H_2SO_4 in the NF permeate, making thus it necessary to remove all Fe(III) before the NF stage. This can be achieved by Fe(III) precipitation at pH ca. 4.0 with the addition of an alkali agent (e.g. caustic soda, ammonia, soda ash or hydrated lime). However, because REEs can easily precipitate with basaluminite ($Al_4SO_4(OH)_{10}{\cdot}5H_2O$) after the NF stage at pH 4.0 (Ayora et al., 2016), Fe(III) precipitation must be accomplished at pH<4.0. Once Fe is precipitated, it would be recommended to decrease the pH down to 1.0 using, e.g. the permeate rich in H_2SO_4 to ensure that NF membranes are positively charged and that they effectively concentrate REE in the feed tank.

4.3. Predicting the performance of NF270 and Desal DL at different operation parameters

As shown in the previous section, the model was capable of predicting the concentration in the permeate and feeding tank solution within the evaluated %permeate recovery range. Because of mechanical limitations of the experimental set-up, a parametric study was carried out to study the effect of ΔP (10, 20, 40 and 60 bar) within a range of %permeate recovery (0-80%) on metal rejection (and thus concentration factors) and sulphuric acid recovery in the permeate with the composition of the solution containing 500 mg/L Fe(III).

Table 2 collects the concentration factor of the elements in the feed solution (i.e. metals, REEs and sulphuric acid) at the ΔP mentioned above, respectively.

For all the ΔP evaluated, the transport of double and triple-charged metallic cations through the studied membranes was effectively hindered by Donnan and dielectric exclusion phenomena, leading to higher concentration factors when %permeate recovery increased. As mentioned before, the transport of HSO_4^- was favoured by the membrane charge at the low

working pH (1.0), which forced H^+ to be also transported to achieve electroneutrality conditions in the permeate. As a result, a permeate rich in sulphuric acid was obtained. Rejections of H^+ were around 20% lower for Desal DL than for NF270, representing a drawback for the former in the recovery of sulphuric acid in the permeate. **Figure 7.a** collects the sulphuric acid concentration in the permeate. NF270 would allow to obtain a higher sulphuric acid concentration in the permeate than Desal DL at the same conditions (pressure, %permeate recovery).

For example, at 10 bar and 80% of permeate recovery, acid concentration in the permeate was 6.6 g/L and 6.2 g/L for NF270 and Desal DL, respectively. By increasing the pressure, lower acid concentration in the permeate would be achieved (**Fig. 7.a**), but the molar flux of acid increased (**Fig. 7.b**).

Regarding the effect of ΔP on concentration factors (see **Table 2**), similar metal concentration factors were achieved at all ΔP tested (10, 20, 40 and 60 bar). The only difference observed between experiments run at different ΔP was that trans-membrane fluxes increased with ΔP (Fig. 8.c). A comparison between membranes showed that both membranes exhibited high metal rejections, leading to similar concentration factors for the different evaluated ΔP and %permeate.

In the light of these findings, it could be anticipated that NF270 was a more suitable membrane for acid recovery, especially working at ΔP of 10 bar, because H^+ permeation through this membrane was higher than for the Desal DL one. At this ΔP, the low H^+ rejection favoured to obtain a richer sulphuric acid permeate (6.6 g/L at 80% of permeate recovery). In addition, the high metal rejections (>98%) allowed to concentrate the metals independently of ΔP up to a factor of 5 at 80% permeate recovery.

For all the conditions evaluated, calculation of SI values for minerals with potential to cause scaling and inorganic fouling (collected in **Table S5**). SI values for the mineral phases of

jurbanite ($AlOHSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$) were close to zero, indicating that their precipitation on the membrane was plausible.

5. Conclusions

Polyamide-based NF membranes have shown their potential for their integration in the treatment of AMWs since they allow the recovery of sulphuric acid as permeate and concentrate the metals and REEs in the feed tank solution. The recovered sulphuric can be beneficial as it can be reused on the pre-processing stages and additionally lowers the cost of alkalis. Both membranes (NF270 and Desal DL) exhibited a similar behaviour due to their similar active layer, but the first one is preferred since it presents higher water permeability. Results showed that the electric fields originated between the membrane and dissolved species govern the separation (Donnan and dielectric exclusion). Therefore, metallic ions were effectively rejected by the membrane (>98%) whereas sulphuric acid was transported (H^+ rejections below 30%).

The set of membrane permeances from previous works was fitted as a function of the proton and total sulphate concentration. With such expressions, it could be possible to take into account the effect of solution composition within the separation.

Finally, a solution to the lack of NF prediction tools for the design and integration of NF technology in the treatment of AMWs applications has been developed. This model can be used to predict the behaviour of any effluent in continuous mode (with recirculation only of the retentate) by knowing how the membrane permeances. The algorithm integrating the SED model and reactive transport has proven its applicability to determine the metal concentration factors and the sulphuric acid recovery at different % permeate recovery ratios. In addition, the equations previously developed, allowed to take into account the effect of feed solution composition in the separation process. Additionally, the prediction of the acidity and total

sulphate concentration are critical factors to determine the potential scaling and inorganic fouling events. The use of NF membranes as a technology for liquid effluents management in the mining industry could promote the reduction of the large volumes of waters that need to be treated and, at the same time, be helpful in reducing the metal and non metal discharges to the environment.

Acknowledgements

This research was supported by the Waste2Product project (CTM2014-57302-R) and by the R2MIT project (CTM2017-85346-R) financed by the Spanish Ministry of Economy and Competitiveness (MINECO) and the Catalan Government (2017-SGR-312), Spain. MINECO supported the work of Julio López and Xanel Vecino within the scope of the grant (BES-2015-075051) and the Juan de la Cierva contract (IJCI-2016-27445), respectively. We also want to thank the contribution of Dow Chemical for the supply of the membranes; to C. Ayora (IDAEA-CSIC) for AMW supply and helpful discussion on AMW treatments, to T. Susín for his help during the modelling stage; to L. Vilaplana for her help during the experimental work and to A. Espriu-Gascón and A. Díaz for the ICP analysis.

Nomenclature

a_0, a_1, a_2	Fitting parameters in Eq. 4 (-)
c	Concentration (mol/L)
IAP	Ionic activity product
j_i	Species flux across the membrane (mol/(L·µm/s))
J_v	Solvent flux across the membrane (µm/s)
$K_{T,I}$	Chemical equilibrium constant
K_{so}	Solubility constant of the mineral
k_w	Hydraulic permeability of the membrane (µm/(s·bar))
P_i	Membrane permeance (µm/s)
Q	Flow (L/min)
SI	Saturation index (-)
V	Tank volume (L)
x	Dimensionless position in the membrane (-)

X	H^+ or Fe(III) concentration in the tank in Eq. 4 (mol/L)
z	Valence charge (-)
ΔP	Trans-membrane pressure (bar)
$\Delta\pi$	Difference of osmotic pressure across the membrane (bar)
γ	Activity coefficient (-)
φ	Dimensionless virtual electrostatic potential in the membrane (-)

Subscripts

f	Feed
i	Species i
p	Permeate
r	Retentate
t	Time

References

Amaya-Vías, D., Tataru, L., Herce-Sesa, B., López-López, J.A., López-Ramírez, J.A., 2019. Metals removal from acid mine drainage (Tinto River, SW Spain) by water gap and air gap membrane distillation. J. Memb. Sci. 582, 20–29. https://doi.org/10.1016/j.memsci.2019.03.081

Ayora, C., Macías, F., Torres, E., Lozano, A., Carrero, S., Nieto, J.M., Pérez-López, R., Fernández-Martínez, A., Castillo-Michel, H., 2016. Recovery of Rare Earth Elements and Yttrium from Passive-Remediation Systems of Acid Mine Drainage. Environ. Sci. Technol. 50, 8255–8262. https://doi.org/10.1021/acs.est.6b02084

Bason, S., Kaufman, Y., Freger, V., 2010. Analysis of Ion Transport in Nanofiltration Using Phenomenological Coefficients and Structural Characteristics. J. Phys. Chem B 114, 3510–3517. https://doi.org/10.1021/jp911615n

Binnemans, K., Jones, P.T., Blanpain, B., Van Gerven, T., Yang, Y., Walton, A., Buchert, M., 2013. Recycling of rare earths: A critical review. J. Clean. Prod. 51, 1–22. https://doi.org/10.1016/j.jclepro.2012.12.037

Cánovas, C.R., Olías, M., Nieto, J.M., Sarmiento, A.M., Cerón, J.C., 2007. Hydrogeochemical characteristics of the Tinto and Odiel Rivers (SW Spain). Factors controlling metal contents. Sci. Total Environ. 373, 363–382. https://doi.org/10.1016/j.scitotenv.2006.11.022

Dow Chemical, C., n.d. FILMTEC NF270 Nanofiltration Elements for Commercial Systems.

European Commission, 2018. Report on Critical Raw Materials and the Circular Economy PART 3/3, Publications Office of the European Union. https://doi.org/10.1097/PPO.0b013e3181b9c5d5

Foureaux, A.F.S., Reis, E.O., Lebron, Y., Moreira, V., Santos, L. V., Amaral, M.S., Lange, L.C.,

2019. Rejection of pharmaceutical compounds from surface water by nanofiltration and reverse osmosis. Sep. Purif. Technol. 212, 171–179. https://doi.org/10.1016/j.seppur.2018.11.018

Jha, M.K., Kumari, A., Panda, R., Rajesh Kumar, J., Yoo, K., Lee, J.Y., 2016. Review on hydrometallurgical recovery of rare earth metals. Hydrometallurgy 165, 2–26. https://doi.org/10.1016/j.hydromet.2016.01.035

Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. Sci. Total Environ. 338, 3–14. https://doi.org/10.1016/j.scitotenv.2004.09.002

Kallioinen, M., Sainio, T., Lahti, J., Pihlajamäki, A., Koivikko, H., Mattila, J., Mänttäri, M., 2016. Effect of extended exposure to alkaline cleaning chemicals on performance of polyamide (PA) nanofiltration membranes. Sep. Purif. Technol. 158, 115–123. https://doi.org/10.1016/j.seppur.2015.12.015

Kim, S.H., Kwak, S.-Y., Suzuki, T., 2005. Evidence to demonstrate the flux-enhancement mechanism in morphology-controlled thin-film-composite (TFC)membrane. Environ. Sci. Technol. 39, 1764–1770.

Kose Mutlu, B., Cantoni, B., Turolla, A., Antonelli, M., Hsu-Kim, H., Wiesner, M.R., 2018. Application of nanofiltration for Rare Earth Elements recovery from coal fly ash leachate: Performance and cost evaluation. Chem. Eng. J. 349, 309–317. https://doi.org/10.1016/j.cej.2018.05.080

López, J., Reig, M., Gibert, O., Cortina, J.L., 2019a. Recovery of sulphuric acid and added value metals (Zn, Cu and rare earths) from acidic mine waters using nanofiltration membranes. Sep. Purif. Technol. 212, 180–190. https://doi.org/10.1016/j.seppur.2018.11.022

López, J., Reig, M., Gibert, O., Cortina, J.L.L., 2019b. Integration of nanofiltration membranes in recovery options of rare earth elements from acidic mine waters. J. Clean. Prod. 210, 1249–1260. https://doi.org/10.1016/j.jclepro.2018.11.096

López, J., Reig, M., Gibert, O., Torres, E., Ayora, C., Cortina, J.L., 2018a. Application of nanofiltration for acidic waters containing rare earth elements: Influence of transition elements, acidity and membrane stability. Desalination 430, 33–44. https://doi.org/10.1016/j.desal.2017.12.033

López, J., Reig, M., Yaroshchuk, A., Licon, E., Gibert, O., Cortina, J.L., 2018b. Experimental and theoretical study of nanofiltration of weak electrolytes: SO42–/HSO4–/H+system. J. Memb. Sci. 550, 389–398. https://doi.org/10.1016/j.memsci.2018.01.002

Lozano, A., Ayora, C., Fernández-Martínez, A., 2020. Sorption of rare earth elements on schwertmannite and their mobility in acid mine drainage treatments. Appl. Geochemistry 113, 104499. https://doi.org/10.1016/j.apgeochem.2019.104499

Lozano, A., Ayora, C., Fernández-Martínez, A., 2019. Sorption of rare earth elements onto basaluminite: The role of sulfate and pH. Geochim. Cosmochim. Acta 258, 50–62. https://doi.org/10.1016/j.gca.2019.05.016

Luo, H., Zeng, Y., Cheng, Y., He, D., Pan, X., 2020. Recent advances in municipal landfill leachate: A review focusing on its characteristics, treatment, and toxicity assessment. Sci. Total Environ. 703, 135468. https://doi.org/10.1016/j.scitotenv.2019.135468

MacLennan, S.M., 1989. Rare Earth Elements in sedimentary rocks: Influence of provenance and sedimentary processes. B.R. Lipin G.A. McKay “Geochemistry Mineral. Rare Earth Elem. Rev. Mineral. 169 – 200.

Martí-Calatayud, M.C., Buzzi, D.C., García-Gabaldón, M., Ortega, E., Bernardes, A.M., Tenório, J.A.S., Pérez-Herranz, V., 2014. Sulfuric acid recovery from acid mine drainage by means of electrodialysis. Desalination 343, 120–127. https://doi.org/10.1016/j.desal.2013.11.031

Mullett, M., Fornarelli, R., Ralph, D., 2014. Nanofiltration of mine water: impact of feed pH and membrane charge on resource recovery and water discharge. Membranes (Basel). 4,

163–180. https://doi.org/10.3390/membranes4020163

Niewersch, C., Bloch, A.L.B., Yüce, S., Melin, T., Wessling, M., 2014. Nanofiltration for the recovery of phosphorus — Development of a mass transport model. Desalination 346, 70–78. https://doi.org/10.1016/j.desal.2014.05.011

Niewersch, C., Meier, K., Wintgens, T., Melin, T., 2010. Selectivity of polyamide nanofiltration membranes for cations and phosphoric acid. Desalination 250, 1021–1024. https://doi.org/10.1016/j.desal.2009.09.097

Olías, M., Nieto, J.M., Pérez-López, R., Cánovas, C.R., Macías, F., Sarmiento, A.M., Galván, L., 2016. Controls on acid mine water composition from the Iberian Pyrite Belt (SW Spain). Catena 137, 12–23. https://doi.org/10.1016/j.catena.2015.08.018

Olías, M., Nieto, J.M., Sarmiento, A.M., Cerón, J.C., Cánovas, C.R., 2004. Seasonal water quality variations in a river affected by acid mine drainage: The Odiel River (South West Spain). Sci. Total Environ. 333, 267–281. https://doi.org/10.1016/j.scitotenv.2004.05.012

Puigdomenech, I., 2001. Chemical equilibirum software Hydra/Medusa.

Qiu, M., He, C., 2019. Efficient removal of heavy metal ions by forward osmosis membrane with a polydopamine modified zeolitic imidazolate framework incorporated selective layer. J. Hazard. Mater. 367, 339–347. https://doi.org/10.1016/j.jhazmat.2018.12.096

Reig, M., Vecino, X., Valderrama, C., Gibert, O., Cortina, J.L., 2018. Application of selectrodialysis for the removal of As from metallurgical process waters: Recovery of Cu and Zn. Sep. Purif. Technol. 195, 404–412. https://doi.org/10.1016/j.seppur.2017.12.040

Ricci, B.C., Ferreira, C.D., Aguiar, A.O., Amaral, M.C.S., 2015. Integration of nanofiltration and reverse osmosis for metal separation and sulfuric acid recovery from gold mining effluent. Sep. Purif. Technol. 154, 11–21. https://doi.org/10.1016/j.seppur.2015.08.040

Robinson, R.A., Stokes, R.H., 2002. Electrolyte Solutions, Second Rev. ed. Dover Books on

Chemistry Series.

Saidani, H., Amar, N. Ben, Palmeri, J., Deratani, A., 2010. Interplay between the transport of solutes across nanofiltration membranes and the thermal properties of the thin active layer. Langmuir 26, 2574–2583. https://doi.org/10.1021/la9028723

Sánchez-Andrea, I., Sanz, J.L., Bijmans, M.F.M., Stams, A.J.M., 2014. Sulfate reduction at low pH to remediate acid mine drainage. J. Hazard. Mater. 269, 98–109. https://doi.org/10.1016/j.jhazmat.2013.12.032

Santos, S., Machado, R., Correia, M.J.N., Carvalho, J.R., 2004. Treatment of acid mining waters. Miner. Eng. 17, 225–232. https://doi.org/10.1016/j.mineng.2003.09.015

Schäfer, A.I., Fane, A.G., Waite, T.D., 2005. Nanofiltration - Principles and Applications, Elsevier L. ed.

Simate, G.S., Ndlovu, S., 2014. Acid mine drainage: Challenges and opportunities. J. Environ. Chem. Eng. 2, 1785–1803. https://doi.org/10.1016/j.jece.2014.07.021

Su, X., Song, Y., Li, T., Gao, C., 2017. Effect of feed water characteristics on nanofiltration separating performance for brackish water treatment in the Huanghuai region of China. J. Water Process Eng. 19, 147–155. https://doi.org/10.1016/j.jwpe.2017.07.021

Tang, C.Y., Kwon, Y.N., Leckie, J.O., 2009. Effect of membrane chemistry and coating layer on physiochemical properties of thin film composite polyamide RO and NF membranes. I. FTIR and XPS characterization of polyamide and coating layer chemistry. Desalination 242, 149–167. https://doi.org/10.1016/j.desal.2008.04.003

Technologies, S.W., 2017. DL series industrial high flow nanofiltration elements [WWW Document]. URL https://www.suezwatertechnologies.com/kcpguest/documents/Fact Sheets_Cust/Americas/English/FS1248EN.pdf

U.S. Geological Survey, 2017. PHREEQC Version 3.

Wadekar, S.S., Vidic, R.D., 2018. Comparison of ceramic and polymeric nanofiltration membranes for treatment of abandoned coal mine drainage. Desalination 440, 135–145. https://doi.org/10.1016/j.desal.2018.01.008

Wu, S., Wang, L., Zhao, L., Zhang, P., El-Shall, H., Moudgil, B., Huang, X., Zhang, L., 2018. Recovery of rare earth elements from phosphate rock by hydrometallurgical processes – A critical review. Chem. Eng. J. 335, 774–800. https://doi.org/10.1016/j.cej.2017.10.143

Xie, F., An, T., Dreisinger, D., Doyle, F., 2014. A critical review on solvent extraction of rare earths from aqueous solutions. Miner. Eng. 56, 10–28. https://doi.org/10.1016/j.mineng.2013.10.021

Yaroshchuk, A., Martínez-Lladó, X., Llenas, L., Rovira, M., de Pablo, J., 2011. Solution-diffusion-film model for the description of pressure-driven trans-membrane transfer of electrolyte mixtures: One dominant salt and trace ions. J. Memb. Sci. 368, 192–201. https://doi.org/10.1016/j.memsci.2010.11.037

Yaroshchuk, A.A.E., 2000. Dielectric exclusion of ions from membranes. Adv. Colloid Interface Sci. 85, 193–230. https://doi.org/10.1016/S0001-8686(99)00021-4

Yaroshchuk, A.E., 2002. Rejection of single salts versus transmembrane volume flow in RO/NF: thermodynamic properties, model of constant coefficients, and its modification. J. Memb. Sci. 198, 285–297. https://doi.org/10.1016/S0376-7388(01)00668-8

Yaroshchuk, A.E., 2001. Non-steric mechanisms of nanofiltration : superposition of Donnan and dielectric exclusion. Sep. Purif. Technol. 22-23, 143–158.

Yu, Y., Zhao, C., Yu, L., Li, P., Wang, T., Xu, Y., 2016. Removal of perfluorooctane sulfonates from water by a hybrid coagulation-nanofiltration process. Chem. Eng. J. 289, 7–16. https://doi.org/10.1016/j.cej.2015.12.048

Zhong, C.-M., Xu, Z.-L., Fang, X.-H., Cheng, L., 2007. Treatment of Acid Mine Drainage (AMD) by

1 Ultra-Low-Pressure Reverse Osmosis and Nanofiltration. Environ. Eng. Sci. 24, 1297–
2 1306. https://doi.org/10.1089/ees.2006.0245

3