

1 **Increasing sustainability on the metallurgical industry by**
2 **integration of membrane nanofiltration processes: acid recovery**

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11 **Abstract**

12 The metallurgical industry generates large volumes of toxic effluents characterised, generally,
13 by high acidity and a noticeable content of metals (Fe, Cu and Zn) and non-metals (As, Sb, Bi).
14 The toxicity of these streams makes necessary treatment before its discharge to the environment
15 or reuse. Sustainable management of these effluents must be focused on the recovery of low
16 added valuable by-products (e.g. strong acids) to reduce the wastes generated along with the
17 treatment (e.g. sludge). Nanofiltration offers clear advantages for acid recovery instead of the
18 conventional treatments such as neutralisation and precipitation, due to the high membrane
19 transport ratios of single charged ions and high rejection of multi-charged ions. The
20 performance of a semi-aromatic poly(piperazineamide) membrane (NF270) was evaluated for
21 the treatment of effluents from copper metallurgical process streams of off-gases treatment
22 trains. These streams are characterised by a high acidity (pH<1) due to a mixture of strong
23 (H₂SO₄, HCl) and weak (H₃AsO₄) acids and the presence of metallic species (Fe, Cu, Zn). The
24 membrane performance was evaluated in terms of acid recovery and metal ions rejection taking

1 into account their aqueous speciation in strong acid media. The transport of the species across
2 the membrane was characterised according to the Solution-Electro-Diffusion model. The
3 membrane permeances to aqueous species (both charged and non-charged) in strongly acidic
4 solutions were calculated. NF270 showed good results for strong acid recovery, exhibiting high
5 rejections of the metallic impurities. The implications of the presence of large amounts of As
6 present as H_3AsO_4 should involve a selective removal stage using H_2S or $\text{Na}_2\text{S}_2\text{O}_3$.

7 **Keywords:** nanofiltration; NF270; acidic waters; arsenic; sulphuric acid; hydrochloric acid.

8 **1. Introduction**

9 During the production of primary zinc and copper, the off-gas from the process, which contains
10 dust and sulphur dioxide, is usually cleaned with a scrubber and a wet electrostatic precipitator.
11 Aqueous streams generated in this treatment are enriched with metallic and not metallic species
12 (e.g. As, Sb, Bi, Se) due to the dissolution of soluble dust particles in the washing liquor. The
13 liquid effluent, rich in strong acids (H_2SO_4 , HCl , and HF) and metallic (Fe, Pb, Cd, Zn, Cu, Ni)
14 and non-metallic species present as weak acids (H_3AsO_4 , H_3AsO_3 , H_3SbO_3 , H_2SeO_4) generally
15 requires further treatment, for instance neutralisation with lime and/or sedimentation for solid-
16 liquid separation [1]. This acidic stream may contain typically 1 – 50 wt. % H_2SO_4 , halides such
17 as HCl (0.2-2 g/L) or HF (0.1– 1 g/L, including H_2SiF_6), metals such as copper, zinc and iron
18 (individually up to 2.5 g/L), mercury (up to 0.05 g/L) and lead (up to 0.05g /L). Arsenic may be
19 present up to levels of 10 g/L. Other elements, such as aluminium, nickel, chromium, cadmium,
20 bismuth and antimony, among others, can be present as traces (below 0.05 g/L). Management
21 routes may include the blending of process streams.

22 The presence of these impurities has prevented the recirculation of these streams back to the
23 process without a purification step. The main challenge of metallurgical industries is to reduce
24 the amount of generated wastes (e.g. lime sludge) and their contaminant load, as well as to
25 valorise valuable by-products. Taking that into account, the objective of the purification step

1 would be to recover the maximum amount of acids, mainly sulphuric acid, for further reuse, and
2 to remove at the same time the impurities of the acid. Different techniques have been applied to
3 remove acidity and non-metallic species (e.g. As, Sb, Bi or Se), such as chemical neutralization
4 and precipitation with lime or adsorption and co-precipitation of non-metallic species (As and
5 Se) [2–4]. Removal of As and Se requires the oxidation of As(III) and Se(IV) to As(V) and
6 Se(VI) by strong oxidants (ozone, chlorine, hydrogen peroxide) and subsequent coagulation-
7 precipitation by adding Al or Fe, or ion exchange or electrochemical treatments to remove
8 arsenic as arsine [5–8]. Nevertheless, these techniques require a considerable amount of
9 chemicals and do not involve the recovery of acids.

10 Nowadays, with the focus on the recovery of valuable by-products, other techniques such as
11 electrodialysis [9–11], diffusion dialysis [12,13] and ion-exchange [14,15] have been postulated
12 to recover acids and to remove undesired components. Among these proposed techniques,
13 nanofiltration (NF) is gaining importance for the treatment of acidic waters, mainly due to its
14 properties, exhibiting high rejection of multi-charged ions (e.g. Fe, Zn...), while the transport of
15 single charged ions (e.g. H^+) is favoured. Studies conducted with polyamide-based NF
16 membranes at high sulphuric acid concentrations (pH <2) showed high metal ion rejection
17 (>90%) and low acid rejections [16–20].

18 Scarce information is found on the solutes transport through NF membranes, especially on non-
19 charged ionic species, as it is the case of the fully protonated oxyanions such as As species
20 (H_3AsO_3 for As(III) and H_3AsO_4 for As(V)) or Se species (H_2SeO_3 for Se(IV) and H_2SeO_4 for
21 Se(VI)). Most of the published studies applied reverse osmosis (RO) and NF for the removal of
22 As (As(III) and As(V)) from surface and groundwater [21,22] with typical rejections between
23 50 to 89% for As(III) and from 87 to 93% for As(V). Only one study on the application of
24 NF270 membrane was found in the scientific literature focusing on the removal of metal ions
25 and As(III), with As rejections below 15% from pH 1.5 to 5.0 [23]. However, the description of
26 transport mechanisms through the NF membrane was not provided.

1 Solute transport of both charged and non-charged species across the membrane depends on the
2 membrane active layer properties (e.g. the composition of the active layer, the content of free
3 acid-base groups, acid-base properties, and free volume distribution size), aqueous compositions
4 (acidity and ion concentrations) and the interaction between these two factors. Nevertheless,
5 there is still a lack of modelling tools to scale-up NF for its application to treat acidic waters.
6 Solution-Diffusion (SD) model is widely used to describe the transport of species across NF
7 membranes [24–26], and it is based on i) the membrane presents a free volume instead of fixed
8 pores and; ii) the separation is achieved due to the differences of species diffusivities inside the
9 membrane. The objective of applying these models is to obtain a parameter that describes the
10 transport of species across the membrane, named membrane permeance to species. In some
11 cases, such as the weak electrolytes, ions can be presented as free ions and forming complexes
12 between them, which have a noticeable impact on the separation performance. Some studies
13 have coupled chemical equilibrium reactions with SD model [27,28].

14 The transport of uncharged species has proven to have a large impact on membrane
15 performance [23,27,29–33]. One case of study is the phosphoric acid [27,29,30], which at $\text{pH} < 2$
16 predominates as an uncharged species (H_3PO_4) over the mono-charged anion (H_2PO_4^-).
17 Guastalli et al. [29], when filtering acidic industrial rinsing water containing dissolved
18 aluminium was able to recover the 56% and 77% of phosphoric acid with MPF-34 and Desal-
19 DL, respectively. The transport of phosphoric acid as an uncharged solute through the
20 membrane was related to steric hindrance. Diallo et al. [30] studied the recovery of phosphoric
21 acid at different acid concentrations (0.12, 1.2 and 5.9 mol/L) with MPF-34. They obtained
22 phosphoric acid rejections of 40% at 0.2 mol/L but decreased to almost zero at 5.9 mol/L due to
23 the increase in H_3PO_4 fraction. The membrane exhibited a decrease in the membrane pore size
24 when compared to water at 5.9 mol/L. Moreover, the nonexistence of a concentration
25 polarisation layer implied that no steric retention occurred. This suggested that the electrostatic
26 interactions between H_2PO_4^- and the membrane master the global rejection of phosphoric acid.
27 Another case of study was the recovery of strategic elements (Ge, Mo, Re, Co, Cu and Zn) from

1 aqueous sulphuric acid solutions [31,32]. In the case of neutral species of Mo (H_2MoO_4), its
2 rejection was near to zero, while at pH 6, the deprotonation of the molecule made Mo rejection
3 higher. Furthermore, Ge(IV) (as $\text{Ge}(\text{OH})_4$) rejections were independent of pH and lower than
4 20%. Transport of both uncharged solutes was mainly controlled by diffusive and convective
5 flow, and the higher rejections values for Mo in relation to Ge were related to the higher
6 molecular size. Werner et al. [33] evaluated the transport of In(III) and Ge(IV) and observed
7 rejection values below 15% in acidic media (due to its presence as $\text{Ge}(\text{OH})_4$). It is worthy of
8 mention the behaviour of In(III), which was totally rejected along with the pH range even
9 though at neutral pH it was presented as a non-charged species ($\text{In}(\text{OH})_3$). This contrast was
10 explained by the different molecular size of $\text{Ge}(\text{OH})_4$ and $\text{In}(\text{OH})_3$. Indium is coordinated with
11 three OH^- groups, surrounded by another three water molecules, while $\text{Ge}(\text{OH})_4$ is coordinated
12 in a tetrahedral structure, indicating that $\text{Ge}(\text{OH})_4$ is smaller than $\text{In}(\text{OH})_3$.

13 The main objective of this work is to study the performance of a semiaromatic polyamide NF
14 membrane (NF270) in the treatment of streams generated from the off-gases treatment step of
15 copper metallurgical industry. These streams contain a mixture of $\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_3\text{AsO}_4$ and
16 metallic species (Fe, Cu, Zn, Ni, Co, Cd) and alkaline metals (Na, K, Ca, Mg). Transport of
17 acids and metallic species through the membrane was evaluated under three different total
18 acidity scenarios with pH values from 0.2 to 0.6 and modelled according to SED model coupled
19 with reactive transport to determine the membrane permeances to species. The transport
20 behaviour implications of both fully dissociated strong acids (H_2SO_4 and HCl) and weak acids
21 (H_3AsO_4) with non-dissociated forms in the working conditions ($0.2 < \text{pH} < 0.6$) was critically
22 evaluated in detail.

2. Material and Methods

2.1. Membrane and solutions

The behaviour of NF270 (from Dow Chemical), with an active layer based on a semi-aromatic poly(piperazine amide) (**Figure 1**) was tested. The membrane has ionogenic amine (R-NH₂) and carboxylic (R-COOH) groups, which are responsible for the membrane charge. The pH value where a membrane exhibits no charge is called the isoelectric point (IEP). For the NF270 membrane, the IEP has a value of 2.5 [34].

Experiments were performed with three different effluents from a metallurgical industry (**Table 1**). These streams are characterised by a high acidity (pH<1) due to the high contents of H₂SO₄ and, to a lesser extent, HCl. As it can be seen in **table 1**, the main toxic impurity of the stream is As (present at the g/L level), while metallic ions (Zn, Fe, Cu, among others) were present at lower concentration levels (mg/L). Analysis of the samples by UV spectroscopy and by ion chromatography indicated that As was mainly present (>95%) as As(V) and then, all the transport and modelling study was carried out considering that As is present mainly as As(V).

A chemical speciation analysis was performed by using the Hydra-Medusa software [36] to determine the species present in the solutions. All metals are mainly complexed with sulphate ions, showing lower chemical equilibrium constants for chloride complexation than for sulphate. **Table 2** collects the chemical equilibrium constants for the main species present in solution. Chloride complexes have not been included as their contribution was below 1% of the total molar ratio of a given element.

Figure 2 represents the speciation diagrams for sulphate and arsenate from pH 0 to 1. These elements were the anions with the highest concentrations, apart from chloride. Sulphate is mainly presented as HSO₄⁻, whereas As is as a non-charged species (H₃AsO₄). Speciation diagrams for cations are collected in **Annex I**.

2.2. Experimental set-up

The experiments were carried out in a cross-flow experimental set-up with flat-sheet membranes (0.014 m²) placed in a test cell (GE SEPA™ CF II) with a spacer-filled feed channel. The set-up has a needle and a by-pass valve which allowed to vary the cross-flow velocity (cfv) and the trans-membrane pressure (TMP). The feed solution was kept in a thermostatic 30 L tank at a constant temperature (25 ± 2°C) and was pumped into the membrane cell with high-pressure diaphragm pump (Hydra-Cell, USA). The two outputs of the cell (permeate and concentrate) were recycled tank to keep the same composition in the feed solution. Feed and concentrate lines were equipped with a manometer, and the latter also with a flow-meter. A data acquisition system programmed in LABVIEW® version 8.6 collected the data from the manometers and the flow-meter. A pre-filter cartridge was placed before the discharge of the concentrate into the tank to avoid that erosion products reached the pump and to eliminate microorganisms. Permeate samples were collected with a three-way valve.

The membrane was placed in Milli-Q water overnight to remove its conservation products before performing any experiment. After that, the membrane was compacted firstly with deionised water and after with the solution used in the experiment at 22 bar and cfv of 1 m/s for 2 h. Experiments were carried out at a pre-fixed cfv (0.7 ms/), and TMP was varied from 4.5 to 20 bar. Finally, the set-up was cleaned with deionised water to remove any impurity that may be left inside the cell.

Permeate and feed samples were analysed using Inductively Coupled Plasma Mass (7800 ICP-MS from Agilent Technologies) and Optical Emission Spectrometer (5100 ICP-OES from Agilent Technologies) to determine the concentration of the solution elements. Both kinds of samples were previously filtered (0.2 µm) and acidified with 2% HNO₃ before their analysis by ICP. Ion chromatography (Dionex ICS-1000) was used to measure the concentration of chloride, sodium, potassium and calcium. Cations were analysed with the IONPAC®CS16 cation-exchange column, using 0.03 mol/L methane sulphonic acid as eluent, while chloride

1 was measured with the IONPAC® AS23 anion-exchange column using a mixture of 45 mM
2 Na₂CO₃ and 0.8 mM NaHCO₃ as eluent solution. Previously, the samples were analysed with a
3 conductivity meter and a pH meter during the experiments as preliminary analyses. The acidity
4 of the samples was outside the recommended range (2 to 12) for being measured by pH glass
5 electrodes. Then, values provided by the pH glass electrode were used for experiment
6 monitoring purposes. The concentration of H⁺ of the samples was determined by acid-base
7 titrations with an automated titrator (Excellence Titrator T5 from Metler Toledo), and pH values
8 were calculated using the Davies equation, taking into account the ionic strength of the solution.

9 **3. Ion transport modelling through NF membranes coupled with** 10 **reactive transport**

11 The transport of charged and non-charged species across the NF membrane was described on
12 the basis of the Solution-Electro-Diffusion (SED) model taking into account the reactive
13 transport to include the chemical equilibrium between the different species in solution. The
14 model does not consider the coupling between species and solvent, and it is assumed that
15 species are transported due to a combination of diffusive forces and electromigration (for
16 charged species). The model uses “virtual” concentrations, which are defined as those that are in
17 thermodynamic equilibrium with an infinitely small volume inside the membrane. The use of
18 “virtual” concentrations satisfies the chemical equilibria reactions inside the membrane with
19 the bulk complexation constant [27]. Concentration polarisation was not considered to reduce
20 the mathematical complexity of the system. **Equation 1** describes the species flux across the
21 membrane.

$$j_i = -P_i \cdot \left(\frac{dc_i}{dx} + c_i \cdot \frac{d(\ln \gamma_i)}{dx} + z_i \cdot c_i \cdot \frac{d\phi}{dx} \right) \quad \text{Eq. 1}$$

22 where j_i is the flux of component i through the membrane, x is the dimensionless position in the
23 membrane, P_i is the membrane permeance to species i , c_i , γ_i and z_i are, respectively, the

1 concentration, the activity coefficient and the valence charge of species i , and φ is the
2 dimensionless virtual electrostatic potential in the membrane.

3 Activity coefficients were calculated according to the Davies equation (**Equation 2**), which is
4 valid for ionic strengths (IS) lower than 0.5 mol/L.

$$\log \gamma_i = -A \cdot z_i^2 \cdot \left(\frac{\sqrt{IS}}{1 + \sqrt{IS}} - 0.3 \cdot IS \right) \quad \text{Eq. 2}$$

5 where A is the Debye Hückel parameter with a value of 0.5042.

6 The objective of the model is to characterise the transport of species using the membrane
7 permeance to species i (P_i). This parameter depends on the species and membrane properties, as
8 well as the interactions between them. Partition coefficients and possible changes in the
9 complexation constants are included within the membrane permeances. Moreover, these values
10 are assumed to be constant over the whole length of the membrane [25].

11 The transport of charged species must be subjected to electroneutrality condition (**Equation 3**),
12 as follows:

$$\sum_{i=1}^n (z_i \cdot c_i) = 0 \quad \text{Eq. 3}$$

13 Species in solution must satisfy the condition of chemical equilibrium reactions between them.
14 For that reason, the flux of one species would not be constant along the membrane. Then,
15 species flux equations (**Equation 1**) are solved for each element that makes up the species.

16 Mass balance equations were solved using Matlab® where the membrane permeances to species
17 were calculated to minimise the error between the rejection obtained experimentally and the one
18 from the model. The rejection was defined according to (**Equation 4**), as follows:

$$R = 1 - \frac{C_{i,p}}{C_{i,f}} \quad \text{Eq. 4}$$

19 Where R is the rejection and $C_{i,p}$ and $C_{i,f}$ are the concentrations of the species i in the permeate
20 and feed, respectively.

1 Phenomenological models based on irreversible thermodynamics (such as the SED model)
2 presents some advantages in comparison with nanopore models, such as it is not necessary to
3 provide data about pore size and geometries, surface charge densities and dielectric constants
4 that are hard to measure experimentally. Thus, until a more precise characterization of the
5 complex chemical and pore structure of NF membrane active layer would be possible,
6 alternative engineering models may be preferable for describing NF with a few thermodynamic
7 coefficients that can be determined from experiments [37]. Values of fitted parameters (e.g.
8 permeances) have been discussed in terms of the main mechanisms involved in the solute
9 transport through the membrane active layer.

10 **4. Results and Discussion**

11 **4.1. Performance of NF270 membranes and determination of** 12 **membrane permeance to species**

13 **Figure 2** shows the rejection for all the main elements in solution (symbols), based on the total
14 concentration of each element in solution regardless of its speciation, as a function of the trans-
15 membrane flux, for the three solutions given in Table 1. The predicted rejections (lines)
16 calculated with the SED model (**Eq. 1**) are also shown.

17 **4.1.1. Rejection of species**

18 NF270 showed high metal rejections (>80%) and moderate sulphate, proton and arsenic
19 rejections (<50%), while chloride rejections were negative within all the evaluated trans-
20 membrane flux range. The rejection value of a given species *i* can be explained by a
21 combination of i) the physicochemical properties of the species *i*, ii) the solution composition,
22 which affects the speciation of *i*, and iii) the membrane properties at the evaluated acidities on
23 the basis of the following main phenomena: i) Donnan exclusion; ii) Dielectric exclusion and
24 iii) solutes complexation.

1 Donnan exclusion, based on the fact that the active layer of a membrane may be charged,
2 favours the passage of counter-ions and hinders that of co-ions [38]. At the working pH of 0.2-
3 0.7 (lower than the NF270 membrane IEP value of 2.5) the membrane exhibited a positive
4 charge along its free volume, as it is described schematically in **Figure 4**. The free carboxylic
5 groups were fully protonated (R-COOH), and amine groups were partially protonated (R₂NH₂⁺).
6 This positive membrane active surface favoured the transport of counter-ions (i.e. HSO₄⁻ and Cl⁻
7), while co-ions (cations) were effectively rejected (i.e. metal ions). However, the transport of
8 anions (HSO₄⁻, Cl⁻) must be coupled to the transport of a cation to ensure electroneutrality in the
9 permeate side. Due to its highest concentration and mobility (much higher than those of any
10 other cation present in the system such as metallic species), H⁺ was the cation more prone to
11 permeate through the NF270 membrane. This explains the relatively low H⁺ rejections observed
12 in **Figure 3**.

13 The high rejection values of metal cations were also associated with dielectric exclusion. It is
14 caused by the interaction between ions and the bound electric charges induced by ions at the
15 interfaces in media of different dielectric constants (e.g. bulk solution/polymeric matrix).
16 Moreover, its effect can be more pronounced than that of Donnan exclusion because the ion-
17 exclusion free energy is proportional to the square of the ion charge (while the Donnan
18 exclusion is linear with it) [38]. Then, according to this, the free-form of the metallic ions such
19 as Fe³⁺, Cu²⁺, Zn²⁺, Ni²⁺, Pb²⁺, Ca²⁺ and Mg²⁺ would be more rejected than the single charged
20 species of Na⁺, K⁺ and H⁺.

21 **Annex I** shows the speciation diagrams for all metal ions in the presence of HSO₄⁻ and Cl⁻. In
22 the case of sulphate, the second dissociation of sulphuric acid (pK₂=1.9) imposes that at pH<1.9
23 the main sulphate species in solution is a single charged anion (HSO₄⁻), while at pH>1.9
24 sulphate is found as a double charged ion (SO₄²⁻). Thus, at pH<1.9 like in the present study,
25 sulphate was not removed because i) it was found as HSO₄⁻, which was less affected by
26 dielectric exclusion, and ii) the NF270 membrane exhibited a positive charge, which attracted
27 and favoured the passage of the negatively-charged HSO₄⁻ through it. On the contrary, at

1 pH>2.5, sulphate would be expected to be totally removed because i) it would be found as SO_4^{2-}
2 , which is greatly affected by dielectric exclusion, and ii) the membrane would exhibit a
3 negative charge, which would repel the negatively-charged SO_4^{2-} [15,26].

4 **Figure 5** shows sulphate rejection data over a range of pH of 0.3-5.8 obtained in previous
5 studies [26,28] together with those obtained in the present study to illustrate this trend.
6 Consistently with what has been discussed above, sulphate rejection clearly increased from pH
7 approx. 2 upwards. It is worth mentioning that, as seen in **Figure 5**, HSO_4^- rejection obtained in
8 this study was higher than in the previous study. This apparent discrepancy is explained by the
9 fact that, unlike the previous study, the solution of this one contained Cl^- ions at a high
10 concentration (**Table 1**), which originated a competition between both ions for the passage
11 through the membrane. These lower rejection values of Cl^- compared to HSO_4^- are attributed to
12 the higher charge density of Cl^- resulting in a higher attraction force to the membrane. The
13 presence of positive charges along the free-volume of the membrane structure makes the
14 behaviour of such membranes approach to that of ion-exchange membranes, favouring the
15 transport of Cl^- over that of HSO_4^- .

16 The rejection of As can also be explained by considering its speciation diagram (**Figure 2**). At
17 the experimental conditions (from pH 0.7 to 0.2), As(V) is found in solution mainly as a non-
18 charged species (H_3AsO_4) and, in a lower extent (below 15%), as a single charged anion
19 (H_2AsO_4^-). Following the discussion above, the prevalent non-charged species (H_3AsO_4) was
20 little repelled by the positively-charged membrane, showing rejections always below 45%.
21 When the pH of the solution decreased from 0.64 to 0.28, the fraction of the H_3AsO_4 slightly
22 increased, thus leading to even lower As rejections (below 40%). These two features were
23 responsible for the low As rejection.

24 **Table 3** collects a comparison of acid and metal rejections for different concentrated acidic
25 solutions (pH < 1) for various NF membranes. It can be seen that NF membranes have a good

1 performance to reject metal ions while letting acids permeate through them allowing thus their
2 further recovery.

3 In general, both polyamide (aromatic and semi-aromatic) and polydimethylsiloxane (MPF-34)
4 based membrane active layers have demonstrated to be effective at recovering strong acids as
5 H_2SO_4 , H_3PO_4 and HCl with a low content on metallic impurities.

6 **4.1.2. Membrane permeances to species**

7 The calculated membrane permeances to each species (obtained with **equation 1**) present in all
8 the solutions are collected in **Figure 6**.

9 On one side, the fastest anion in solution to permeate was Cl^- , exhibiting the highest membrane
10 permeance values ($>100 \mu\text{m/s}$); followed by dihydrogen arsenate (H_2AsO_4^-) and hydrogen
11 sulphate (HSO_4^-) with values of $45 \mu\text{m/s}$ and $30 \mu\text{m/s}$, respectively. The higher membrane
12 permeance values for Cl^- than for the two other anions were related to its lower size and charge.

13 On the other side, the fastest cation in solution was H^+ , with a membrane permeance value
14 higher than $100 \mu\text{m/s}$. As discussed above, this value is explained by the high mobility and
15 concentration of H^+ and by the high rejection of metallic cationic (e.g. Zn^{2+} , Fe^{3+} and Pb^{2+} ... and
16 their complexes), which showed membrane permeance values $<0.5 \mu\text{m/s}$ and were thus less
17 prone to permeate through the membrane to satisfy electroneutrality condition in the permeate
18 side. Despite exhibiting high permeance values (much higher than divalent heavy metals), Na^+
19 and K^+ did not compete with H^+ in permeating through the membrane because of their much
20 lower concentration.

21 The permeance values for the different species were in agreement with the Donnan and
22 dielectric exclusion phenomena [38]. For instance, Fe(III), which can form complexes with
23 sulphate, can be present in solution as Fe^{3+} , FeHSO_4^{2+} , FeSO_4^+ and $\text{Fe}(\text{SO}_4)_2^-$. Membrane
24 permeances to those species were found to follow the trend $\text{Fe}^{3+} < \text{FeHSO}_4^{2+} < \text{FeSO}_4^+ <$
25 $\text{Fe}(\text{SO}_4)_2^-$. This trend is consistent with the dielectric exclusion phenomenon, according to
26 which the transport of single charged ions is favoured over the transport of double and triple-

1 charged ions. The trend is further explained by the fact that, at the pH of the experiments, the
2 membrane exhibited a positive surface charge ($\text{pH} < \text{IEP}$), meaning that cations (i.e. Fe^{3+} ,
3 FeHSO_4^{2+} , FeSO_4^+) would be more rejected, whereas anions ($\text{Fe}(\text{SO}_4)_2^-$) would be less rejected.
4 If membrane permeance values to two elements (e.g. Zn and Fe) are compared, they did not
5 always follow the sequence expected from the dielectric exclusion phenomenon. This was
6 attributed to their high concentrations compared to those of the other cations. Other studies have
7 highlighted the dependence of membrane permeance to an ion on its concentration in solution
8 [42–44].

9 According to the chemical speciation, there are also neutral complexes in solution such as
10 ZnSO_4 , CuSO_4 , PbSO_4 and NiSO_4 . The passage of these molecules is not impeded nor favoured
11 by the electric fields of the membrane. Actually, these species are expected to be better
12 transported than the corresponding free-form of the ion (Zn^{2+} , Cu^{2+} , Pb^{2+} and Ni^{2+}). This fact is
13 supported when the membrane permeances to these non-charged species are compared with
14 those of the free-metallic ions.

15 Membrane permeance values were compared with those published previously in the literature.
16 In a previous study, a sulphuric acidic solution ($\text{pH} 1.0$) containing metals were treated with the
17 NF270, and membrane permeances were determined considering complexing reactions [45]. H^+
18 had the highest permeance among cations ($58 \mu\text{m/s}$), while HSO_4^- the highest one among anions
19 ($114 \mu\text{m/s}$). Differences in permeance values between the cited studies and the one presented
20 here could be explained by the different composition of the solution. In this work, H^+
21 concentration was much higher (pH in the range 0.28 - 0.64), leading to permeance values > 100
22 $\mu\text{m/s}$. Moreover, the presence of Cl^- in the solution limited the transport of HSO_4^- , which
23 resulted in lower membrane permeances to HSO_4^- . The obtained membrane permeances to the
24 free-form of the metallic ions (Zn^{2+} , Cu^{2+}) were much lower, which was related to the effect of
25 pH and their different concentration. The effect of the membrane charge on permeance values
26 can be seen by comparing the membrane permeances to Cl^- with those previously published in
27 the literature [35]. At neutral pH , NF270 is negatively charged, thus showing low membrane

1 permeances to Cl^- (between 9 and 21 $\mu\text{m/s}$). In the present study, the membrane was positively
2 charged at the pH values tested, resulting in an increase of the membrane permeance to Cl^- (212
3 – 374 $\mu\text{m/s}$).

4 **4.2. Comparison of recovery of strong and weak electrolytes**

5 NF membranes with two main different properties have been postulated for acid recovery: i)
6 positively charged membranes (e.g. polyamide based active-layer membranes), where the
7 transport of acid is driven by the transport of the anionic acid form (X^-) causing the passage of
8 H^+ to maintain electroneutrality in the permeate side, and; ii) negatively charged membranes to
9 promote the transport of H^+ , while X^- is just co-transported to achieve the electroneutrality
10 condition. However, weak electrolytes presented in solution as fully protonated non-charged
11 species (e.g. H_3AsO_4) are not affected by membrane charge. Instead, its transport is driven by a
12 concentration gradient, with a limited effect of dielectric exclusion. This explains why 70% of
13 the As (as H_3AsO_4) was transported at the previous experiments. The transport of non-charged
14 species has been widely documented in RO membranes, as the case of B(III) as H_3BO_3 , whose
15 speciation depends on the pH and temperature of the solution [46]. However, there are limited
16 examples of the transport of weak acids (e.g. H_3AsO_4 , H_3PO_4) through NF membranes in the
17 literature and the most relevant are summarised in **table 4**.

18 As stressed, the electric fields governate the transport of ions in NF membranes. The fact that
19 one inorganic compound appeared in solution as uncharged ion makes that the membrane
20 cannot reject it, which has been addressed by several authors [23,27,29–33]. One case is the
21 transport of phosphoric acid in NF membranes at $\text{pH}<2$ [27,29,30]. Niewersch et al. [27] treated
22 solutions which contained mixtures of sulphuric and phosphoric acid (pH 1 to 3) with metals
23 and cations (Ca, Mg, Fe, Cu, Ni, Cu). Phosphorus was rejected up to 40% at pH 2, and its
24 rejection decreased at lower pH, which was associated with the transport of the dominant
25 species H_3PO_4 . Rejections near to zero at even high phosphoric acid concentrations (5.9 mol/L)
26 have been noticed by Diallo et al. [30]. Meschke et al. [31,32] related the low rejection of Mo

1 and Ge to their presence as neutral species (i.e. H_2MoO_4 and $\text{Ge}(\text{OH})_4$) and suggested that their
2 transport was mainly controlled by diffusive and convective flow. Werner et al. [33] evaluated
3 the transport of In(III) and Ge(IV) and observed low rejections of Ge(IV) when it was presented
4 as neutral species, while In(III) was totally rejected even when it was presented as a non-
5 charged species ($\text{In}(\text{OH})_3$). This was explained due to the lower size of $\text{Ge}(\text{OH})_4$ than $\text{In}(\text{OH})_3$.
6 For uncharged inorganic species, the steric hindrance becomes the main exclusion mechanism
7 for large molecules. Instead, for species of low molecular weight, its transport is not impeded by
8 the membrane. The fact that the interactions between the electric fields and the ion charges
9 control the separation could make possible that those species to be rejected by the membrane.
10 The only way to achieve that is to shift the pH to modify the membrane charge or the
11 equilibrium among the different species in solution. In the case of the present manuscript, if
12 As(V) must be removed from the solution, it should be recommended to operate at $\text{pH} > 2.5$
13 (NF270 IEP). Under this acidity conditions, the membrane would exhibit a negative charge
14 ($\text{pH} > \text{IEP}$) and the As(V), which would be deprotonated mainly as a mixture of H_2AsO_4^- and
15 HAsO_4^{2-} , would be rejected by the membrane.

16 **5. Conclusions**

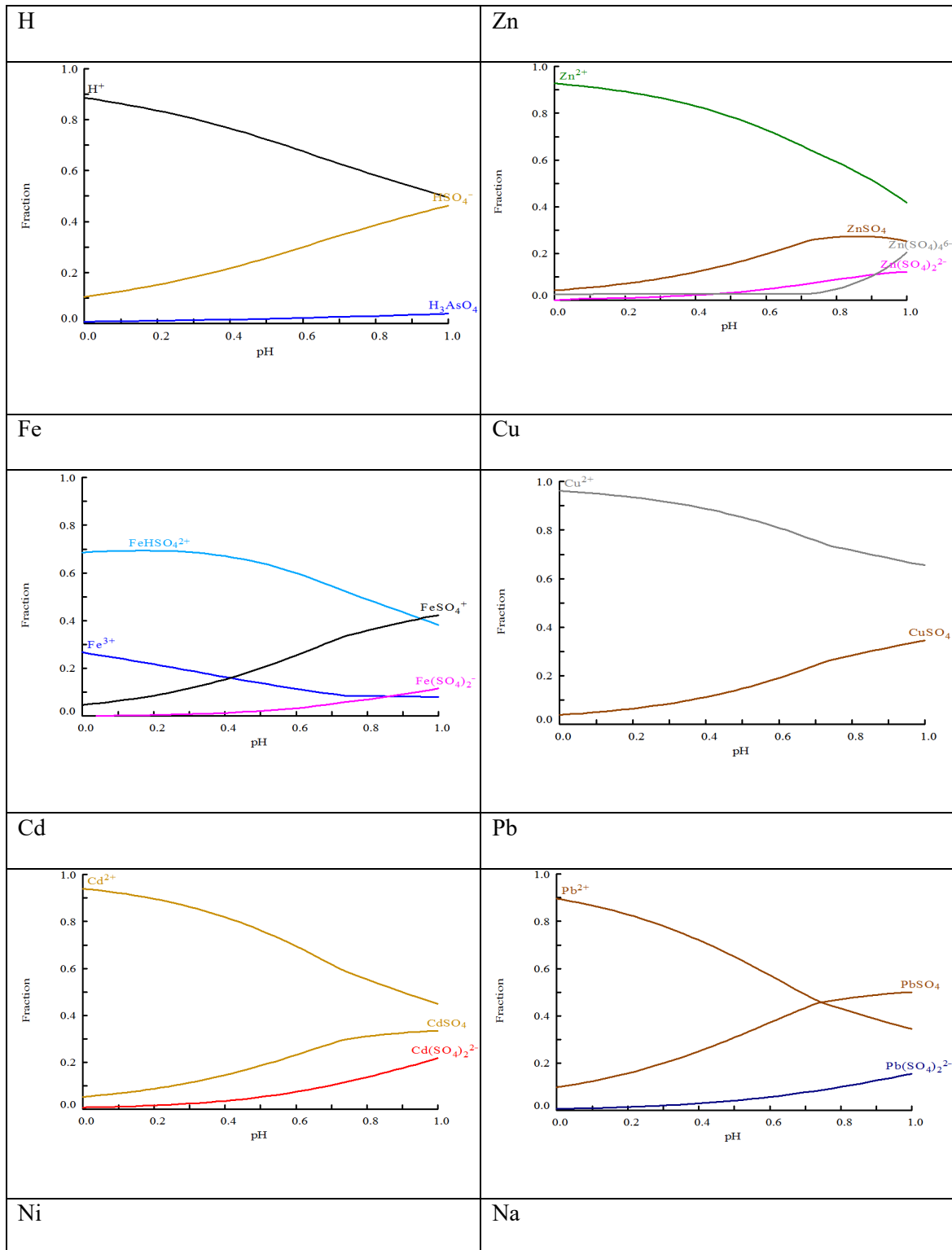
17 The treatment of hydrometallurgical streams using NF offered a good alternative to
18 conventional methods. The experimental data showed it was possible to recover strong acids
19 (H_2SO_4 , HCl) from hydrometallurgical streams by using a semi-aromatic polyamide membrane.
20 NF270 exhibits a positively surface charge at $\text{pH} < 1.0$, which favoured the transport of anions,
21 while impeded the transport of metallic species presented as cations. With the different
22 solutions tested, the membrane exhibited negative chloride rejections and moderate sulphate
23 rejections. Design of processes using more than one NF stage may allow to recover up to 90%
24 of the total strong acids content. Nevertheless, the active layer of these membranes can suffer a
25 hydrolysis process due to the long term exposition to acid, so a stability test should be
26 performed before its use at industrial scale.

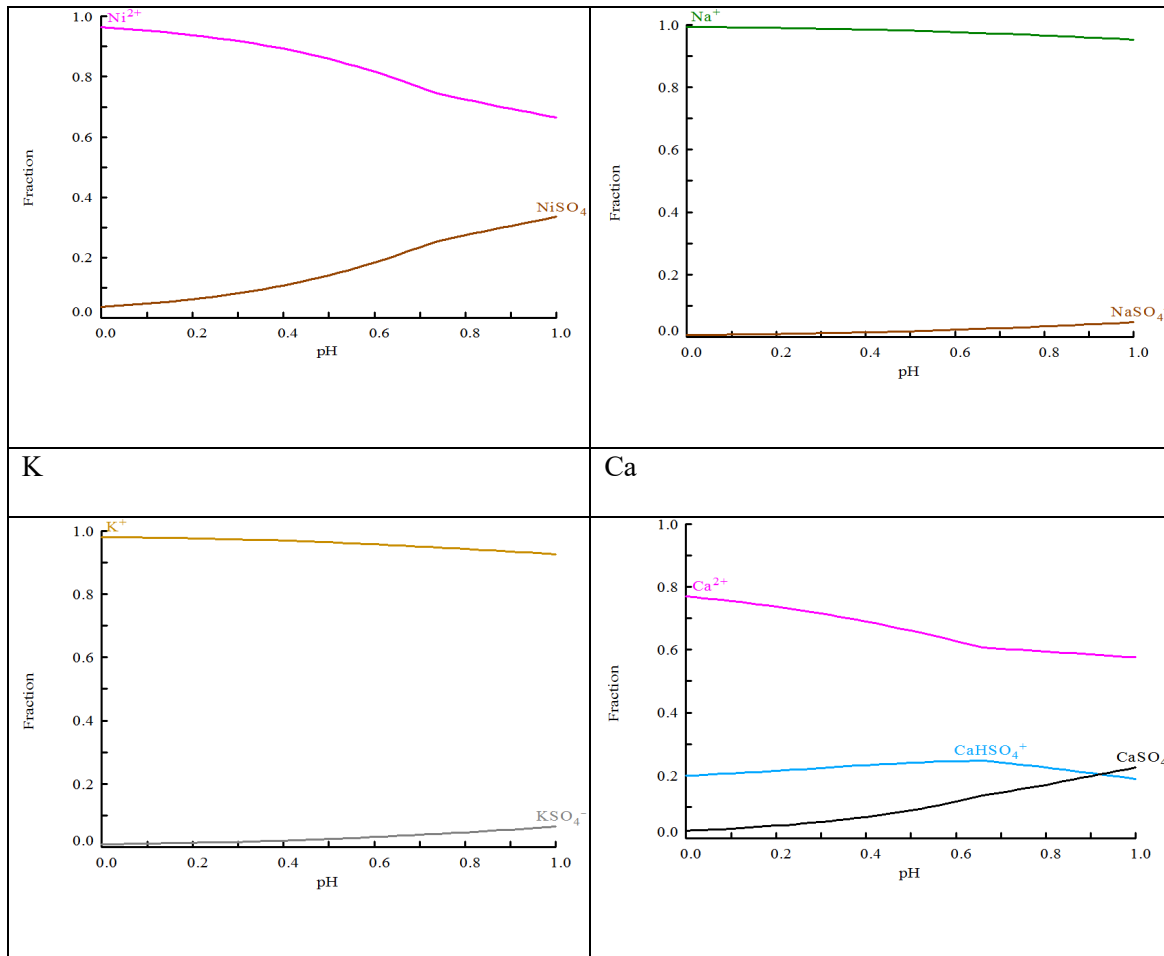
1 In addition, the membrane favoured the transport of a non-metallic species (As) due to its
2 presence as a non-charged species (H_3AsO_4) and not limited by the dielectric and Donnan
3 exclusion. The levels of As will limit then this application, and then a pre-treatment stage may
4 be needed, such as using a reducing agent (e.g. H_2S or $\text{S}_2\text{O}_3^{2-}$) to obtain As(III) and then
5 precipitate As as $\text{As}_2\text{S}_3(\text{s})$ or as a mixture of $\text{S}(\text{s})$ and $\text{As}_2\text{O}_3(\text{s})$.

6 The SED model coupled with reactive transport fitted the experimental rejections properly, and
7 calculated membrane permeances could be used to design stages in full-scale applications.
8 Membrane permeances to the main components (H^+ and HSO_4^-) were consistent with values
9 previously determined for acidic streams from mining and hydrometallurgical applications.

10

1 Annex I - Speciation diagrams





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