Journal of Hazardous Materials

Arsenic impact on the valorisation schemes of acidic mine waters of the Iberian Pyrite Belt: integration of selective precipitation and spiral-wound nanofiltration processes
--Manuscript Draft--

Departament d'Enginyeria Química

UNIVERSITAT POLITÈCNICA DE CATALUNYA

Dr. Professor Jörg Rinklebe

Editor on Journal of Hazardous Materials,

Barcelona, 23/07/2020

Dear Mr,

Please find enclosed the revised version of our manuscript: *"Arsenic impact on the valorisation schemes of acidic mine waters of the Iberian Pyrite Belt: integration of selective precipitation and spiral-wound nanofiltration processes"* by: Julio López, Mònica Reig, Xanel Vecino and José Luis Cortina (**Reference HAZMAT-D-20-06470**).

We have considered all the comments and suggestions made by the reviewers and we hope that the manuscript will now be suitable for publication in **Journal of Hazardous Materials.**

A listed response to the reviewer's comments and a marked original copy is provided on separate sheets.
I look forward to hearing from you.

Yours faithfully,

Dr. Julio López (corresponding author)

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Novelty Statement

We consider that this work fits the scope of the Special Issue. Hereby, we present the treatment of acid mine waters containing 2 mg/L As (and also Cd, Pb and Se). The novelty is the proposed treatment train, based on (i) chemical oxidation, (ii) precipitation and (iii) nanofiltration, which made possible to achieve a water recovery ratio up to 80% with As concentration values below 70 µg/L that can be discharged to the medium according to the mining effluent discharge legislation or be re-used in industrial applications. Additionally, the rare earth elements recovered make the process sustainable.

ANSWERS TO THE REVIEWERS

Ref: HAZMAT-D-20-06470

Title: *Arsenic impact on the valorisation schemes of acidic mine waters of the Iberian Pyrite Belt: integration of selective precipitation and spiral-wound nanofiltration processes*

Journal: Journal of Hazardous Materials

Dear Proff. Jörg Rinklebe,

Thank you for your invitation to resubmit our manuscript after addressing all reviewer comments. We have completed the review of your manuscript, and a summary of the raised comments and the comments and changes made could be found in the next pages below. We have considered all issues mentioned in the reviewers' comments, and we have outlined every change made point by point, and provide suitable rebuttals for any comments not addressed. The revised manuscript is now submitted for your consideration with all the corrections made.

I look forward to receiving your comments.

Kind regards,

Julio Lopez

Comments from Editors and Reviewers:

Reviewer #1: General comments

This paper reports the application of membrane nanofiltration coupled with an oxidation/precipitation step for the treatment of acid mine waters, a topic poorly investigated in the pertinent literature. Nanofiltration experiments were performed in both a closed-recirculation and stages in opern-recirculation mode at different pressures.

Relationships among water trans-membrane flux, elements removal and operating conditions are critically discussed. The obtained results are very promising for the practical implementation of the proposed technology for the treatment of acid mine waters.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

Specific comments

2. Materials and methods

Page 6 line 134. Did the Authors experimentally verify the formation of schwertmannite

precipitate, e.g. by means of XRD analysis?

During more than one decade we have been working with Dr. C. Ayora and Dr. J. M. Nieto in the treatment of acidic mine waters. They have demonstrated that working with these waters, iron precipitated as schwertmannite (see the references below). In the present work, this phase was not characterized. Then, the sentence has been modified accordingly (see page 6).

C.R. Cánovas, S. Peiffer, F. Macías, M. Olías, J.M. Nieto, Geochemical processes in a highly acidic pit lake of the Iberian Pyrite Belt (SW Spain), Chem. Geol. 395 (2015) 144–153. doi:10.1016/j.chemgeo.2014.12.007.

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

D.C. Fernández-Remolar, R. V. Morris, J.E. Gruener, R. Amils, A.H. Knoll, The Río Tinto Basin, Spain: Mineralogy, sedimentary geobiology, and implications for interpretation of outcrop rocks at Meridiani Planum, Mars, Earth Planet. Sci. Lett. 240 (2005) 149–167. doi:10.1016/j.epsl.2005.09.043.

2.3 Spiral-wound nanofiltration

Page 6 line 143. Please specify whether the constant feed concentration refers to the stream obtained after mixing the raw feed with concentrate and permeate or uniquely to the raw feed (i.e. without mixing).

As suggested by the reviewer, the sentence has been modified accordingly (see page 6).

3.2 Spiral-wound nanofltration experiments

Figure 3-b. Please correct "cupper" with "copper".

As indicated by the review, there was a type error in Figure 3-b. The word "cooper" has been modified properly.

Reviewer #2: The paper is about water remediation. The authors tried to removal arsenic by three stepped treatment. Oxidation, precipitation and nanofiltration steps were used for this purpose. The authors investigated especially the pressure effect on water recovery. They paper can be accepted in its current form.

We acknowledge the positive judgment of the reviewer.

Reviewer #3: This paper provides useful information on the efficiency of nanofiltration membrane technology for the treatment of acidic mine waters of the Iberian Pyrite Belt. The

results showed that As ion removal performance of the membrane technology was not high enough. Therefore, an additional chemical process was utilized for the removal of As and Fe ions before the main treatment step. The result of this case study is of interest and I recommend further consideration of this paper. However, I have left some minor comments for improving the paper quality.

We would like to thank the reviewer for her/his detailed and accurate revision of the manuscript. All the queries have been taken into account and, accordingly, the required modifications have been made.

Comments:

1. Please revise the title to project the main goal of the current paper.

As suggested by the reviewer, the title has been modified accordingly to "*Arsenic impact on the valorisation schemes of acidic mine waters of the Iberian Pyrite Belt: integration of selective precipitation and spiral-wound nanofiltration processes*".

2. Please include full vendor information on the material used.

Vendor information has been included in the reagents section (see page 5).

3. Please move some of the less important figures and tables to a supplementary file so the main results could be presented in the manuscript with more focus.

As suggested by the reviewer, Tables 2 and 5 and Figure 2 have been moved to the supplementary file.

4. Please revise the application of abbreviations. Each abbreviation should be defined in its first use.

As indicated by the reviewer, abbreviations have been revised along the manuscript in order to define all them the first time that they are used.

5. Please add full sampling data including approach and date.

AMW sampling was not carried out by the authors of the paper. As indicated in the acknowledgements section, the sampling was carried out by Dr. C. Ayora (IDAEA, CSIC) running on-site acid-mine drainage remediation trials. Samples of 50 L, contained in PVD containers, were received it at university.

Graphical abstract

Abstract

Arsenic and selenium presence in acid mine waters (AMWs) limits its disposal due to environmental regulations. The focus to solve the economic infeasibility is directed to sustainable solutions, promoting resource recovery. In fact, rare earth elements (REEs) recovery is proposed in most of the Iberian Pyrite Belt AMWs. However, the presence of arsenic and selenium may impact in the REEs recovery. Among different alternatives, nanofiltration (NF) provides a concentration stage on REEs recovery, reduces the nominal flow and removes hazardous species. In this work, Iberian Pyrite Belt AMWs with up-to 10 mg/L REEs, containing arsenic (2 mg/L), were treated with a NF membrane. Firstly, AMWs were pre-treated with H_2O_2/NaOH, to oxidise Fe(II) to Fe(II) and As(III) to As(V), promoting their removal and avoiding their potential precipitation at the membrane. Subsequently, NF pressure effect (6 to 20 bar) was studied, removing metals (>95%), whereas arsenic rejections ranged from 60 to 71%. Then, water recovery potential was evaluated at 10, 15 and 22 bar by reproducing a 10-stages NF plant. Results showed that the proposed treatment could be an alternative for arsenic and selenium removal (70 µg/L and 0.5 µg/L permeate concentrations, respectively) to achieve mining discharge limits according to regulations.

Keywords: ESNA; rare earth elements; valorisation; hazardous materials; water discharge

Highlights

- AMWs disposal is limited due to arsenic and selenium environmental regulations
- NF is proposed as a sustainable alternatively for traditional AMWs treatments
- Chemical precipitation was conducted before NF for Fe and As oxidation and removal
- REEs recovery, hazardous species removal and flow reduction was achieved by NF
- As & Se concentration was reduced below discharge limits by the proposed treatment

1 **Arsenic impact on the valorisation schemes of acidic mine waters**

2 **of the Iberian Pyrite Belt: integration of selective precipitation**

3 **and spiral-wound nanofiltration processes**

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Abstract

Arsenic and selenium presence in acid mine waters (AMWs) limits its disposal due to environmental regulations. The focus to solve the economic infeasibility is directed to sustainable solutions, promoting resource recovery. In fact, rare earth elements (REEs) recovery is proposed in most of the Iberian Pyrite Belt AMWs. However, the presence of arsenic and selenium may impact in the REEs recovery. Among different alternatives, nanofiltration (NF) provides a concentration stage on REEs recovery, reduces the nominal flow and removes hazardous species. In this work, Iberian Pyrite Belt AMWs with up-to 10 mg/L REEs, containing arsenic (2 mg/L), were treated with a NF membrane. Firstly, AMWs were pre-treated with H_2O_2/NaOH, to oxidise Fe(II) to Fe(II) and As(III) to As(V), promoting their removal and avoiding their potential precipitation at the membrane. Subsequently, NF pressure effect (6 to 20 bar) was studied, removing metals (>95%), whereas arsenic rejections ranged from 60 to 71%. Then, water recovery potential was evaluated at 10, 15 and 22 bar by reproducing a 10-stages NF plant. Results showed that the proposed treatment could be an alternative for arsenic and selenium removal (70 µg/L and 0.5 µg/L permeate concentrations, respectively) to achieve mining discharge limits according to regulations.

Keywords: ESNA; rare earth elements; valorisation; hazardous materials; water discharge

1. Introduction

Acidic Mine Waters (AMWs) are formed when sulphide minerals, mainly those related to iron (e.g. pyrite (FeS_2), marcasite, (FeS_2), and pyrrhotite (FeS)), are oxidised in contact with water or oxygen. AMWs generation takes place at both operating and abandoned poly-sulphide mining sites, as well as galleries, mine workings, open pits and waste rock piles [1–3]. The generation process produces sulphuric acid, which can dissolve the soil minerals and then, an acidic effluent, rich in dissolved ferrous and non-ferrous metal sulphates (e.g. Fe, Al, Zn and Cu), non-metals (e.g. As, Se) and a minor amount of rare earth elements (REEs), which is released to the environment [4,5]. One of the most known cases of AMWs generation can be found in the Iberian Pyrite Belt (south of Spain), which is one of the largest sources of pyrite in the world, and up to 150 different kinds of AMWs can be found in the Odiel and Tinto basins. These waters are characterised by low pH (1-3) and concentrations up to 35 g/L Fe, 3.5 g/L Al, 675 mg/L Cu and 798 mg/L Zn, among others [6,7]. It was found that the concentration of REEs is around 80 mM, which is high in comparison to that of natural waters (0.08 mM) [8–10]. Therefore, the presence of valuable compounds (e.g. Cu, Zn, REEs) in AMWs has made that research is being towards its recovery.

The presence of arsenic in these waters is related to the leaching process of arsenic-containing non-ferrous minerals (copper, lead, zinc, gold or uranium) when entering in contact with the sulphuric acid present in AMWs [11]. The removal of arsenic has become a challenge because of the health and environmental effects that it represents. The World Health Organisation (WHO) has set up a limit of 10 µg/L in the drinkable water, and for example, its concentration in unpolluted surface and groundwater varies from 1 to 10 µg/L [12]. However, in the case of AMWs from the Iberian Pyrite Belt basins, it can range from 10 to 104000 µg/L with a mean value of 8634 µg/L. Additionally, selenium may be present up to 2000 µg/L [13]. Such content of arsenic, which can be up to 5 orders of magnitude higher than the WHO limits, has made necessary treating AMWs properly before its disposal. Various governments adopted an upper limit of 10 µg/L and 50 µg/L for arsenic and selenium, respectively for drinking water, while these limits are higher for effluent discharge (10 – 200 µg/L for arsenic and 2 – 100 µg/L for selenium) [14]. Differences in regulations are due to the source type and solution composition, environmental and hydraulic conditions (stream flow-rates and natural habitat) and the toxicity that they may produce in the different living organisms [15].

Usually, the presence of non-metals (e.g. arsenic or selenium) may require a previously pre-treatment to oxidase them (e.g. As(V) and Se(VI)) with strong oxidants, such as ozone, chlorine

64 or hydrogen peroxide, among others. After that, they are removed by a coagulation-

65 precipitation process with aluminium or iron, or through ion exchange or electrochemical

66 treatments to remove arsenic as $AsH_3(g)$ [11,12,16]. Other treatments, such as neutralisation

67 with lime or adsorption and co-precipitation of non-metallic species can be used [17–19].

68 However, these alternatives require a huge amount of chemicals for carrying out the

69 separation process, the potential recovery of valuable components may be reduced, and the

70 residual levels of toxic species do not fulfil most of the industrial effluent or environmental

71 discharge limits.

72 Nowadays, membrane technologies are being used as an alternative to conventional

73 treatments for dealing with acidic effluents, both industrial and AMWs, as they offer: i) high

74 water recovery ratio and additional concentration factor for resource recovery options and ii)

75 high water quality with low presence of toxic metal and non-metal species, which allows to

76 meet the environmental discharge limits. Studies about the application of reverse osmosis

77 (RO), nanofiltration (NF), and electrodialysis (ED) can be found for arsenic removal [20–24].

78 Among different membrane technologies, NF can be used for treating AMWs, exhibiting high

79 rejections of multivalent ions (e.g. metals, non-metals), while the transport of monovalent

80 species is favoured (e.g. H^+, HSO_4^-, Na^+, Cl^-). NF has been proved to be useful for treating

81 AMWs. Metals can be effectively rejected (>90%), while water can be obtained as permeate

82 [25,26], and if the feed solution to be treated has a moderate acidity (pH=1), acid can be

83 obtained as permeate as well [27,28]. However, most of the published studies for arsenic

84 removal are for surface and groundwater, with rejections between 50% to 89% and from 87%

85 to 93% for As(III) and As(V), respectively [20,21]. Only a few works dealing with arsenic

86 removal from acidic waters are found in the literature. Al-Rashdi et al. [22] evaluated the

87 removal of metal ions (e.g. Cu, Mn, Cd, Pb) and As(III) with the NF270 polyamide-based

88 membrane. The effect of pH was studied and As(III) rejections were below 15% from pH 1.5 to

89 5. López et al. [24] studied the same membrane for treating a copper smelter effluent. They

90 achieved high metal rejections (>80%), while the arsenic permeated (rejections below 40%)

91 because of its presence as a non-charged species (H_3AsO_4). In addition, special attention

92 should be paid to other toxic components, such as cadmium chromium, lead and selenium.

93 In this work, AMWs from *La Poderosa* mine (Iberian Pyrite Belt) containing up to 10 mg REEs/L,

94 was treated with a commercial polyamide-based nanofiltration membrane (ESNA1-LF-LD-

95 4040) under spiral-wound (SW) configuration. This acidic water was characterised by a pH 2.0-

96 2.2 and by the presence of metals (e.g. iron, copper, zinc) and toxic metallic (e.g. cadmium,

97 lead and chromium) and non-metallic elements (e.g. arsenic, selenium). Previous to the

98 treatment with SW-NF, H_2O_2 and NaOH were added to the AMWs for iron, arsenic and
99 selenium removal to avoid scaling at the membrane surface. The effect of the pressure (6-20
100 bar) in elements rejections was investigated by SW-NF in a closed-loop configuration. Finally, a
101 membrane test was carried out reproducing a treatment plant consisting of ten SW-NF
102 modules in series at three different pressures (10, 15 and 22 bar). The aim of this final test was
103 to evaluate the water recovery, the concentration factor and the permeate water quality, as
104 this treated water could be discharged to natural water receiving bodies or used in industrial
105 applications. The concentration of the toxic metals and non-metals was followed along the
106 treatment stages, and the values achieved in the treated stream (i.e. permeate) were analysed
107 according to the different regulations, covering from industrial discharge limits to
108 environmental protection standards for natural ecosystems.

2. Materials and methods

2.1. Reagents

111 Hydrogen peroxide (35% (v/v), H_2O_2) was used to oxidise Fe(II) to Fe(III), As(III) to As(V) and
112 Se(IV) to Se(VI), and NaOH (pellets) was used for adjusting pH. Hydrochloric acid (37%, HCl)
113 was used for membrane cleaning. All chemicals were analytical grade reagents from Sigma
114 Aldrich.

2.2. Acidic mine waters

116 The AMWs treated in this work was from *La Poderosa* mine located in the Iberian Pyrite Belt
117 (South-West of Spain, Huelva). The pH of AMWs was between 2.0-2.2, and they presented high
118 metal concentrations due to the oxidation of sulphide minerals. **Table 1** shows the initial water
119 composition from *La Poderosa* mine. Also, the AMWs showed an orange-brown colour due to
120 very high iron concentrations in solution [29].

121 As shown in **Table 1**, AMWs were mainly composed of iron, sodium and sulphur (higher
122 concentration values than 1100 mg/L). Other main elements present in AMWs were
123 aluminium, calcium, magnesium, copper, zinc and manganese. Besides, arsenic, REEs
124 (neodymium, gadolinium, samarium, praseodymium, and dysprosium, among others), cobalt,
125 cadmium and others minor elements were also present in concentration values from 3000 to 5
126 µg/L.

2.2.1. Pre-treatment of AMWs: Fe and As removal

128 Previously to the treatment of the AMWs with SW-NF, iron was removed to prevent scaling at

129 the membrane surface. Moreover, in this stage, arsenic can be removed because it co-

130 precipitates with Fe(III) as $FeAsO_4(s)$. In fact, Carrero et al. [30] indicated that Fe(III) mineral

131 phases precipitation, as nano-crystalline structures in AMWs, implied an important removal of

132 anionic trace elements, such as arsenic. In this case, the main removal mechanism for arsenate

133 and selenite is the combination of surface complexes and oxyanion exchange. In this case, iron

134 was removed from AMWs by the oxidation of Fe(II) to Fe(III) with H_2O_2, adding 1 mL of H_2O_2

135 35% (v/v) per 1 L of acidic mine water, and increasing the pH up to 3.7-3.8 with NaOH (2 M)

136 [2,27]. Finally, the precipitates (according to the literature is mainly schwertmannite

137 [$Fe_8O_8(OH)_{8-2x}(SO_4)_x \cdot nH_2O$, where $1 \leq x \leq 1.75$] [6,31,32]), solids and colloidal matter were

138 removed first by gravity filtration using a filter paper (Whatman № 42, 2.5 µm) following a

139 second filtration with quartz sand column.

2.3. Spiral-wound nanofiltration

2.3.1. Experimental design

142 Two types of experiments were carried out by a SW-NF set-up: i) NF closed-recirculation mode

143 and ii) NF stages in open-recirculation mode. **Figure 1** represents both types of experiments.

144 In the first set (**Figure 1.a**), both concentrate and permeate streams were recirculated to the

145 feed tank, maintaining a constant feed concentration (i.e. feed composition along the

146 experiments was the same as the initial one, due to mixing again the permeate and

147 concentrate streams in the feed tank). The trans-membrane pressure (TMP) was increased (2

148 by 2 bar) from 6 to 20 bar. Samples from the permeate stream were collected and analysed at

149 different TMP. Also, initial and final feed samples were collected from the feed tank to check

150 feed concentration evolution.

151 The second set of experiments (**Figure 1.b**) was carried out mimicking SW-NF in a pressure

152 vessel containing ten SW membrane modules. For this purpose, both generated output

153 streams (concentrate and permeate) were collected in different tanks, and only the

154 concentrate taken from one stage was used as feed solution for the next one. In this case, as

155 membrane stabilisation procedure, before feeding the concentrate in the next membrane

156 stage, the solution was circulated through the system for 5 min. TMP tested in the open-loop

157 configuration were 10, 15 and 20 bar. Samples from concentrate and permeate streams were

158 collected and analysed in each membrane filtration step.

2.3.2. SW-NF set-up

159   **2.3.2. SW-NF set-up**

160   The experimental set-up used for SW-NF membrane tests with AMWs is described elsewhere

161   [33,34]. Before starting the experiments, deionised water was pumped through the membrane

162   modules at the maximum TMP (22 bar) during 1.5 h to achieve membrane steadiness.

163   Afterwards, this procedure was repeated with feed solution at 22 bar for 2 h to ensure that the

164   membrane density was kept constant during the full experiment. This process implied the

165   membrane compaction.

166   The SW-NF membrane used for all experiments was ESNA1-LF-LD-4040, purchased from

167   Hydranautics (USA) [35]. The surface material of the membrane is a composite aromatic

168   polyamide, and it has a surface-active area of 7.43 m^2. This membrane is a polyamide-based

169   membrane with an iso-electric point (IEP) of 4.5 [36,37].

170   After pressurisation steps (with deionised water and feed solution), the feed solution (50 L)

171   was pumped into the membrane module passing previously through a pre-filter cartridge (100

172   μm). TMP was gradually varied from 6 bar to 20 bar in the closed-configuration experiments,

173   whereas the TMP was fixed (at 10, 15 and 20 bar) in the open-configuration ones. In both

174   cases, two output streams were obtained, the permeate and the concentrate. Although in the

175   first step of experiments (**Figure 1.a**) both were recirculated into the feed tank, whereas in the

176   second set (**Figure 1.b**) both were collected and separated in different product tanks.

177   During the experiments, several parameters such as pressure, flow, conductivity, pH and

178   temperature were monitored.

179   Once an experiment was finished, the membrane was cleaned by the following steps: 1) with

180   deionised water at 10 bar for 30 min; 2) with new deionised water at 22 bar for 1.5 h; 3) with

181   diluted HCl (pH=2.1-2.5) at 10 bar for 30 min, and 4) with fresh deionised water at 22 bar for

182   1.5 h.

183   The hydraulic water permeability of the membrane after experiments was compared with the

184   virgin membrane value to ensure that the membrane was cleaned successfully.

2.3.3. SW-NF data analysis

185   **2.3.3. SW-NF data analysis**

186   The TMP was calculated taking into account the system pressures around the membrane stack,

187   as follows equation (1) [38]:

$$TMP\ (bar) = \frac{P_F + P_C}{2} - P_P \qquad (1)$$

188   where P_F is the feed pressure entering into the test cell (bar), P_C is the outgoing pressure in the

189   concentrate stream (bar) and P_P is the outgoing pressure in the permeate stream (bar).

190   During the experimental tests, the trans-membrane flux (J_v) was also calculated by Equation (2)

191   [22,38]:

$$J_v \left(\frac{L}{m^2 \cdot h} \right) = \frac{Q_P}{A} \tag{1}$$

192   where Q_P is the permeate flow (L/h) and A is the active membrane area (m^2).

193   Water permeability constant (K_w) can be obtained with the following equation (3) when

194   filtering deionised water [22]:

$$K_w \left(\frac{L}{m^2 \cdot h \cdot bar} \right) = \frac{J_v}{TMP} \tag{3}$$

195   where J_v is the permeate flux (L/h·m^2) and the TMP is the trans-membrane pressure (bar).

196   For closed-recirculation experiments, equation (4) was used to determine the obtained

197   rejection (R) percentage [38]:

$$R\ (\%) = \frac{C_F - C_P}{C_F} \cdot 100 \tag{4}$$

198   where C_F and C_P are the concentration of each element in the feed and permeate solution

199   (mg/L), respectively.

200   On the other hand, for open-circulation assays, as the feed concentration changed at each

201   filtration stage, the equation (4) can be depicted as equation (5):

202    $R_1\ (\%) = \frac{C_F - C_{P1}}{C_F} \cdot 100 \ ; R_2\ (\%) = \frac{C_{c1} - C_{P2}}{C_{c1}} \cdot 100 \ ; ... ; R_n\ (\%) = \frac{C_{c(n-1)} - C_{P(n)}}{C_{c(n-1)}} \cdot 100$ (5)

203   where C_F, C_P and C_C are the concentration of each element in the feed, permeate and

204   concentrate solution (mg/L), respectively, and n is the number of stages performed.

205   Additionally, for open-circulation tests, the concentration factor (CF) of each element was

206   calculated taking into account the equation (6) [34]:
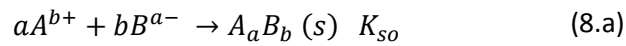
$$CF = \frac{C_c}{C_P} \tag{6}$$

207   where C_C and C_F are the concentration in the concentrate and feed solution (mg/L),

208   respectively.

209 The performance of the membrane in open-recirculation tests was represented as a function
210 of permeate recovery, defined as follows equation (7):

$$Permeate\ recovery\ (\%) = \frac{V_{t=o} - V_t}{V_{t=o}} \cdot 100 \qquad (7)$$

211 where $V_{t=0}$ (50 L) and V_t are the volumes of the feed tank solutions at the beginning of the
212 experiment and at time t, respectively.

213 Finally, from the chemical composition of the open-recirculation tests, a chemical analysis
214 using PHREEQC (U.S. Geological Survey) [39] was performed to assess the scaling potential at
215 the membrane surface. Then, for a precipitation reaction (equation 8.a), the saturation
216 indexes (SI) were calculated according to equation 8.b:

$$aA^{b+} + bB^{a-} \rightarrow A_aB_b\ (s)\ \ K_{so} \qquad (8.a)$$

$$SI = \log\left(\frac{IAP}{K_{so}}\right)\log\left(\frac{[A]^a \cdot [B]^b}{K_{sp}}\right) \qquad (8.b)$$

217 where IAP is the ion activity product and K_{so} is the precipitation constant. If SI>0, the solution is
218 supersaturated, whereas SI<0 the solution is undersaturated. In the case that SI=0, the solution
219 is saturated.

2.4. Analytical methodology

221 The initial AMWs, the pre-treated AMWs and samples after experiments were analysed by
222 Inductively Coupled Plasma (ICP) combined with Optical Emission Spectroscopy (ICP-OES,
223 Agilent 5100) and Mass Spectrometry (ICP-MS, Agilent 7800) to determine solution
224 composition (e.g. transition metals, non-metals and REEs). Samples were filtered (0.2 μm) and
225 acidified with 2% HNO_3 before their analysis by ICP. The pH was monitored with a pH-meter
226 (GLP 21, Crison).

3. Results and discussion

3.1. Acid mine waters pre-treatment for iron and arsenic removal

229 **Table S1** (Supplementary material) shows the removal percentage of each element present in
230 the acidic mine waters at pH 3.7-3.8 during the iron and arsenic removal step.

231 The pre-treatment of AMWs allowed to remove 99±1% of iron, 84±2% of arsenic, and 63±13%
232 of selenium, followed by 36±2% of sodium, 26±3% of cobalt, 25±2% of cadmium, 22±2% of
233 aluminium, 16±2% of nickel and 16±2% of manganese. The elimination percentage of other

234   metals and REEs was lower (between 6.2±0.6% magnesium to <0.2% calcium, zinc, among

235   others). Therefore, the AMWs pre-treatment to remove iron for reducing the expected scaling

236   in the NF stage was effective and also a reduction of two toxic elements as arsenic and

237   selenium was partially achieved.

238   Results are in agreement with previous studies with AMWs, where >98% Fe and partial

239   removal of Al(III) were reported by Wei. et al. [40] after oxidation of Fe(II) to Fe(III) in the

240   presence of H_2O_2 as oxidising agent and sub-sequent precipitation at pH 3.5. Additionally,

241   Carrero et al. [30] observed that during the precipitation of Fe(III) and Al(III) as

242   hydroxysulphates, As(V) and Se(VI) can also co-precipitate or be adsorbed. Besides, the rest of

243   the main metal ions (Zn(II) and Cu(II)) in solution did not precipitate, as well as the REEs, which

244   are pursued to be recovered in a later stage. These results can also be compared with the

245   previous studies, such as the one by Lozano et al. [41], who reported that REEs precipitates

246   above pH by sorption onto basaluminite.

247   It was assumed that arsenic and selenium are at their highest oxidation state after the addition

248   of H_2O_2 as As(V) and Se(VI). Both elements are as anionic forms as described in **Annex A**. After

249   the selective precipitation stage at pH 4, partial removal of 84.2±2.0% and 62.0±3.0% for

250   arsenic and selenium was achieved, respectively. Carrero et al. [30] reported that the

251   formation of iron and aluminium nano-crystalline structures in AMWs is responsible for the

252   removal of trace non-metal elements (i.e. arsenic, selenium). They concluded that anion

253   exchange with structural sulphate ions was the main mechanism for $HSeO_4^-$, whereas a

254   combination of surface complexation and anion exchange was responsible for $H_2AsO_4^-$

255   removal. They also found that the $H_2AsO_4^-$ sorption capacity in basaluminite was two times

256   higher than in schwertmannite, but also three times higher than the $HSeO_4^-$ sorption capacity

257   in both minerals. Then, the removal of both arsenic and selenium in iron and aluminium sludge

258   can be beneficial for the final discharge to the medium of the treated AMWs. However, an

259   evaluation of the disposal of the sludge is required.

260   In consequence, the composition of the AMWs after their pre-treatment to remove the iron is

261   summarised in **Table 2**.

262   As showed in **Table 2**, the AMWs to be treated by SW-NF contained similar values as the initial

263   one but with less iron (9±1 mg/L), and a much lower arsenic concentration (322±18 μg/L in

264   comparison with an initial concentration of approximately 2041±294 μg/L). Thus, the AMWs

265   treated by SW-NF contained a high amount of sulphur (1747±135 mg/L), present in solution as

266 sulphate, sodium (1250±110 mg/L) and metals, such as aluminium (195±29 mg/L), copper

267 (78±7.5 mg/L) and zinc (78±6 mg/L); and low concentration of REEs ranged from 2816±187

268 µg/L (Ce) to 5±1 mg/L (Sc).

3.2. Spiral-wound nanofiltration experiments

3.2.1. Effect of trans-membrane pressure on elements rejections

271 The effect of TMP on the elements rejections with the solution after Fe removal pre-treatment

272 was studied. **Figure S1** shows the dependence of permeate flux on TMP, and **Figure 2**

273 represents the rejections for each element in solution.

274 As can be seen in **Figure S1** the flux increases linearly with the TMP, and can be described by

275 the following phenomenological equation:

$$J_v = k_W \cdot (TMP - \Delta\pi) \tag{9}$$

276 where k_w is the hydraulic membrane permeability (L/(m^2·h·bar)) and $\Delta\pi$ is the average osmotic

277 pressure of the solution (bar).

278 Accordingly, this membrane has a hydraulic permeability of 2.31 L/(m^2·h·bar), whereas the

279 osmotic pressure of the solution can be estimated to be 2.78 bar (J_v = 0).

280 **Figure 2.a** collects the rejections for the elements at initial concentrations below 1 mg/L,

281 whereas **Figure 2.b** shows the rejections for those elements with concentration values above

282 that concentration. This last figure, shows the rejection for REEs, which corresponds to the

283 following elements: cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum,

284 lutetium, neodymium, praseodymium, samarium, scandium, terbium, thulium, ytterbium and

285 yttrium. In order to distinguish properly the tendencies of major components, whose transport

286 directly influences the one of trace species, the y-axis (i.e. rejection) is displayed from 90% to

287 100% (**Figure 2.b**).

288 The SW-NF membrane exhibited good performance for trivalent and divalent metal removal

289 (i.e. aluminium, iron, copper and calcium, among others), providing rejection values higher

290 than 99%. Below the metal rejections, the corresponding one to sulphate (97-99%) and sodium

291 (95-98%) can be found. These high rejections contrast with those obtained for proton (80-90%)

292 and arsenic (60-71%), which exhibited much lower values.

293 The obtained rejections can be explained with the basis of the main membrane mechanisms:

294 Donnan and dielectric exclusions.

295   The Donnan exclusion postulates that the membrane presents a superficial charge because of

296   the protonation and deprotonation of the active layer functional groups. Thus, membranes

297   active layers in based to polyamide chemistry, depending on the solution pH, exhibit a positive

298   or negative surface charge [42,43]. The pH value at which the membrane has no superficial

299   charge is defined as the IEP. Below the IEP, the membrane presents a positive surface charge,

300   which attracts the anions in solution (counter-ions) and repels the cations (co-ions). Above the

301   IEP, the transport of cations is favoured because of the membrane negative charge [25].

302   However, the Donnan exclusion is not able to explain the membrane selectivity regarding the

303   rejections for multivalent and monovalent elements. Instead, the dielectric exclusion

304   postulates that the difference of dielectric constants (polymeric matrix/bulk solution) causes

305   an interaction between the ions in solution and the bound electric charges induced in the

306   membrane. The dielectric exclusion explains the membrane selectivity because the ion-

307   exclusion free energy is proportional to the square of the ion charge, whereas in the Donnan

308   exclusion, such dependence is linear [44,45].

309   Both phenomena explain the obtained results in this work. The ESNA1-LF-LD-4040 is a

310   polyamide-based membrane with free ionisable amine (R-NH$_2$) and carboxylic (R-COOH)

311   groups, whose protonation or deprotonation confers the membrane a net surface charge. The

312   pH of the solution was below the IEP (i.e. 4.0<4.5), then the amine and carboxylic groups were

313   partially and fully protonated, respectively (i.e. R-NH$_3^+$/R-COOH) [36,37]. Accordingly, the

314   positive membrane surface charge favoured the transport of anions, whereas the cations were

315   repelled. In addition, the dielectric exclusion hindered the transport of multivalent ions. These

316   two facts explained why the multivalent metals were highly rejected by the membrane (>99%).

317   The fact that the membrane favoured the transport of anions explained why sulphate

318   rejections were lower than the metal ones (97-99%). However, because of the major presence

319   of sulphate as a bivalent anion (e.g. SO$_4^{2-}$, see **Annex A**), it was highly rejected because of

320   dielectric exclusion. In addition, the fact that arsenic was mainly present as monovalent

321   species (i.e. H$_2$AsO$_4^-$) resulted in lower rejections (60-71%). The fact that anions permeated

322   across the membrane implied that a stoichiometric number of cations must permeate to

323   accomplish the electro-neutrality condition. In this case, the preferred ones to be transported

324   were sodium and proton, which exhibited lower rejections than metals (i.e. 95-98% and 80-

325   90% for sodium and proton, respectively) because of dielectric exclusion.

326   The ESNA1-LF-LD-4040 membrane showed not only potential use for treating AMWs, but also

327   to remove hazardous materials such as arsenic, cadmium, chromium, lead and selenium. **Table**

328   **3** collects the feed and permeate composition of these elements at three different TMP.

329   It must be highlighted that no studies about the performance of this membrane in SW

330   configuration were found in the literature. However, other similar polymeric commercial NF

331   membranes have been applied for the treatment of AMWs, and the results were in agreement

332   with the ones above-mentioned. For example, Al-Zoubi et al. [46] optimised the performance

333   of polyamide-based membranes (Alfalaval NF99 and Osmonics DK) for the treatment of an

334   AMWs (pH=2.6, 1.2 g/L aluminium, 2.3 g/L copper, 14 g/L sulphate). In that work, rejection for

335   metals was higher than 98%, whereas the one for sulphate was around 80%. In a subsequent

336   study [47], they obtained transition metal rejections higher than 98% for NF99 and DK, with

337   rejections higher than 98% for sulphate with a different AMWs. In addition, they were able to

338   obtain a permeate richer in acid than the feed stream (e.g. pH 2.7 vs 2.5). Al-Rashdi et al. [22]

339   studied the removal of transition metal ions (e.g. copper, manganese, cadmium, lead and

340   arsenic, all at 1000 mg/L) with NF270 membrane. At a pressure of 4 bar and pH=4, the

341   following rejection sequence was obtained: copper (99%) > cadmium (70%) > lead (60%) >

342   manganese (30%) > arsenic (12%). The low rejection of arsenic (As(III)) was explained because

343   of its presence of H_3AsO_3 (neutral specie). Besides, it must be highlighted that at pH=4, the

344   membrane was near to its IEP (3.5-4.0), which could explain the low rejections for the other

345   metals.

346   Urase et al. [20] studied the effect of pH on the rejection of arsenate (AsO_4^{3-}) and arsenite

347   (AsO_3^{3-}) with the ES-10 membrane. For example, arsenite rejections shifted from 50 to 89%

348   when the pH increased from 3 to 10. Instead, rejections for arsenate barely varied (87-93%).

349   These changes in arsenite rejections were explained with the arsenic speciation. At pH=3,

350   arsenite can be found as H_3AsO_3, whereas arsenate is present as $H_2AsO_4^-$. The increase in pH

351   leads to the deprotonation of both species ($H_2AsO_3^-$ pK=9.24, $HAsO_4^{2-}$ pK=6.94), which were

352   rejected by the negatively charged membrane.

353   Recently, Wadekar and Vidic [48] treated the drainage of an abandoned coal mine with a

354   semiaromatic polymeric (NF270) and a ceramic membrane (TiO_2, molecular weight cut-off

355   (MWCO) of 500 Da). The effluent was characterised by a pH=7.8, 151 mg/L calcium, 110 mg/L

356   sodium, 70 µg/L arsenic and 55 µg/L selenium, among others. NF270 was able to reject

357   multivalent metals (>96%), while the ceramic membrane exhibited lower rejections (50-70%).

358   Selenium was rejected 30-40% by the ceramic membrane, whereas the NF270 removed it

359   effectively (>90%). The lowest rejection for both membranes was for the arsenic, with values

360   in the range 10-20% and 30-35% for the ceramic membrane and NF270, respectively.

361   **3.2.2. Projection of a SW-NF treatment stage in a resource recovery scheme**
362   **from a REE-rich AMWs**

363   From the data obtained previously, it was decided to mimic a full-scale vessel with the SW-NF

364   module by recirculating and filtering the concentrate stream sequentially in 10 steps. This

365   experiment was performed at three different TMPs (10, 15 and 22 bar) with the pre-treated

366   AMWs. The objective was to optimise the water recovery ratio and the water quality for direct

367   discharge into natural water bodies or potential water re-use by varying the TMP.

368   **Figure 3** shows the obtained permeate flux, as well as the permeate recovery achieved along

369   with the whole treatment with 10 SW-NF steps at the above-mentioned TMPs. As expected,

370   the higher the pressure, the higher the permeate flux. The high rejections provided by the

371   membrane caused an increase in the osmotic pressure along with the treatment, thus

372   decreasing the effective pressure gradient and then the permeate flux. In addition, higher

373   pressures favoured the recovery of more water with the same membrane steps. For example,

374   working at 22 bar water recovery reached a value of 83%, whereas at 10 bar was 54%, both

375   after 10 SW-NF steps.

376   **Figure 4** collects the obtained rejections for each membrane step at the three TMP evaluated

377   (10, 15 and 22 bar). Due to the fact that cerium, cobalt, magnesium, nickel, scandium, thorium,

378   yttrium, aluminium, calcium, copper, iron, magnesium and zinc were effectively rejected by

379   the membrane (>99%), these elements were grouped as metals for simplicity.

380   As observed in **Figure 2**, metals, cadmium, chromium, lead and REEs were effectively rejected

381   at the first SW-NF step (>99%) for all tested TMP. However, the fact that these metals became

382   more concentrated in solution after several SW-NF steps, increased the concentration gradient

383   (driving force) across the membrane, and then favoured slightly their passage (rejections >95%

384   at all TMP tested) as can be seen in **Figure 4**. Sodium rejections were lower because of being a

385   monovalent species, and dropped from 96% to 85% for all the TMP tested. Arsenic showed a

386   different trend, and their rejections were around 80% at 10 bar, ranged from 86 to 79% at 15

387   bar and from 91% to 75% at 22 bar.

388   At the end of the experiment, metals in solution get concentrated with CF of 2.15 ± 0.02 (10

389   bar, 54% permeate recovery), 2.97 ± 0.14 (15 bar, 67% permeate recovery) and 5.78 ± 0.08 (22

390   bar, 83% permeate recovery). Arsenic(V) species presented a different CF due to their lower

391   rejections: 1.80 (10 bar), 1.87 (15 bar) and 2.36 (22 bar). It should be stressed the fact that

392   while elements in solution get concentrated, precipitation of solid phases may occur,

393   especially at the membrane surface because of concentration polarisation. Therefore, a

chemical speciation analysis was performed to determine the potential scaling by means of the saturation indexes. Due to the fact that concentration polarisation may increase the concentration at the membrane, a factor of 10 over the composition of the concentrate stream was considered. This analysis was carried out with the last step of the experiment at 22 bar. **Table S2** shows the potential mineral phases to precipitate at the solution as well as at the membrane surface. As can be seen, the precipitation of sulphate minerals, especially those containing sulphate (anglesite, anhydrite, glauberite, gypsum and schwertmannite), were the most likely to happen. In the case of schwertmannite, despite having a high SI (higher than 10), it should be reminded that the iron concentration at the beginning of the process was residual (9±1mg/L). Therefore, if the treatment of AMWs is going to be implemented, the addition of anti-scalants should be considered to ensure a long useful life of the membranes. Additionally, acid cleanings would be recommended to remove any solid phase that may occur.

Finally, the composition of the harmful elements in the permeate of the AMWs at the end of the SW-NF process was evaluated (**Table 4**). As can be seen, the concentration of the hazardous components was quite lower in comparison with the initial ones, with values even lower than 1 µg/L for chromium and selenium. Higher concentrations of cadmium and lead (2-9 µg/L) were achieved with SW-NF, whereas the arsenic exhibited the highest ones (64 - 71 µg/L).

These values can be compared with the discharge limits from legislation concerning the industry, the criteria for superficial water and also the recommended limits for drinkable water (see **Table 5**). The Spanish legislation concerning the water quality of superficial water bodies R.D. 817/2015 (based on European Union Directive 2008/105/CE) has very restrictive limits for arsenic (50 µg/L), cadmium (0.25 µg/L), chromium (50 µg/L), lead (7.2 µg/L) and selenium (1 µg/L) in rivers and lakes. From the permeate composition, the only elements that surpass the recommended limits are cadmium and arsenic, although the arsenic concentration was quite close to the discharge criteria. Furthermore, the Spanish Law 5/2002 established the limits for industrial discharges to the public sanitation systems with a higher threshold of emissions than the R.D. 817/2015. Legislation from Canada (SOR/2002-222) and USA (40 CFR Part 440) was also consulted regarding the threshold of hazardous substances in the mining industry effluents. Despite being more restrictive than the Spanish legislation, the composition of the permeate fits within the recommended limits. Moreover, the European Union has listed the concentration achievable during the treatment of mining effluents by the use of Best Available Technologies, and as can be seen the permeate concentrations fall within them. Finally, the

427 limits of WHO were also consulted but they are more stringent if the water is directly used for

428 human consumption.

429 The concentration of arsenic in the permeate can be reduced by operating the SW-NF at

430 higher pH. By working at pH>5, the $H_2AsO_4^-$ starts deprotonated to $HAsO_4^{2-}$ and at pH>pK (pK =

431 6.94 [20]), the double-charge arsenate species predominates in solution. Additionally, the pH

432 of the solution would be higher than the IEP, thus the membrane would be positively charged.

433 Therefore, according to the Donnan and dielectric exclusions, the anions (especially multi-

434 charge ones) would be completely rejected by the membrane. This matches with the results

435 from Urase et al. [20], who observed an increase in As(V) rejections from 87% at pH 3 to 93%

436 at pH 10 with ES-10 NF membrane, and from Figoli et al. [49], who obtained a shift in As(V)

437 rejections moving from pH 3 to 10 (from 94% to 98.4% for NF90 and from 74% to 88% for

438 N30F). High As(V) rejections (>95%) at pH 8.1–8.2 were obtained with SW-NF membranes

439 (NF300) by Saitúa et al. [50]. However, despite of rejecting arsenic, the transport of cadmium

440 and lead may increase across the membrane because of its negatively charged surface and also

441 the REEs co-precipitate with the aluminum, which can comprise the environmental

442 sustainability of the process.

443 The proposed treatment showed an alternative to traditional methods (**Figure 5**). The

444 traditional methods (mostly based on neutralisation/precipitation or sulphate reduction in

445 wetlands) can recover the total amount of water. However, the neutralisation/precipitation

446 method generates a sludge-rich in water with a 2-4% of solid content. This hazardous waste

447 should be treated properly due to the high concentration of toxic elements (e.g. arsenic and

448 metals). On the other side, the reduction of sulphate, accompanied by metal precipitation, also

449 generates a voluminous sludge [2,4,51]. The proposed treatment of the AMWs from *La*

450 *Poderosa* based on the removal of iron and arsenic at pH=4 (as As sorption onto

451 schwertmannite) by chemical precipitation and the subsequent filtration with the ESNA1-LF-LD

452 may be a choice for: i) producing water with quality standards on arsenic, selenium and other

453 metal ions making it compatible for discharge into the medium as environmental water or

454 being re-used in other industrial uses; ii) concentrating up to five times the REEs and the

455 transition metals for further valorisation schemes. With the evaluated 80% water recovery

456 factor, the inlet flow-rate may be recovered as permeate with concentrations that make it

457 suitable for industrial re-use or direct discharge to the rivers according to the legislation (**Table**

458 **5**). Additionally, it can provide a reduction of the waste generated (i.e. sludge), but also a

459 generation of a revenue stream (i.e. the concentrate as an enriched-REE stream) than can

460 make this environmentally sustainable process as economically viable. This economic viability

461 will be linked to the fact that REEs have been included as "Critical Raw Materials" for the

462 European Union [52] and their recovery from secondary resources, such as AMWs, has been

463 converted in mandatory as it is the need to recover phosphorous from the urban wastewater

464 cycle [53] after the phosphatic rock was also included on the Critical raw material list [52] and

465 its recovery is promoted by the Circular Economy Programme [54].

4. Conclusions

467 The proposed treatment (based on iron removal by chemical precipitation and SW-NF) showed

468 its potential for a sustainable treatment of REE-enriched AMWs, where the levels of arsenic

469 and selenium in the treated water (i.e. permeate) reached industrial water discharge limits. At

470 the AMWs pH, the polyamide active layer of the membrane was positively charged (pH<IEP,

471 4.5) and was able to reject all the metals by more than 95% because of the electric fields

472 (Donnan and dielectric exclusions), whereas the arsenic, present as As(V), presented lower

473 rejections (60-71%) because of its presence as $H_2AsO_4^-$. The fact that As(V) was present as a

474 single-charge anion did not impede its transport across the membrane because of Donann and

475 dielectric exclusions. Additionally, other elements present in the AMWs should be considered

476 in the water quality such as cadmium, chromium, lead and selenium because of their toxicity.
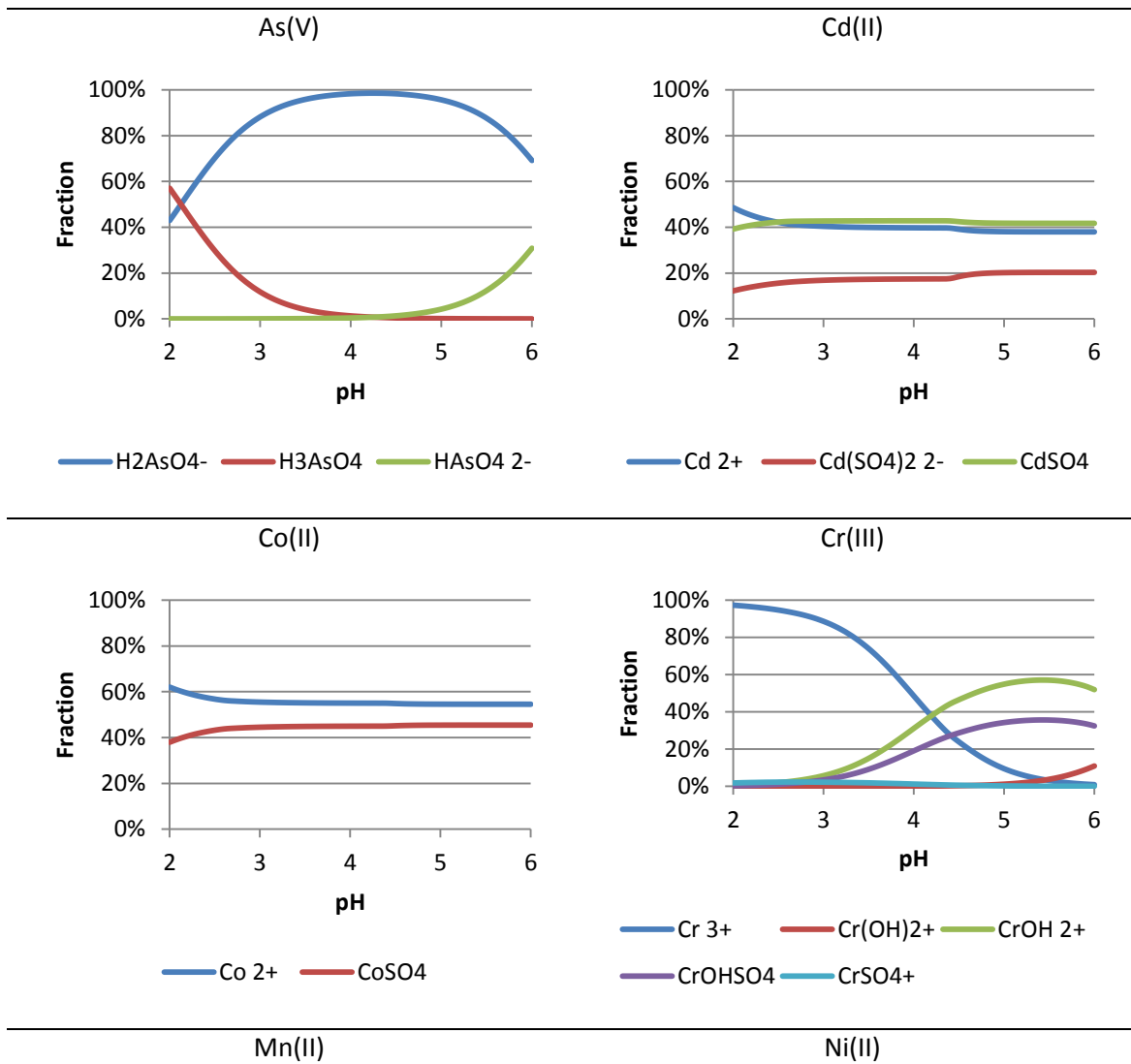
477 The treatment of an AMWs was conducted by mimicking a SW-NF plant based on 10 stages,

478 showing that it was possible to achieve a water recovery of around 80% of the nominal flow.

479 Three different pressures were tested (10, 15, and 22 bar), and the highest one provided the

480 highest permeate flux (i.e., 83% of permeate recovery at 22 bar). By analysing the chemical

481 composition of the recovered water, it was observed that the permeate contained around 65

482 μg/L of arsenic (in comparison to 2041 μg/L of the raw AMWs). The concentration of other

483 elements, such as selenium and chromium (initial concentrations of 32 and 17 μg/L,

484 respectively) was reduced to values lower than 0.5 μg/L in the NF permeate. Additionally, 4%

485 of the lead was able to permeate (3-9 μg/L), whereas only a 2% of the cadmium in the feed

486 solution passed across the NF membrane (5 μg/L in the permeate). These low concentrations

487 (below the discharge limits) showed the potential of SW-NF membranes for the recovery of

488 high-quality water (recovery of 83%). Therefore, the proposed treatment based on (i) chemical

489 oxidation, (ii) Fe(III) and As(V) precipitation and (iii) SW-NF showed its potential for producing

490 high-quality water (according to environmental laws). However, the chemical speciation

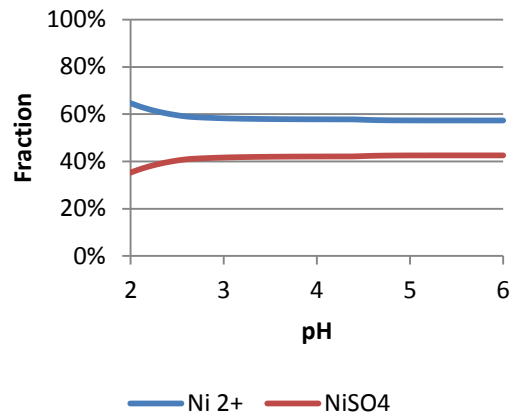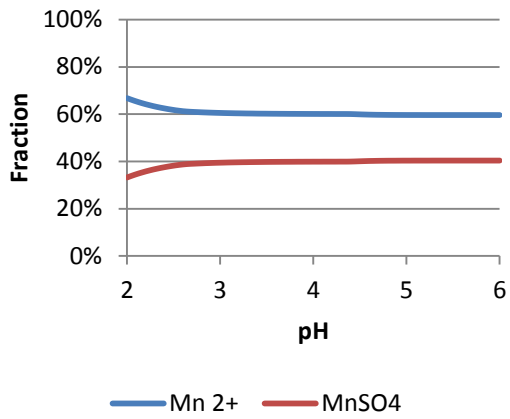491 analysis revealed that at this high recovery, scaling may occur at the membrane, mainly caused

492   by calcium sulphates. Therefore, it would be recommended the use of anti-scalants and acidic
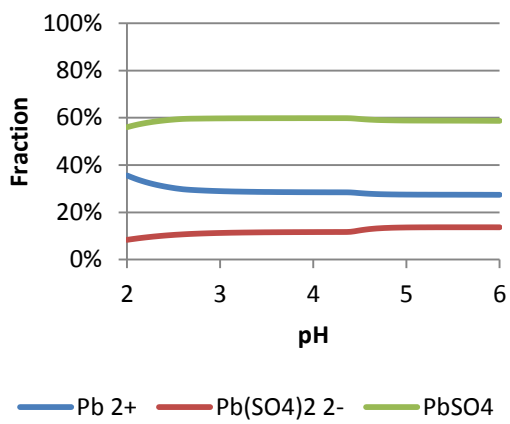
493   cleaning at large scale.

494 Acknowledgements

502 Annex A. Speciation diagrams

Mn 2+ ——— MnSO4   Ni 2+ ——— NiSO4

Pb(II)

Se(VI)

Pb 2+ ——— Pb(SO4)2 2- ——— PbSO4   SeO4 2- ——— HSeO4-

Y(III)

REEs(III)

Y 3+ ——— Y(SO4)2- ——— YSO4+   REE 3+ ——— REE(SO4)2- ——— REESO4+

Al(III)

Ca(II)

Legend (top-left plot): Al 3+, Al(SO4)2-, Al2(OH)2 4+, Al3(OH)4 5+, AlHSO4 2+, AlOH 2+, AlSO4+

Legend (top-right plot): Ca 2+, CaSO4

Cu(II)

Fe(II)

Legend (middle-left plot): Cu 2+, CuSO4

Legend (middle-right plot): Fe 2+, FeSO4

Mg(II)

S(VI)

Legend (bottom-left plot): Mg 2+, MgSO4

Legend (bottom-right plot): SO4 2-, Al(SO4)2-, AlSO4+, CaSO4, CuSO4, HSO4-, MgSO4, NaSO4-, YSO4+

Zn(II)

Na(I)

20

Zn 2+   Zn(SO4)2 2-   ZnSO4   Na+   NaSO4-

503

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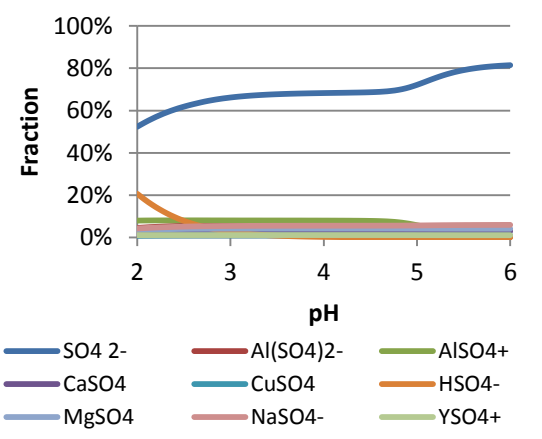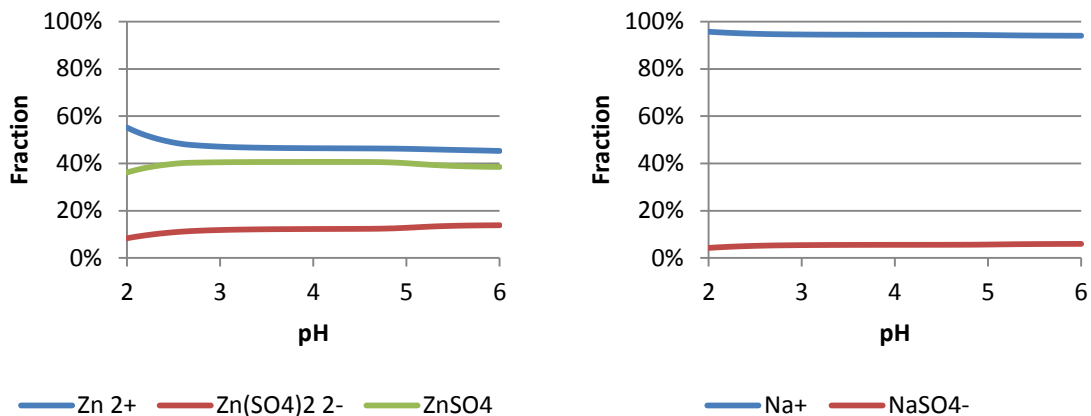516   Trans. 28 (2012) 109–114. doi:10.3303/CET1228019.

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657

Table

Table 1. *Acidic mine water composition from La Poderosa Mine (Huelva, SW Spain).*

Main elements	mg/L	Minor elements	µg/L	Minor elements	µg/L
Iron (Fe)	1141±105	Cerium (Ce)	2948±356	Erbium (Er)	139±10
Sodium (Na)	1951±189	Arsenic (As)	2041±294	Lead (Pb)	113±9
Sulphur (S)	1817±176	Neodymium (Nd)	1745±177	Ytterbium (Yb)	99±8
Aluminium (Al)	251±42	Yttrium (Y)	1629±153	Terbium (Tb)	79±7
Calcium (Ca)	154±27	Cobalt (Co)	1434±148	Europium (Eu)	69±7
Magnesium (Mg)	127±16	Lanthanum (La)	1097±125	Holmium (Ho)	61±5
Copper (Cu)	82±10	Gadolinium (Gd)	498±56	Thorium (Th)	29±4
Zinc (Zn)	78±11	Samarium (Sm)	455±45	Chromium (Cr)	17±4
Manganese (Mn)	5±1	Praseodymium (Pr)	399±39	Thulium (Tm)	16±3
		Cadmium (Cd)	398±29	Lutetium (Lu)	12±2
		Dysprosium (Dy)	367±16	Selenium (Se)	32±3
		Nickel (Ni)	147±10	Scandium (Sc)	5±1

Table 2. *Acidic mine water composition from La ponderosa Mine after treatment with NaOH and H_2O_2 for iron removal.*

Main elements	mg/L	Minor elements	µg/L	Minor elements	µg/L
Iron (Fe)	9±1	Cerium (Ce)	2816±187	Erbium (Er)	139±25
Sodium (Na)	1250±110	Arsenic (As)	322±18	Lead (Pb)	213±15
Sulphur (S)	1747±135	Neodymium (Nd)	1743±143	Ytterbium (Yb)	98±11
Aluminium (Al)	195±29	Yttrium (Y)	1624±100	Terbium (Tb)	74±7.8
Calcium (Ca)	154±17	Cobalt (Co)	1057±57	Europium (Eu)	69±6
Magnesium (Mg)	120±10	Lanthanum (La)	1087±63	Holmium (Ho)	58±4
Copper (Cu)	78±7.5	Gadolinium (Gd)	482±50	Thorium (Th)	29±3
Zinc (Zn)	78±6	Samarium (Sm)	429±46	Chromium (Cr)	17±1
Manganese (Mn)	4±1	Praseodymium (Pr)	391±45	Thulium (Tm)	16±4
		Cadmium (Cd)	300±2.0	Lutetium (Lu)	11±2
		Dysprosium (Dy)	354±25	Selenium (Se)	12±4
		Nickel (Ni)	123±16	Scandium (Sc)	5±1

Table 3. Composition of the feed solution and permeate samples at 10, 15 and 22 bar in µg/L of the hazardous components of the AMW treated with the ESNA1-LF-LD-4040 membrane.

	Arsenic	Cadmium	Chromium	Lead	Selenium
Feed solution	322 ± 18	300 ± 2	17 ± 1	213 ± 15	12 ± 4
10 bar	129 ± 21	2.2 ± 0.9	0.04 ± 0.01	2.6 ± 0.3	3.9 ± 1.4
15 bar	118 ± 18	1.5 ± 0.1	0.12 ± 0.01	2.3 ± 1.4	3.2 ± 0.4
22 bar	107 ± 18	1.3 ± 0.1	0.08 ± 0.01	2.1 ± 0.2	2.2 ± 0.3

Table 4. *Composition of the feed and average permeate samples in µg/L of the hazardous components of the AMW treated with the ESNA1-LF-LD-4040 membrane after 10 steps.*

	Arsenic	Cadmium	Chromium	Lead	Selenium
Feed solution	322 ± 18	300 ± 2	17 ± 1	213 ± 15	12 ± 4
10 bar (54% permeate recovery)	63.6 ± 18	5.9 ± 0.9	0.13 ± 0.01	2.9 ± 0.3	0.1 ± 0.01
15 bar (67% permeate recovery)	64.5 ± 14	5.2 ± 0.3	0.19 ± 0.03	8.7 ± 0.6	0.4 ± 0.01
22 bar (83% permeate recovery)	70.8 ± 21	3.5 ± 0.4	0.15 ± 0.02	5.4 ± 0.3	0.2 ± 0.01

Table 5. *Legislation concerning the discharge limits (in µg/L) of hazardous components*

	Spain (R.D. 817/2015 [53])		Spain (Law 5/2002 [54])	European Union (Directive 2010/75/EU [55])	United States of America (40 CFR Part 440 [56])	Canada (SOR/2002-222 [57])	WHO limit in drinkable water [58]
	Rivers, lakes and connected water bodies	Other water bodies	Industrial effluents				
Arsenic	50	25	1000	10-100	500	500	10
Cadmium	0.08-0.25	0.2	500	10-100	50	n.d.	3
Chromium(III)	50	n.d.	5000	10-300	n.d.	n.d.	50
Chromium(VI)		5				n.d.	
Lead	7.2	7.2	1000	50-300	300	200	10
Selenium	1	10	500	n.d.	n.d.	n.d.	10
Copper	5-120[1]	25	5000	50-500	150	300	2000
Zinc	30-500[1]	60	10000	100-2000	500	500	<3000[2]
Nickel	20	20	5000	50-1000	100	500	70

n.d.: no data

[1]Depending on water hardness. The lowest value corresponds to hardness lower than 10 mg/L $CaCO_3$, whereas the highest one is for hardness higher than 100 mg/L $CaCO_3$

[2] Value not given. However, concentrations higher than 3 mg/L may not be acceptable for consumers

Figure

FIGURE CAPTIONS

Figure 1. Schematic representation of the two types of SW-NF experiments: a) closed-recirculation mode and b) open-recirculation mode.

Figure 2. Effect of trans-membrane pressure on rejections for the elements at (a) trace (<1 mg/L) and (b) dominant (>1 mg/L) levels for the ESNA1-LF-LD-4040 membrane.

Figure 3. (a) Trans-membrane flux and (b) permeate recovery for the reproduction of a full-scale vessel with SW-NF at 10, 15 and 22 bar.

Figure 4. Rejection values for the different elements along the full-scale vessel with 10 SW-NF steps at (a) 10, (b) 15 and (c) 22 bar.

Figure 5. Comparison of traditional (environmental oriented) and sustainable (resource and water recovery oriented) management.
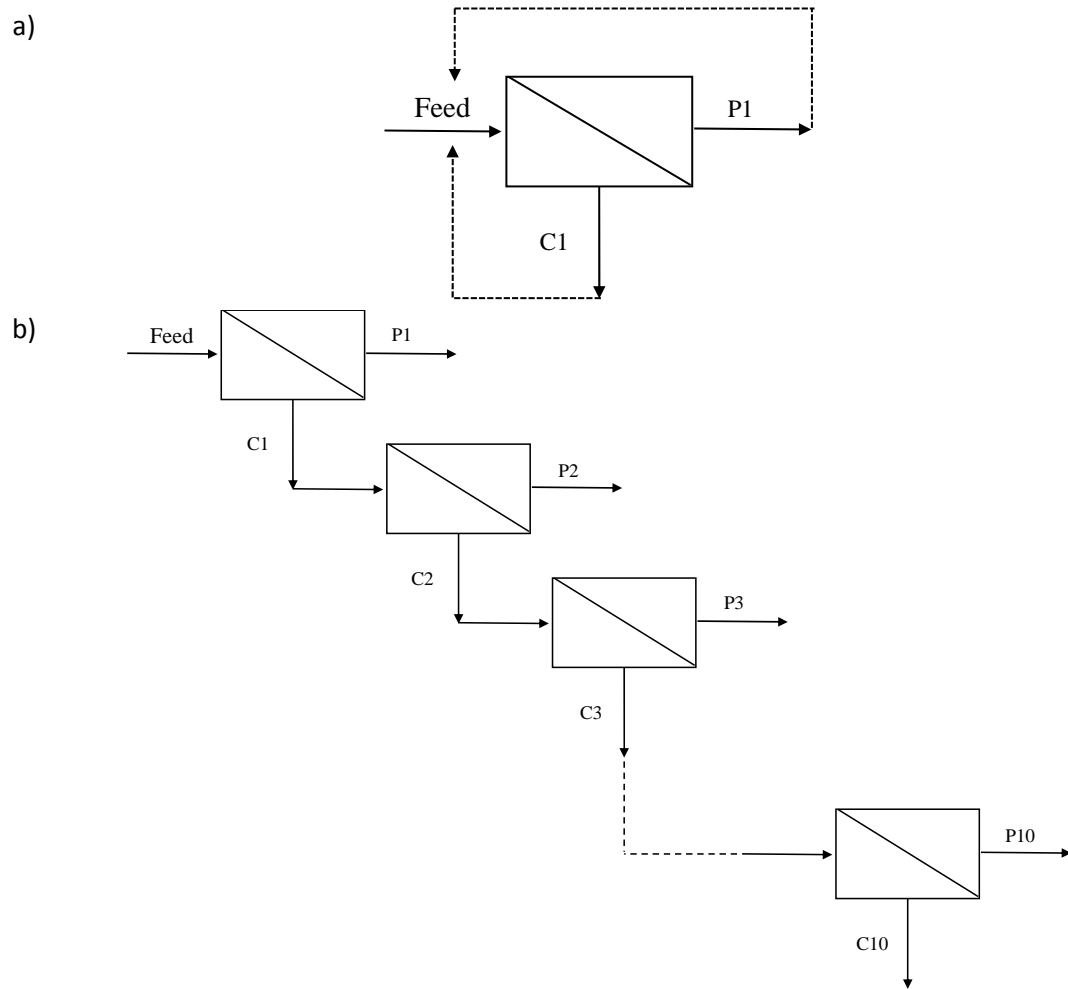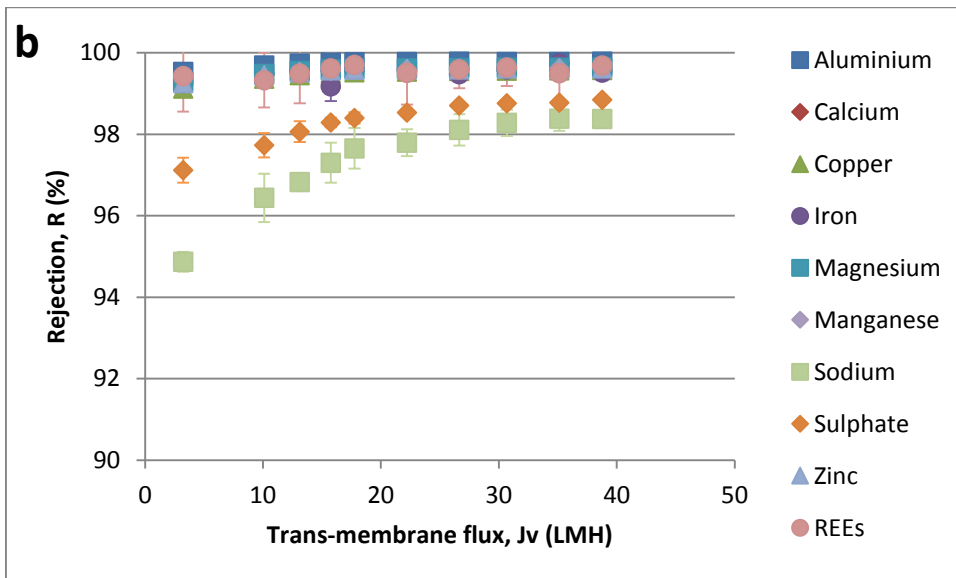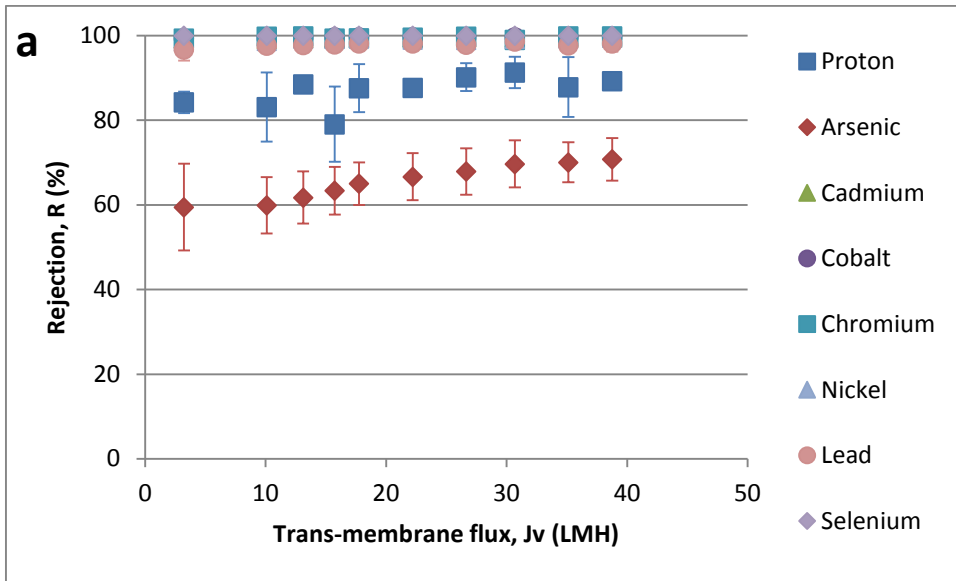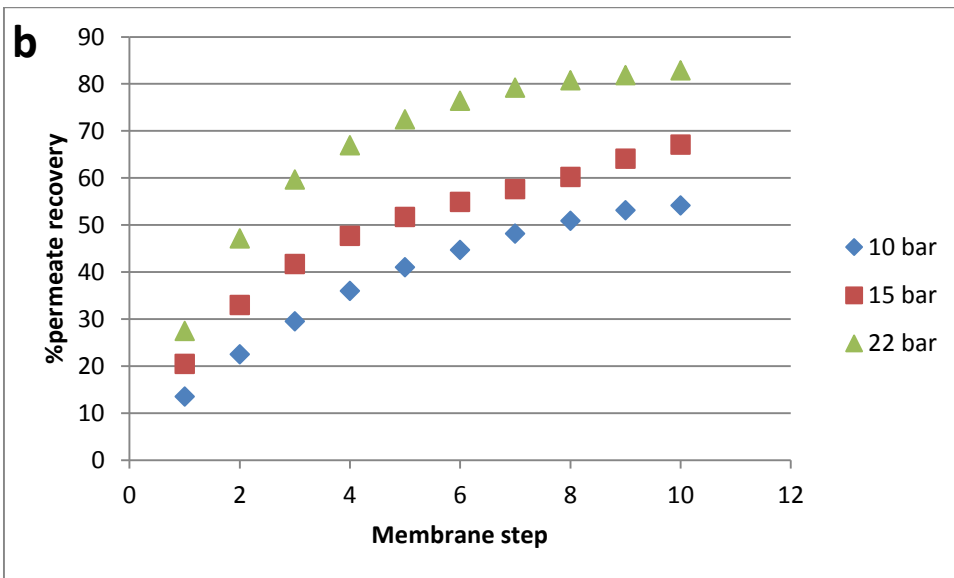
a)

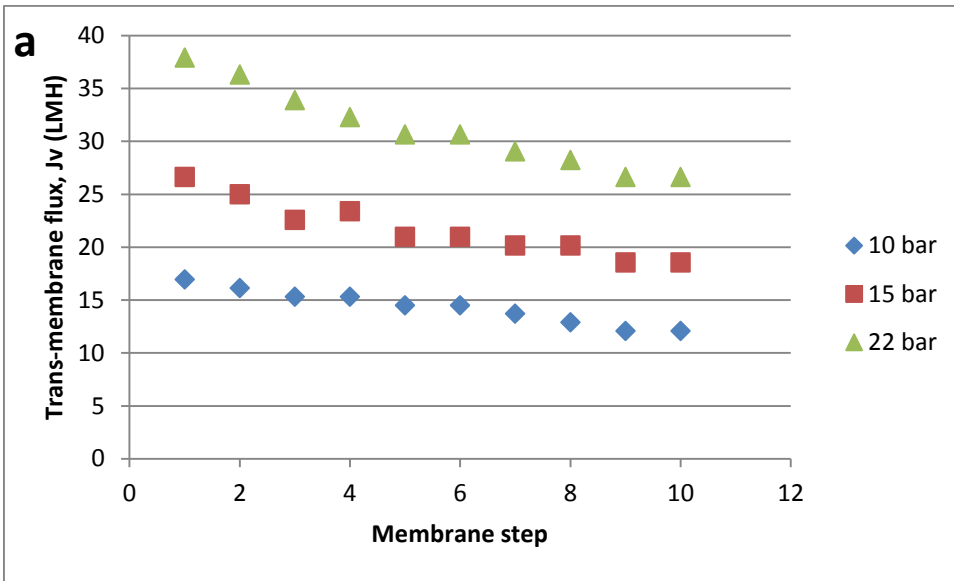
b)

Figure 1

Figure 2

Figure 3
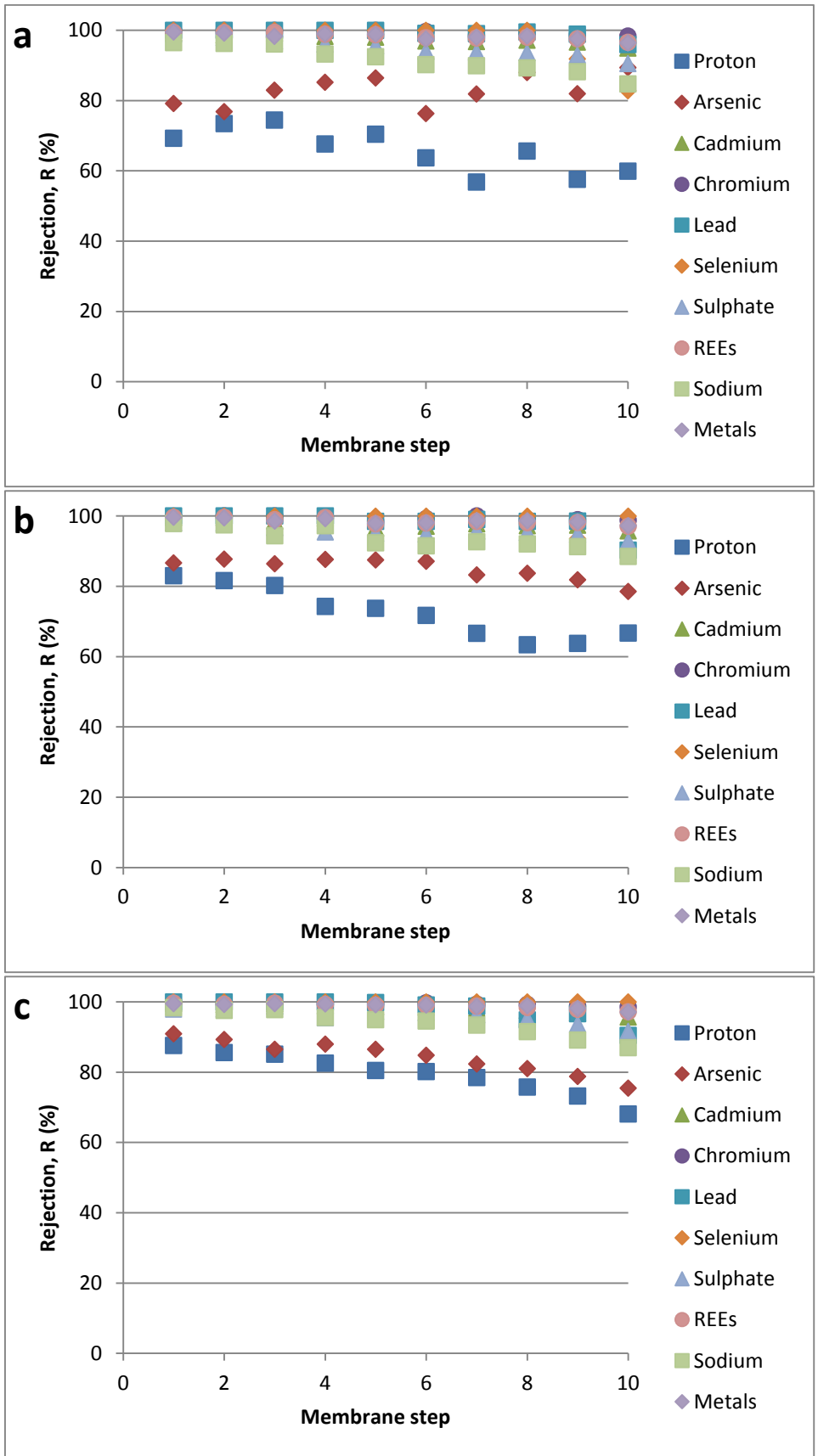
Figure 4
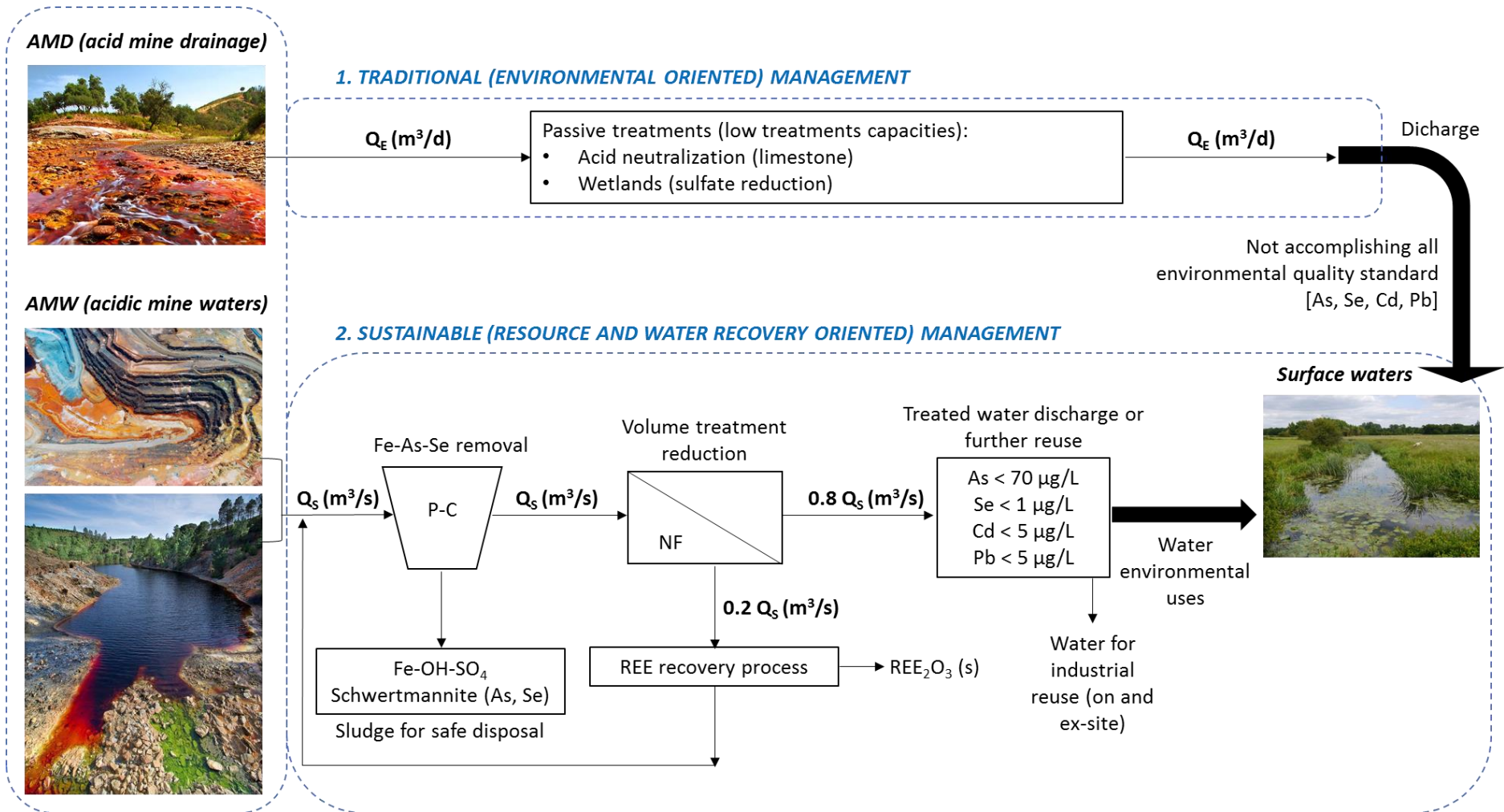
Figure 5

Credit Author Statement

J. López: Formal analysis, Investigation, Software, Validation, Writing – original draft, review and editing

M. Reig: Formal analysis, Investigation, Methodology, Validation, Writing – original draft, review and editing

X. Vecino: Formal analysis, Investigation, Methodology, Validation, Writing – original draft, review and editing

J.L. Cortina: Conceptualization, Funding acquisition, Investigation, Project administration, resources, supervision, writing – review and editing.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Arsenic impact on the valorisation schemes of acidic mine waters of the Iberian Pyrite Belt: integration of selective precipitation and spiral-wound nanofiltration processes

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Supplementary material

Table S1. *Main elements removal (%) by the pre-treatment step for iron and arsenic removal.*

| Main elements	%	Minor elements	%	Minor elements	%
Iron (Fe)	99±1	Cerium (Ce)	5±2	Erbium (Er)	<0.2
Sodium (Na)	36±2	Arsenic (As)	84±2	Lead (Pb)	<0.2
Sulphur (S)	4±1	Neodymium (Nd)	<0.1	Ytterbium (Yb)	<0.3
Aluminium (Al)	22±2	Yttrium (Y)	<0.2	Terbium (Tb)	5±1
Calcium (Ca)	<0.2	Cobalt (Co)	26±3	Europium (Eu)	<0.2
Magnesium (Mg)	6±1	Lanthanum (La)	<0.4	Holmium (Ho)	4±1
Copper (Cu)	6±1	Gadolinium (Gd)	3±1	Thorium (Th)	<0.2
Zinc (Zn)	<0.1	Samarium (Sm)	6±1	Chromium (Cr)	<0.2
Manganese (Mn)	16±2	Praseodymium (Pr)	2±1	Thulium (Tm)	<0.20
		Cadmium (Cd)	25±2	Lutetium (Lu)	5±1
		Dysprosium (Dy)	4±1	Selenium (Se)	63±13
		Nickel (Ni)	16±2	Scandium (Sc)	>0.2
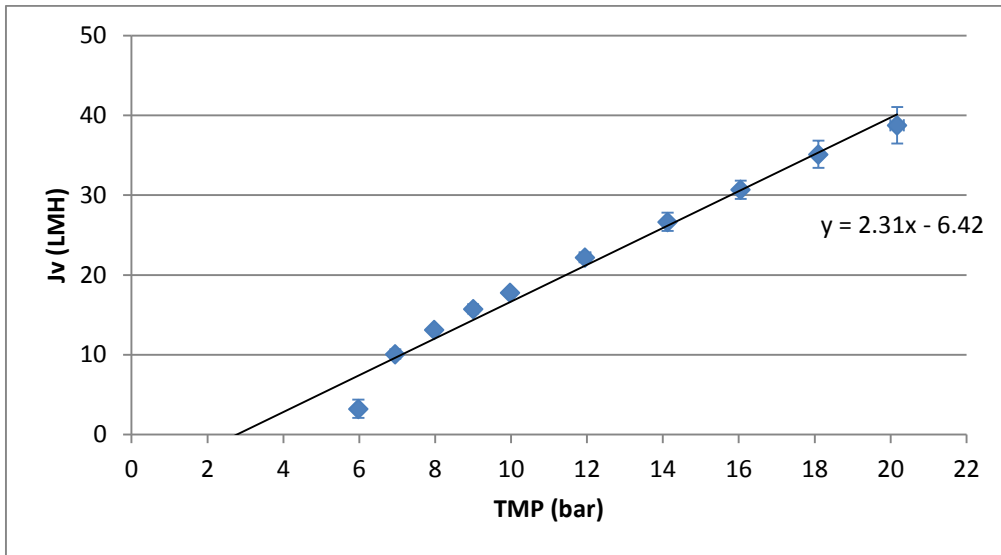
Figure S1. *Effect of trans-membrane pressure on trans-membrane flux for the ESNA1-LF-LD-4040 membrane. Linear regression of trans-membrane water flux (J_v) as a function of transmembrane pressure according to equation 9.*

Table S2. *Most likely mineral phases to precipitate at the membrane surface (calculated with PHREEQC)*

Mineral phase		Saturation index	
Name	Chemical formula	Concentrate	Membrane
$Al_2(SO_4)_3(s)$		-31.5	-29.6
$Al_2(SO_4)_3 \cdot 6H_2O(s)$		-14.2	-12.4
Anglesite	$PbSO_4(s)$	1.0	2.3
Anhydrite	$CaSO_4(s)$	0.1	1.3
Bassanite	$CaSO_4 \cdot 0.5H_2O(s)$	-0.6	0.6
Basaluminite	$(Al_4(OH)_{10}SO_4)$	-4.1	-2.8
$CaSO_4 \cdot 0.5H_2O\ (\beta)$		-0.8	0.4
Diaspore	$AlHO_2(s)$	-0.3	-0.1
Ettringite	$Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O(s)$	-48.3	-42.9
Glauberite	$Na_2Ca(SO_4)_2(s)$	-2.3	1.3
Gibbsite	$Al(OH)_3(s)$	-0.9	-0.7
Gypsum	$CaSO_4 \cdot 2H_2O(s)$	0.2	1.4
$Na_4Ca(SO_4)_3 \cdot 2H_2O(s)$		-5.3	0.6
Pyrolusite	$MnO_2(s)$	-6.8	-6.6
Schwertmannite	$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}(s)$	10.7	12.3

1 **Arsenic impact on the valorisation schemes of acidic mine waters**

2 **of the Iberian Pyrite Belt: integration of selective precipitation**

3 **and spiral-wound nanofiltration processes**

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11

12

Abstract

Arsenic and selenium presence in acid mine waters (AMWs) limits its disposal due to environmental regulations. The focus to solve the economic infeasibility is directed to sustainable solutions, promoting resource recovery. In fact, rare earth elements (REEs) recovery is proposed in most of the Iberian Pyrite Belt AMWs. However, the presence of arsenic and selenium may impact in the REEs recovery. Among different alternatives, nanofiltration (NF) provides a concentration stage on REEs recovery, reduces the nominal flow and removes hazardous species. In this work, Iberian Pyrite Belt AMWs with up-to 10 mg/L REEs, containing arsenic (2 mg/L), were treated with a NF membrane. Firstly, AMWs were pre-treated with H_2O_2/NaOH, to oxidise Fe(II) to Fe(II) and As(III) to As(V), promoting their removal and avoiding their potential precipitation at the membrane. Subsequently, NF pressure effect (6 to 20 bar) was studied, removing metals (>95%), whereas arsenic rejections ranged from 60 to 71%. Then, water recovery potential was evaluated at 10, 15 and 22 bar by reproducing a 10-stages NF plant. Results showed that the proposed treatment could be an alternative for arsenic and selenium removal (70 µg/L and 0.5 µg/L permeate concentrations, respectively) to achieve mining discharge limits according to regulations.

Keywords: ESNA; rare earth elements; valorisation; hazardous materials; water discharge

1. Introduction

Acidic Mine Waters (AMWs) are formed when sulphide minerals, mainly those related to iron (e.g. pyrite (FeS_2), marcasite, (FeS_2), and pyrrhotite (FeS)), are oxidised in contact with water or oxygen. AMWs generation takes place at both operating and abandoned poly-sulphide mining sites, as well as galleries, mine workings, open pits and waste rock piles [1–3]. The generation process produces sulphuric acid, which can dissolve the soil minerals and then, an acidic effluent, rich in dissolved ferrous and non-ferrous metal sulphates (e.g. Fe, Al, Zn and Cu), non-metals (e.g. As, Se) and a minor amount of rare earth elements (REEs), which is released to the environment [4,5]. One of the most known cases of AMWs generation can be found in the Iberian Pyrite Belt (south of Spain), which is one of the largest sources of pyrite in the world, and up to 150 different kinds of AMWs can be found in the Odiel and Tinto basins. These waters are characterised by low pH (1-3) and concentrations up to 35 g/L Fe, 3.5 g/L Al, 675 mg/L Cu and 798 mg/L Zn, among others [6,7]. It was found that the concentration of REEs is around 80 mM, which is high in comparison to that of natural waters (0.08 mM) [8–10]. Therefore, the presence of valuable compounds (e.g. Cu, Zn, REEs) in AMWs has made that research is being towards its recovery.

The presence of arsenic in these waters is related to the leaching process of arsenic-containing non-ferrous minerals (copper, lead, zinc, gold or uranium) when entering in contact with the sulphuric acid present in AMWs [11]. The removal of arsenic has become a challenge because of the health and environmental effects that it represents. The World Health Organisation (WHO) has set up a limit of 10 µg/L in the drinkable water, and for example, its concentration in unpolluted surface and groundwater varies from 1 to 10 µg/L [12]. However, in the case of AMWs from the Iberian Pyrite Belt basins, it can range from 10 to 104000 µg/L with a mean value of 8634 µg/L. Additionally, selenium may be present up to 2000 µg/L [13]. Such content of arsenic, which can be up to 5 orders of magnitude higher than the WHO limits, has made necessary treating AMWs properly before its disposal. Various governments adopted an upper limit of 10 µg/L and 50 µg/L for arsenic and selenium, respectively for drinking water, while these limits are higher for effluent discharge (10 – 200 µg/L for arsenic and 2 – 100 µg/L for selenium) [14]. Differences in regulations are due to the source type and solution composition, environmental and hydraulic conditions (stream flow-rates and natural habitat) and the toxicity that they may produce in the different living organisms [15].

Usually, the presence of non-metals (e.g. arsenic or selenium) may require a previously pre-treatment to oxidase them (e.g. As(V) and Se(VI)) with strong oxidants, such as ozone, chlorine

64   or hydrogen peroxide, among others. After that, they are removed by a coagulation-

65   precipitation process with aluminium or iron, or through ion exchange or electrochemical

66   treatments to remove arsenic as AsH_3(g) [11,12,16]. Other treatments, such as neutralisation

67   with lime or adsorption and co-precipitation of non-metallic species can be used [17–19].

68   However, these alternatives require a huge amount of chemicals for carrying out the

69   separation process, the potential recovery of valuable components may be reduced, and the

70   residual levels of toxic species do not fulfil most of the industrial effluent or environmental

71   discharge limits.

72   Nowadays, membrane technologies are being used as an alternative to conventional

73   treatments for dealing with acidic effluents, both industrial and AMWs, as they offer: i) high

74   water recovery ratio and additional concentration factor for resource recovery options and ii)

75   high water quality with low presence of toxic metal and non-metal species, which allows to

76   meet the environmental discharge limits. Studies about the application of reverse osmosis

77   (RO), nanofiltration (NF), and electrodialysis (ED) can be found for arsenic removal [20–24].

78   Among different membrane technologies, NF can be used for treating AMWs, exhibiting high

79   rejections of multivalent ions (e.g. metals, non-metals), while the transport of monovalent

80   species is favoured (e.g. H^+, HSO_4^-, Na^+, Cl^-). NF has been proved to be useful for treating

81   AMWs. Metals can be effectively rejected (>90%), while water can be obtained as permeate

82   [25,26], and if the feed solution to be treated has a moderate acidity (pH=1), acid can be

83   obtained as permeate as well [27,28]. However, most of the published studies for arsenic

84   removal are for surface and groundwater, with rejections between 50% to 89% and from 87%

85   to 93% for As(III) and As(V), respectively [20,21]. Only a few works dealing with arsenic

86   removal from acidic waters are found in the literature. Al-Rashdi et al. [22] evaluated the

87   removal of metal ions (e.g. Cu, Mn, Cd, Pb) and As(III) with the NF270 polyamide-based

88   membrane. The effect of pH was studied and As(III) rejections were below 15% from pH 1.5 to

89   5. López et al. [24] studied the same membrane for treating a copper smelter effluent. They

90   achieved high metal rejections (>80%), while the arsenic permeated (rejections below 40%)

91   because of its presence as a non-charged species (H_3AsO_4). In addition, special attention

92   should be paid to other toxic components, such as cadmium chromium, lead and selenium.

93   In this work, AMWs from *La Poderosa* mine (Iberian Pyrite Belt) containing up to 10 mg REEs/L,

94   was treated with a commercial polyamide-based nanofiltration membrane (ESNA1-LF-LD-

95   4040) under spiral-wound (SW) configuration. This acidic water was characterised by a pH 2.0-

96   2.2 and by the presence of metals (e.g. iron, copper, zinc) and toxic metallic (e.g. cadmium,

97   lead and chromium) and non-metallic elements (e.g. arsenic, selenium). Previous to the

98 treatment with SW-NF, H_2O_2 and NaOH were added to the AMWs for iron, arsenic and

99 selenium removal to avoid scaling at the membrane surface. The effect of the pressure (6-20

100 bar) in elements rejections was investigated by SW-NF in a closed-loop configuration. Finally, a

101 membrane test was carried out reproducing a treatment plant consisting of ten SW-NF

102 modules in series at three different pressures (10, 15 and 22 bar). The aim of this final test was

103 to evaluate the water recovery, the concentration factor and the permeate water quality, as

104 this treated water could be discharged to natural water receiving bodies or used in industrial

105 applications. The concentration of the toxic metals and non-metals was followed along the

106 treatment stages, and the values achieved in the treated stream (i.e. permeate) were analysed

107 according to the different regulations, covering from industrial discharge limits to

108 environmental protection standards for natural ecosystems.

2. Materials and methods

2.1. Reagents

111 Hydrogen peroxide (35% (v/v), H_2O_2) was used to oxidise Fe(II) to Fe(III), As(III) to As(V) and

112 Se(IV) to Se(VI), and NaOH (pellets) was used for adjusting pH. Hydrochloric acid (37%, HCl)

113 was used for membrane cleaning. All chemicals were analytical grade reagents from Sigma

114 Aldrich.

2.2. Acidic mine waters

116 The AMWs treated in this work was from *La Poderosa* mine located in the Iberian Pyrite Belt

117 (South-West of Spain, Huelva). The pH of AMWs was between 2.0-2.2, and they presented high

118 metal concentrations due to the oxidation of sulphide minerals. **Table 1** shows the initial water

119 composition from *La Poderosa* mine. Also, the AMWs showed an orange-brown colour due to

120 very high iron concentrations in solution [29].

121 As shown in **Table 1**, AMWs were mainly composed of iron, sodium and sulphur (higher

122 concentration values than 1100 mg/L). Other main elements present in AMWs were

123 aluminium, calcium, magnesium, copper, zinc and manganese. Besides, arsenic, REEs

124 (neodymium, gadolinium, samarium, praseodymium, and dysprosium, among others), cobalt,

125 cadmium and others minor elements were also present in concentration values from 3000 to 5

126 µg/L.

2.2.1. Pre-treatment of AMWs: Fe and As removal

Previously to the treatment of the AMWs with SW-NF, iron was removed to prevent scaling at the membrane surface. Moreover, in this stage, arsenic can be removed because it co-precipitates with Fe(III) as $FeAsO_4(s)$. In fact, Carrero et al. [30] indicated that Fe(III) mineral phases precipitation, as nano-crystalline structures in AMWs, implied an important removal of anionic trace elements, such as arsenic. In this case, the main removal mechanism for arsenate and selenite is the combination of surface complexes and oxyanion exchange. In this case, iron was removed from AMWs by the oxidation of Fe(II) to Fe(III) with H_2O_2, adding 1 mL of H_2O_2 35% (v/v) per 1 L of acidic mine water, and increasing the pH up to 3.7-3.8 with NaOH (2 M) [2,27]. Finally, the precipitates (according to the literature is mainly schwertmannite $[Fe_8O_8(OH)_{8-2x}(SO_4)_x \cdot nH_2O$, where $1 \leq x \leq 1.75]$ [6,31,32]), solids and colloidal matter were removed first by gravity filtration using a filter paper (Whatman Nº 42, 2.5 μm) following a second filtration with quartz sand column.

2.3. Spiral-wound nanofiltration

2.3.1. Experimental design

Two types of experiments were carried out by a SW-NF set-up: i) NF closed-recirculation mode and ii) NF stages in open-recirculation mode. **Figure 1** represents both types of experiments.

In the first set (**Figure 1.a**), both concentrate and permeate streams were recirculated to the feed tank, maintaining a constant feed concentration (i.e. feed composition along the experiments was the same as the initial one, due to mixing again the permeate and concentrate streams in the feed tank). The trans-membrane pressure (TMP) was increased (2 by 2 bar) from 6 to 20 bar. Samples from the permeate stream were collected and analysed at different TMP. Also, initial and final feed samples were collected from the feed tank to check feed concentration evolution.

The second set of experiments (**Figure 1.b**) was carried out mimicking SW-NF in a pressure vessel containing ten SW membrane modules. For this purpose, both generated output streams (concentrate and permeate) were collected in different tanks, and only the concentrate taken from one stage was used as feed solution for the next one. In this case, as membrane stabilisation procedure, before feeding the concentrate in the next membrane stage, the solution was circulated through the system for 5 min. TMP tested in the open-loop configuration were 10, 15 and 20 bar. Samples from concentrate and permeate streams were collected and analysed in each membrane filtration step.

2.3.2. SW-NF set-up

159 160 The experimental set-up used for SW-NF membrane tests with AMWs is described elsewhere
161 [33,34]. Before starting the experiments, deionised water was pumped through the membrane
162 modules at the maximum TMP (22 bar) during 1.5 h to achieve membrane steadiness.
163 Afterwards, this procedure was repeated with feed solution at 22 bar for 2 h to ensure that the
164 membrane density was kept constant during the full experiment. This process implied the
165 membrane compaction.

166 The SW-NF membrane used for all experiments was ESNA1-LF-LD-4040, purchased from
167 Hydranautics (USA) [35]. The surface material of the membrane is a composite aromatic
168 polyamide, and it has a surface-active area of 7.43 m^2. This membrane is a polyamide-based
169 membrane with an iso-electric point (IEP) of 4.5 [36,37].

170 After pressurisation steps (with deionised water and feed solution), the feed solution (50 L)
171 was pumped into the membrane module passing previously through a pre-filter cartridge (100
172 μm). TMP was gradually varied from 6 bar to 20 bar in the closed-configuration experiments,
173 whereas the TMP was fixed (at 10, 15 and 20 bar) in the open-configuration ones. In both
174 cases, two output streams were obtained, the permeate and the concentrate. Although in the
175 first step of experiments (**Figure 1.a**) both were recirculated into the feed tank, whereas in the
176 second set (**Figure 1.b**) both were collected and separated in different product tanks.

177 During the experiments, several parameters such as pressure, flow, conductivity, pH and
178 temperature were monitored.

179 Once an experiment was finished, the membrane was cleaned by the following steps: 1) with
180 deionised water at 10 bar for 30 min; 2) with new deionised water at 22 bar for 1.5 h; 3) with
181 diluted HCl (pH=2.1-2.5) at 10 bar for 30 min, and 4) with fresh deionised water at 22 bar for
182 1.5 h.

183 The hydraulic water permeability of the membrane after experiments was compared with the
184 virgin membrane value to ensure that the membrane was cleaned successfully.

2.3.3. SW-NF data analysis

185 186 The TMP was calculated taking into account the system pressures around the membrane stack,
187 as follows equation (1) [38]:

$$TMP \ (bar) = \frac{P_F + P_C}{2} - P_P \qquad (1)$$

188   where P_F is the feed pressure entering into the test cell (bar), P_C is the outgoing pressure in the

189   concentrate stream (bar) and P_P is the outgoing pressure in the permeate stream (bar).

190   During the experimental tests, the trans-membrane flux (J_v) was also calculated by Equation (2)

191   [22,38]:

$$J_v \left(\frac{L}{m^2 \cdot h} \right) = \frac{Q_P}{A} \qquad (1)$$

192   where Q_P is the permeate flow (L/h) and A is the active membrane area (m^2).

193   Water permeability constant (K_w) can be obtained with the following equation (3) when

194   filtering deionised water [22]:

$$K_w \left(\frac{L}{m^2 \cdot h \cdot bar} \right) = \frac{J_v}{TMP} \qquad (3)$$

195   where J_v is the permeate flux (L/h·m^2) and the TMP is the trans-membrane pressure (bar).

196   For closed-recirculation experiments, equation (4) was used to determine the obtained

197   rejection (R) percentage [38]:

$$R\ (\%) = \frac{C_F - C_P}{C_F} \cdot 100 \qquad (4)$$

198   where C_F and C_P are the concentration of each element in the feed and permeate solution

199   (mg/L), respectively.

200   On the other hand, for open-circulation assays, as the feed concentration changed at each

201   filtration stage, the equation (4) can be depicted as equation (5):

202      $R_1\ (\%) = \frac{C_F - C_{P1}}{C_F} \cdot 100 \,; R_2\ (\%) = \frac{C_{c1} - C_{P2}}{C_{c1}} \cdot 100 \,; ...; R_n\ (\%) = \frac{C_{c(n-1)} - C_{P(n)}}{C_{c(n-1)}} \cdot 100$ (5)

203   where C_F, C_P and C_C are the concentration of each element in the feed, permeate and

204   concentrate solution (mg/L), respectively, and n is the number of stages performed.

205   Additionally, for open-circulation tests, the concentration factor (CF) of each element was

206   calculated taking into account the equation (6) [34]:
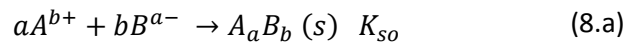
$$CF = \frac{C_c}{C_P} \qquad (6)$$

207   where C_C and C_F are the concentration in the concentrate and feed solution (mg/L),

208   respectively.

209 The performance of the membrane in open-recirculation tests was represented as a function
210 of permeate recovery, defined as follows equation (7):

$$Permeate\ recovery\ (\%) = \frac{V_{t=o} - V_t}{V_{t=o}} \cdot 100 \qquad (7)$$

211 where $V_{t=0}$ (50 L) and V_t are the volumes of the feed tank solutions at the beginning of the
212 experiment and at time t, respectively.

213 Finally, from the chemical composition of the open-recirculation tests, a chemical analysis
214 using PHREEQC (U.S. Geological Survey) [39] was performed to assess the scaling potential at
215 the membrane surface. Then, for a precipitation reaction (equation 8.a), the saturation
216 indexes (SI) were calculated according to equation 8.b:

$$aA^{b+} + bB^{a-} \rightarrow A_aB_b\ (s)\ \ K_{so} \qquad (8.a)$$

$$SI = \log\left(\frac{IAP}{K_{so}}\right)\log\left(\frac{[A]^a \cdot [B]^b}{K_{sp}}\right) \qquad (8.b)$$

217 where IAP is the ion activity product and K_{so} is the precipitation constant. If SI>0, the solution is
218 supersaturated, whereas SI<0 the solution is undersaturated. In the case that SI=0, the solution
219 is saturated.

2.4. Analytical methodology

221 The initial AMWs, the pre-treated AMWs and samples after experiments were analysed by
222 Inductively Coupled Plasma (ICP) combined with Optical Emission Spectroscopy (ICP-OES,
223 Agilent 5100) and Mass Spectrometry (ICP-MS, Agilent 7800) to determine solution
224 composition (e.g. transition metals, non-metals and REEs). Samples were filtered (0.2 μm) and
225 acidified with 2% HNO_3 before their analysis by ICP. The pH was monitored with a pH-meter
226 (GLP 21, Crison).

3. Results and discussion

3.1. Acid mine waters pre-treatment for iron and arsenic removal

229 **Table S1** (Supplementary material) shows the removal percentage of each element present in
230 the acidic mine waters at pH 3.7-3.8 during the iron and arsenic removal step.

231 The pre-treatment of AMWs allowed to remove 99±1% of iron, 84±2% of arsenic, and 63±13%
232 of selenium, followed by 36±2% of sodium, 26±3% of cobalt, 25±2% of cadmium, 22±2% of
233 aluminium, 16±2% of nickel and 16±2% of manganese. The elimination percentage of other

234   metals and REEs was lower (between 6.2±0.6% magnesium to <0.2% calcium, zinc, among
235   others). Therefore, the AMWs pre-treatment to remove iron for reducing the expected scaling
236   in the NF stage was effective and also a reduction of two toxic elements as arsenic and
237   selenium was partially achieved.

238   Results are in agreement with previous studies with AMWs, where >98% Fe and partial
239   removal of Al(III) were reported by Wei. et al. [40] after oxidation of Fe(II) to Fe(III) in the
240   presence of H_2O_2 as oxidising agent and sub-sequent precipitation at pH 3.5. Additionally,
241   Carrero et al. [30] observed that during the precipitation of Fe(III) and Al(III) as
242   hydroxysulphates, As(V) and Se(VI) can also co-precipitate or be adsorbed. Besides, the rest of
243   the main metal ions (Zn(II) and Cu(II)) in solution did not precipitate, as well as the REEs, which
244   are pursued to be recovered in a later stage. These results can also be compared with the
245   previous studies, such as the one by Lozano et al. [41], who reported that REEs precipitates
246   above pH by sorption onto basaluminite.

247   It was assumed that arsenic and selenium are at their highest oxidation state after the addition
248   of H_2O_2 as As(V) and Se(VI). Both elements are as anionic forms as described in **Annex A**. After
249   the selective precipitation stage at pH 4, partial removal of 84.2±2.0% and 62.0±3.0% for
250   arsenic and selenium was achieved, respectively. Carrero et al. [30] reported that the
251   formation of iron and aluminium nano-crystalline structures in AMWs is responsible for the
252   removal of trace non-metal elements (i.e. arsenic, selenium). They concluded that anion
253   exchange with structural sulphate ions was the main mechanism for $HSeO_4^-$, whereas a
254   combination of surface complexation and anion exchange was responsible for $H_2AsO_4^-$
255   removal. They also found that the $H_2AsO_4^-$ sorption capacity in basaluminite was two times
256   higher than in schwertmannite, but also three times higher than the $HSeO_4^-$ sorption capacity
257   in both minerals. Then, the removal of both arsenic and selenium in iron and aluminium sludge
258   can be beneficial for the final discharge to the medium of the treated AMWs. However, an
259   evaluation of the disposal of the sludge is required.

260   In consequence, the composition of the AMWs after their pre-treatment to remove the iron is
261   summarised in **Table 2**.

262   As showed in **Table 2**, the AMWs to be treated by SW-NF contained similar values as the initial
263   one but with less iron (9±1 mg/L), and a much lower arsenic concentration (322±18 µg/L in
264   comparison with an initial concentration of approximately 2041±294 µg/L). Thus, the AMWs
265   treated by SW-NF contained a high amount of sulphur (1747±135 mg/L), present in solution as

266   sulphate, sodium (1250±110 mg/L) and metals, such as aluminium (195±29 mg/L), copper

267   (78±7.5 mg/L) and zinc (78±6 mg/L); and low concentration of REEs ranged from 2816±187

268   µg/L (Ce) to 5±1 mg/L (Sc).

269   ## 3.2. Spiral-wound nanofiltration experiments

270   ### 3.2.1. Effect of trans-membrane pressure on elements rejections

271   The effect of TMP on the elements rejections with the solution after Fe removal pre-treatment

272   was studied. **Figure S1** shows the dependence of permeate flux on TMP, and **Figure 2**

273   represents the rejections for each element in solution.

274   As can be seen in **Figure S1** the flux increases linearly with the TMP, and can be described by

275   the following phenomenological equation:

$$J_v = k_W \cdot (TMP - \Delta\pi) \tag{9}$$

276   where k_w is the hydraulic membrane permeability (L/(m^2·h·bar)) and $\Delta\pi$ is the average osmotic

277   pressure of the solution (bar).

278   Accordingly, this membrane has a hydraulic permeability of 2.31 L/(m^2·h·bar), whereas the

279   osmotic pressure of the solution can be estimated to be 2.78 bar ($J_v = 0$).

280   **Figure 2.a** collects the rejections for the elements at initial concentrations below 1 mg/L,

281   whereas **Figure 2.b** shows the rejections for those elements with concentration values above

282   that concentration. This last figure, shows the rejection for REEs, which corresponds to the

283   following elements: cerium, dysprosium, erbium, europium, gadolinium, holmium, lanthanum,

284   lutetium, neodymium, praseodymium, samarium, scandium, terbium, thulium, ytterbium and

285   yttrium. In order to distinguish properly the tendencies of major components, whose transport

286   directly influences the one of trace species, the y-axis (i.e. rejection) is displayed from 90% to

287   100% (**Figure 2.b**).

288   The **SW-NF** membrane exhibited good performance for trivalent and divalent metal removal

289   (i.e. aluminium, iron, copper and calcium, among others), providing rejection values higher

290   than 99%. Below the metal rejections, the corresponding one to sulphate (97-99%) and sodium

291   (95-98%) can be found. These high rejections contrast with those obtained for proton (80-90%)

292   and arsenic (60-71%), which exhibited much lower values.

293   The obtained rejections can be explained with the basis of the main membrane mechanisms:

294   Donnan and dielectric exclusions.

295 The Donnan exclusion postulates that the membrane presents a superficial charge because of

296 the protonation and deprotonation of the active layer functional groups. Thus, membranes

297 active layers in based to polyamide chemistry, depending on the solution pH, exhibit a positive

298 or negative surface charge [42,43]. The pH value at which the membrane has no superficial

299 charge is defined as the IEP. Below the IEP, the membrane presents a positive surface charge,

300 which attracts the anions in solution (counter-ions) and repels the cations (co-ions). Above the

301 IEP, the transport of cations is favoured because of the membrane negative charge [25].

302 However, the Donnan exclusion is not able to explain the membrane selectivity regarding the

303 rejections for multivalent and monovalent elements. Instead, the dielectric exclusion

304 postulates that the difference of dielectric constants (polymeric matrix/bulk solution) causes

305 an interaction between the ions in solution and the bound electric charges induced in the

306 membrane. The dielectric exclusion explains the membrane selectivity because the ion-

307 exclusion free energy is proportional to the square of the ion charge, whereas in the Donnan

308 exclusion, such dependence is linear [44,45].

309 Both phenomena explain the obtained results in this work. The ESNA1-LF-LD-4040 is a

310 polyamide-based membrane with free ionisable amine ($R-NH_2$) and carboxylic ($R-COOH$)

311 groups, whose protonation or deprotonation confers the membrane a net surface charge. The

312 pH of the solution was below the IEP (i.e. 4.0<4.5), then the amine and carboxylic groups were

313 partially and fully protonated, respectively (i.e. $R-NH_3^+$/$R-COOH$) [36,37]. Accordingly, the

314 positive membrane surface charge favoured the transport of anions, whereas the cations were

315 repelled. In addition, the dielectric exclusion hindered the transport of multivalent ions. These

316 two facts explained why the multivalent metals were highly rejected by the membrane (>99%).

317 The fact that the membrane favoured the transport of anions explained why sulphate

318 rejections were lower than the metal ones (97-99%). However, because of the major presence

319 of sulphate as a bivalent anion (e.g. SO_4^{2-}, see **Annex A**), it was highly rejected because of

320 dielectric exclusion. In addition, the fact that arsenic was mainly present as monovalent

321 species (i.e. $H_2AsO_4^-$) resulted in lower rejections (60-71%). The fact that anions permeated

322 across the membrane implied that a stoichiometric number of cations must permeate to

323 accomplish the electro-neutrality condition. In this case, the preferred ones to be transported

324 were sodium and proton, which exhibited lower rejections than metals (i.e. 95-98% and 80-

325 90% for sodium and proton, respectively) because of dielectric exclusion.

326 The ESNA1-LF-LD-4040 membrane showed not only potential use for treating AMWs, but also

327 to remove hazardous materials such as arsenic, cadmium, chromium, lead and selenium. **Table**

328 **3** collects the feed and permeate composition of these elements at three different TMP.

329   It must be highlighted that no studies about the performance of this membrane in SW

330   configuration were found in the literature. However, other similar polymeric commercial NF

331   membranes have been applied for the treatment of AMWs, and the results were in agreement

332   with the ones above-mentioned. For example, Al-Zoubi et al. [46] optimised the performance

333   of polyamide-based membranes (Alfalaval NF99 and Osmonics DK) for the treatment of an

334   AMWs (pH=2.6, 1.2 g/L aluminium, 2.3 g/L copper, 14 g/L sulphate). In that work, rejection for

335   metals was higher than 98%, whereas the one for sulphate was around 80%. In a subsequent

336   study [47], they obtained transition metal rejections higher than 98% for NF99 and DK, with

337   rejections higher than 98% for sulphate with a different AMWs. In addition, they were able to

338   obtain a permeate richer in acid than the feed stream (e.g. pH 2.7 vs 2.5). Al-Rashdi et al. [22]

339   studied the removal of transition metal ions (e.g. copper, manganese, cadmium, lead and

340   arsenic, all at 1000 mg/L) with NF270 membrane. At a pressure of 4 bar and pH=4, the

341   following rejection sequence was obtained: copper (99%) > cadmium (70%) > lead (60%) >

342   manganese (30%) > arsenic (12%). The low rejection of arsenic (As(III)) was explained because

343   of its presence of H_3AsO_3 (neutral specie). Besides, it must be highlighted that at pH=4, the

344   membrane was near to its IEP (3.5-4.0), which could explain the low rejections for the other

345   metals.

346   Urase et al. [20] studied the effect of pH on the rejection of arsenate (AsO_4^{3-}) and arsenite

347   (AsO_3^{3-}) with the ES-10 membrane. For example, arsenite rejections shifted from 50 to 89%

348   when the pH increased from 3 to 10. Instead, rejections for arsenate barely varied (87-93%).

349   These changes in arsenite rejections were explained with the arsenic speciation. At pH=3,

350   arsenite can be found as H_3AsO_3, whereas arsenate is present as $H_2AsO_4^-$. The increase in pH

351   leads to the deprotonation of both species ($H_2AsO_3^-$ pK=9.24, $HAsO_4^{2-}$ pK=6.94), which were

352   rejected by the negatively charged membrane.

353   Recently, Wadekar and Vidic [48] treated the drainage of an abandoned coal mine with a

354   semiaromatic polymeric (NF270) and a ceramic membrane (TiO_2, molecular weight cut-off

355   (MWCO) of 500 Da). The effluent was characterised by a pH=7.8, 151 mg/L calcium, 110 mg/L

356   sodium, 70 μg/L arsenic and 55 μg/L selenium, among others. NF270 was able to reject

357   multivalent metals (>96%), while the ceramic membrane exhibited lower rejections (50-70%).

358   Selenium was rejected 30-40% by the ceramic membrane, whereas the NF270 removed it

359   effectively (>90%). The lowest rejection for both membranes was for the arsenic, with values

360   in the range 10-20% and 30-35% for the ceramic membrane and NF270, respectively.

3.2.2. Projection of a SW-NF treatment stage in a resource recovery scheme from a REE-rich AMWs

From the data obtained previously, it was decided to mimic a full-scale vessel with the SW-NF module by recirculating and filtering the concentrate stream sequentially in 10 steps. This experiment was performed at three different TMPs (10, 15 and 22 bar) with the pre-treated AMWs. The objective was to optimise the water recovery ratio and the water quality for direct discharge into natural water bodies or potential water re-use by varying the TMP.

Figure 3 shows the obtained permeate flux, as well as the permeate recovery achieved along with the whole treatment with 10 SW-NF steps at the above-mentioned TMPs. As expected, the higher the pressure, the higher the permeate flux. The high rejections provided by the membrane caused an increase in the osmotic pressure along with the treatment, thus decreasing the effective pressure gradient and then the permeate flux. In addition, higher pressures favoured the recovery of more water with the same membrane steps. For example, working at 22 bar water recovery reached a value of 83%, whereas at 10 bar was 54%, both after 10 SW-NF steps.

Figure 4 collects the obtained rejections for each membrane step at the three TMP evaluated (10, 15 and 22 bar). Due to the fact that cerium, cobalt, magnesium, nickel, scandium, thorium, yttrium, aluminium, calcium, copper, iron, magnesium and zinc were effectively rejected by the membrane (>99%), these elements were grouped as metals for simplicity.

As observed in **Figure 2**, metals, cadmium, chromium, lead and REEs were effectively rejected at the first SW-NF step (>99%) for all tested TMP. However, the fact that these metals became more concentrated in solution after several SW-NF steps, increased the concentration gradient (driving force) across the membrane, and then favoured slightly their passage (rejections >95% at all TMP tested) as can be seen in **Figure 4**. Sodium rejections were lower because of being a monovalent species, and dropped from 96% to 85% for all the TMP tested. Arsenic showed a different trend, and their rejections were around 80% at 10 bar, ranged from 86 to 79% at 15 bar and from 91% to 75% at 22 bar.

At the end of the experiment, metals in solution get concentrated with CF of 2.15 ± 0.02 (10 bar, 54% permeate recovery), 2.97 ± 0.14 (15 bar, 67% permeate recovery) and 5.78 ± 0.08 (22 bar, 83% permeate recovery). Arsenic(V) species presented a different CF due to their lower rejections: 1.80 (10 bar), 1.87 (15 bar) and 2.36 (22 bar). It should be stressed the fact that while elements in solution get concentrated, precipitation of solid phases may occur, especially at the membrane surface because of concentration polarisation. Therefore, a

chemical speciation analysis was performed to determine the potential scaling by means of the saturation indexes. Due to the fact that concentration polarisation may increase the concentration at the membrane, a factor of 10 over the composition of the concentrate stream was considered. This analysis was carried out with the last step of the experiment at 22 bar. **Table S2** shows the potential mineral phases to precipitate at the solution as well as at the membrane surface. As can be seen, the precipitation of sulphate minerals, especially those containing sulphate (anglesite, anhydrite, glauberite, gypsum and schwertmannite), were the most likely to happen. In the case of schwertmannite, despite having a high SI (higher than 10), it should be reminded that the iron concentration at the beginning of the process was residual (9±1mg/L). Therefore, if the treatment of AMWs is going to be implemented, the addition of anti-scalants should be considered to ensure a long useful life of the membranes. Additionally, acid cleanings would be recommended to remove any solid phase that may occur.

Finally, the composition of the harmful elements in the permeate of the AMWs at the end of the SW-NF process was evaluated (**Table 4**). As can be seen, the concentration of the hazardous components was quite lower in comparison with the initial ones, with values even lower than 1 µg/L for chromium and selenium. Higher concentrations of cadmium and lead (2-9 µg/L) were achieved with SW-NF, whereas the arsenic exhibited the highest ones (64 - 71 µg/L).

These values can be compared with the discharge limits from legislation concerning the industry, the criteria for superficial water and also the recommended limits for drinkable water (see **Table 5**). The Spanish legislation concerning the water quality of superficial water bodies R.D. 817/2015 (based on European Union Directive 2008/105/CE) has very restrictive limits for arsenic (50 µg/L), cadmium (0.25 µg/L), chromium (50 µg/L), lead (7.2 µg/L) and selenium (1 µg/L) in rivers and lakes. From the permeate composition, the only elements that surpass the recommended limits are cadmium and arsenic, although the arsenic concentration was quite close to the discharge criteria. Furthermore, the Spanish Law 5/2002 established the limits for industrial discharges to the public sanitation systems with a higher threshold of emissions than the R.D. 817/2015. Legislation from Canada (SOR/2002-222) and USA (40 CFR Part 440) was also consulted regarding the threshold of hazardous substances in the mining industry effluents. Despite being more restrictive than the Spanish legislation, the composition of the permeate fits within the recommended limits. Moreover, the European Union has listed the concentration achievable during the treatment of mining effluents by the use of Best Available Technologies, and as can be seen the permeate concentrations fall within them. Finally, the

427 limits of WHO were also consulted but they are more stringent if the water is directly used for
428 human consumption.

429 The concentration of arsenic in the permeate can be reduced by operating the SW-NF at
430 higher pH. By working at pH>5, the $H_2AsO_4^-$ starts deprotonated to $HAsO_4^{2-}$ and at pH>pK (pK =
431 6.94 [20]), the double-charge arsenate species predominates in solution. Additionally, the pH
432 of the solution would be higher than the IEP, thus the membrane would be positively charged.
433 Therefore, according to the Donnan and dielectric exclusions, the anions (especially multi-
434 charge ones) would be completely rejected by the membrane. This matches with the results
435 from Urase et al. [20], who observed an increase in As(V) rejections from 87% at pH 3 to 93%
436 at pH 10 with ES-10 NF membrane, and from Figoli et al. [49], who obtained a shift in As(V)
437 rejections moving from pH 3 to 10 (from 94% to 98.4% for NF90 and from 74% to 88% for
438 N30F). High As(V) rejections (>95%) at pH 8.1–8.2 were obtained with SW-NF membranes
439 (NF300) by Saitúa et al. [50]. However, despite of rejecting arsenic, the transport of cadmium
440 and lead may increase across the membrane because of its negatively charged surface and also
441 the REEs co-precipitate with the aluminum, which can comprise the environmental
442 sustainability of the process.

443 The proposed treatment showed an alternative to traditional methods (**Figure 5**). The
444 traditional methods (mostly based on neutralisation/precipitation or sulphate reduction in
445 wetlands) can recover the total amount of water. However, the neutralisation/precipitation
446 method generates a sludge-rich in water with a 2-4% of solid content. This hazardous waste
447 should be treated properly due to the high concentration of toxic elements (e.g. arsenic and
448 metals). On the other side, the reduction of sulphate, accompanied by metal precipitation, also
449 generates a voluminous sludge [2,4,51]. The proposed treatment of the AMWs from *La*
450 *Poderosa* based on the removal of iron and arsenic at pH=4 (as As sorption onto
451 schwertmannite) by chemical precipitation and the subsequent filtration with the ESNA1-LF-LD
452 may be a choice for: i) producing water with quality standards on arsenic, selenium and other
453 metal ions making it compatible for discharge into the medium as environmental water or
454 being re-used in other industrial uses; ii) concentrating up to five times the REEs and the
455 transition metals for further valorisation schemes. With the evaluated 80% water recovery
456 factor, the inlet flow-rate may be recovered as permeate with concentrations that make it
457 suitable for industrial re-use or direct discharge to the rivers according to the legislation (**Table
458 5**). Additionally, it can provide a reduction of the waste generated (i.e. sludge), but also a
459 generation of a revenue stream (i.e. the concentrate as an enriched-REE stream) than can

make this environmentally sustainable process as economically viable. This economic viability will be linked to the fact that REEs have been included as "Critical Raw Materials" for the European Union [52] and their recovery from secondary resources, such as AMWs, has been converted in mandatory as it is the need to recover phosphorous from the urban wastewater cycle [53] after the phosphatic rock was also included on the Critical raw material list [52] and its recovery is promoted by the Circular Economy Programme [54].

4. Conclusions

The proposed treatment (based on iron removal by chemical precipitation and SW-NF) showed its potential for a sustainable treatment of REE-enriched AMWs, where the levels of arsenic and selenium in the treated water (i.e. permeate) reached industrial water discharge limits. At the AMWs pH, the polyamide active layer of the membrane was positively charged (pH<IEP, 4.5) and was able to reject all the metals by more than 95% because of the electric fields (Donnan and dielectric exclusions), whereas the arsenic, present as As(V), presented lower rejections (60-71%) because of its presence as $H_2AsO_4^-$. The fact that As(V) was present as a single-charge anion did not impede its transport across the membrane because of Donann and dielectric exclusions. Additionally, other elements present in the AMWs should be considered in the water quality such as cadmium, chromium, lead and selenium because of their toxicity.
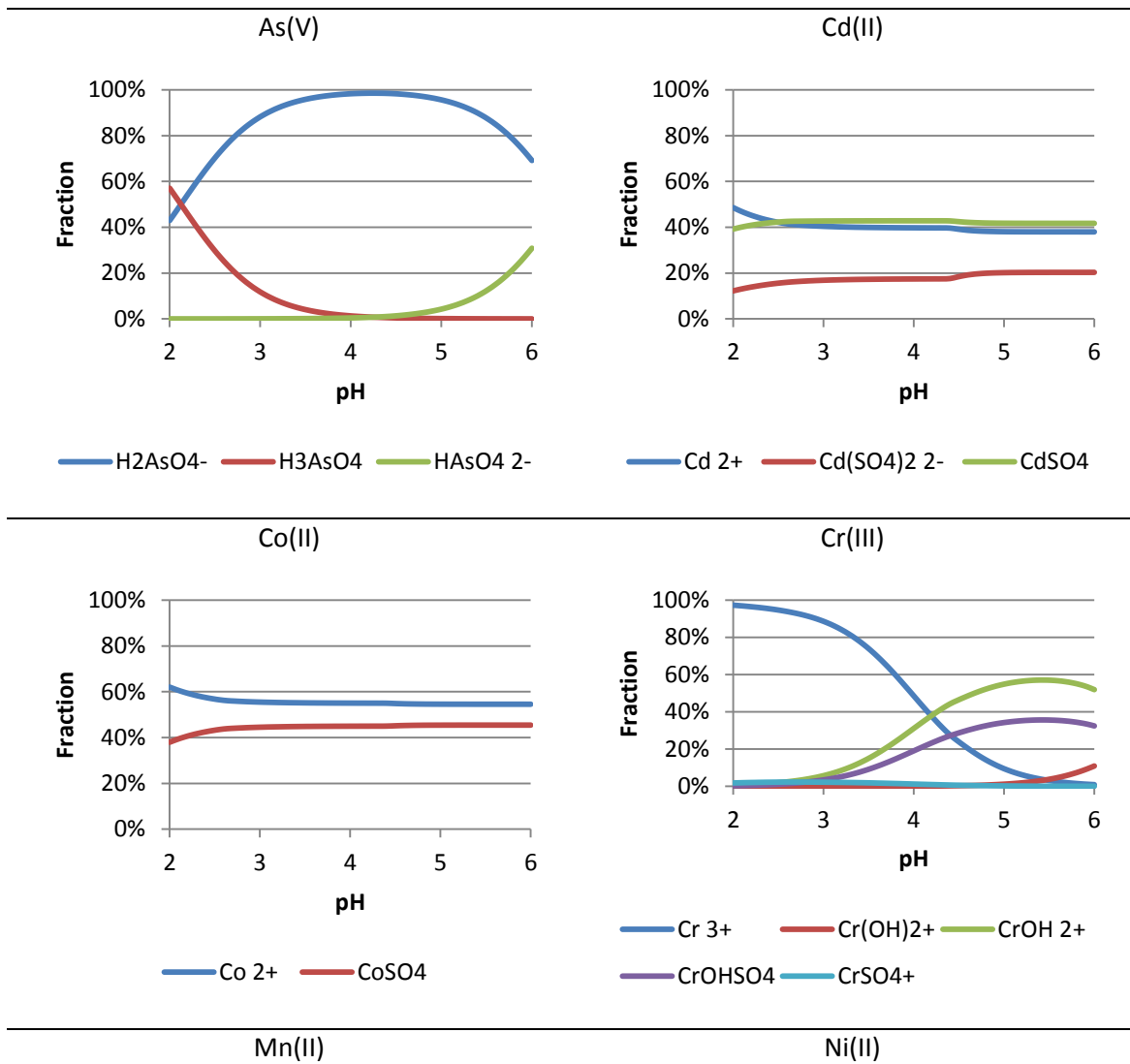
The treatment of an AMWs was conducted by mimicking a SW-NF plant based on 10 stages, showing that it was possible to achieve a water recovery of around 80% of the nominal flow. Three different pressures were tested (10, 15, and 22 bar), and the highest one provided the highest permeate flux (i.e., 83% of permeate recovery at 22 bar). By analysing the chemical composition of the recovered water, it was observed that the permeate contained around 65 µg/L of arsenic (in comparison to 2041 µg/L of the raw AMWs). The concentration of other elements, such as selenium and chromium (initial concentrations of 32 and 17 µg/L, respectively) was reduced to values lower than 0.5 µg/L in the NF permeate. Additionally, 4% of the lead was able to permeate (3-9 µg/L), whereas only a 2% of the cadmium in the feed solution passed across the NF membrane (5 µg/L in the permeate). These low concentrations (below the discharge limits) showed the potential of SW-NF membranes for the recovery of high-quality water (recovery of 83%). Therefore, the proposed treatment based on (i) chemical oxidation, (ii) Fe(III) and As(V) precipitation and (iii) SW-NF showed its potential for producing high-quality water (according to environmental laws). However, the chemical speciation analysis revealed that at this high recovery, scaling may occur at the membrane, mainly caused
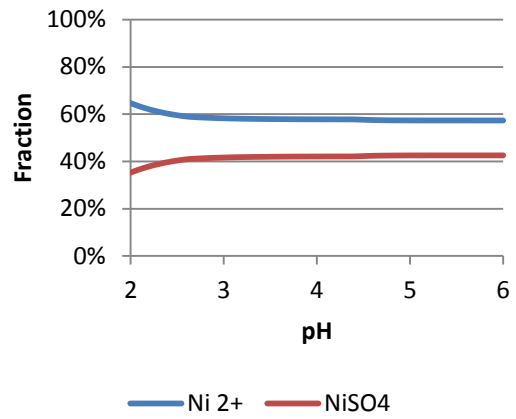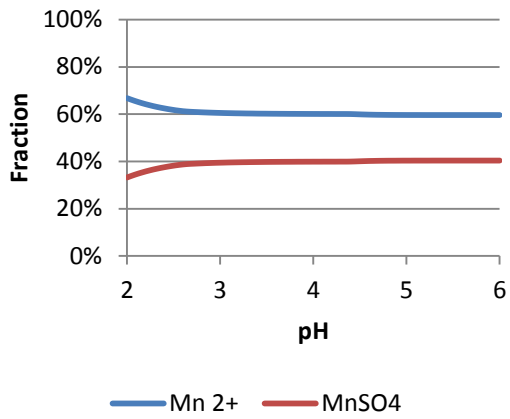
492   by calcium sulphates. Therefore, it would be recommended the use of anti-scalants and acidic

493   cleaning at large scale.

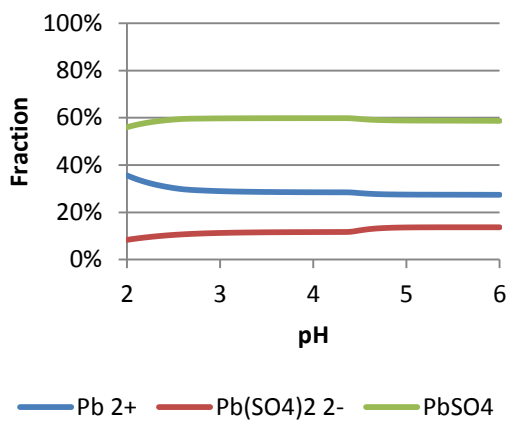502 # Annex A. Speciation diagrams

As(V) — H2AsO4-, H3AsO4, HAsO4 2-

Cd(II) — Cd 2+, Cd(SO4)2 2-, CdSO4
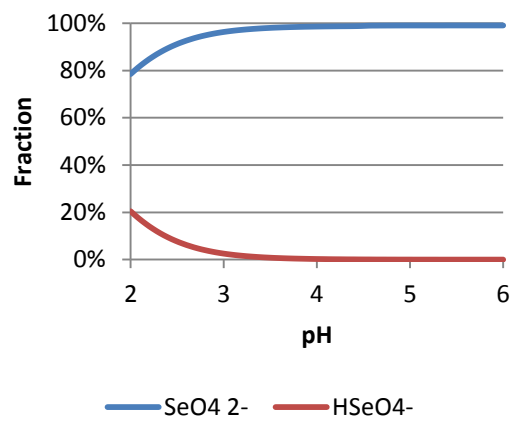
Co(II) — Co 2+, CoSO4

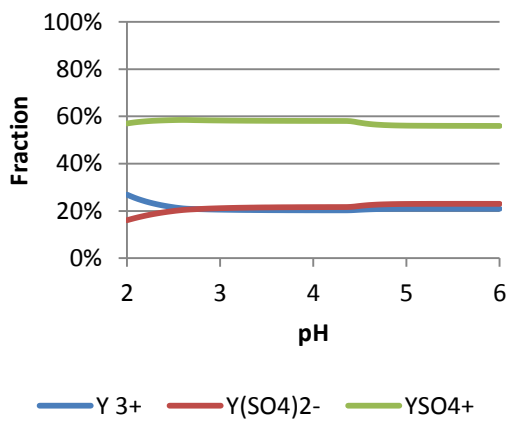Cr(III) — Cr 3+, Cr(OH)2+, CrOH 2+, CrOHSO4, CrSO4+

Mn(II)

Ni(II)

Pb(II)

Se(VI)

Y(III)

REEs(III)

Al(III)

Ca(II)

Al

Fraction

100% 80% 60% 40% 20% 0%

pH 2 3 4 5 6

Legend: Al 3+ | Al(SO4)2- | Al2(OH)2 4+ | Al3(OH)4 5+ | AlHSO4 2+ | AlOH 2+ | AlSO4+

Ca

Fraction

100% 80% 60% 40% 20% 0%

pH 2 3 4 5 6

Legend: Ca 2+ | CaSO4

Cu(II)

Fraction

100% 80% 60% 40% 20% 0%

pH 2 3 4 5 6

Legend: Cu 2+ | CuSO4

Fe(II)

Fraction

100% 80% 60% 40% 20% 0%

pH 2 3 4 5 6

Legend: Fe 2+ | FeSO4

Mg(II)

Fraction

100% 80% 60% 40% 20% 0%

pH 2 3 4 5 6

Legend: Mg 2+ | MgSO4

S(VI)

Fraction

100% 80% 60% 40% 20% 0%

pH 2 3 4 5 6

Legend: SO4 2- | Al(SO4)2- | AlSO4+ | CaSO4 | CuSO4 | HSO4- | MgSO4 | NaSO4- | YSO4+

Zn(II)

Na(I)

Zn 2+   Zn(SO4)2 2-   ZnSO4   Na+   NaSO4-

503

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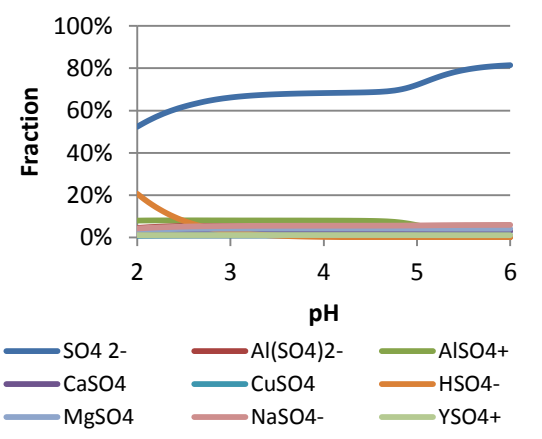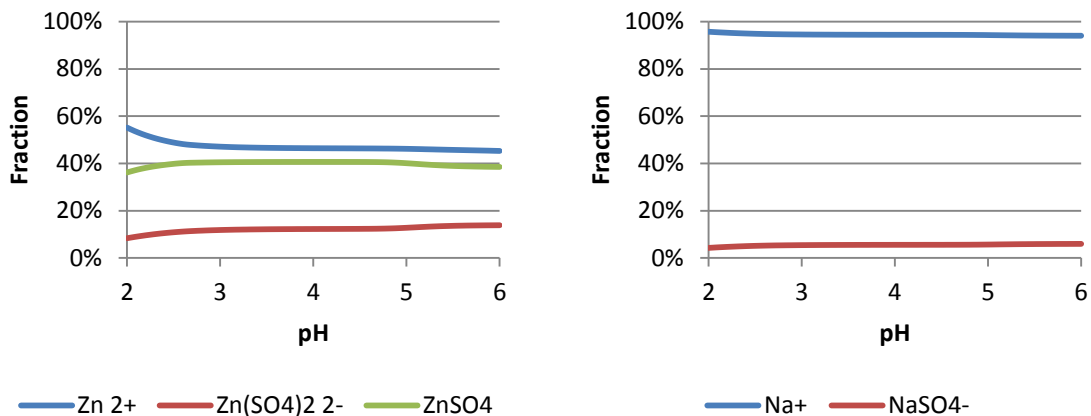512   Elsevier, 2014: pp. 131–190. doi:10.1016/B978-0-08-095975-7.00905-0.

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