Potential for water and metal recovery from acid mine drainage by combining hybrid membrane processes with selective metal precipitation

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ABSTRACT

Acid mining drainage has a serious impact on the environment. Forward osmosis allows the concentration of acid mine waters to favor the formation of enrichment sludges and subsequent selective metal precipitation. In this work, a methodology was proposed to treat mining effluents from the Iberian Pyrite Belt. Forward osmosis experiments were performed using different osmotic pressures from 0.5M to 2.5M NaCl to evaluate water fluxes and recovery. The water recovery obtained was in the range of 50-80%, and the flux remained above 5 $(L{\bullet}m^{-2}{\bullet}h^{-1})$. Four combined processes were modelled to determine the feasibility of eliminating water and precipitating metals. Furthermore, a new hybrid membrane process was proposed to recover at least 75% of water with recovery yields of Al, Fe, Cu, Zn and Mn of greater than 70%. A water production cost of 2.01 \$/m^3 and a specific energy consumption of 8.03 kWh$_e$/m^3 were estimated for the hybrid process.

1. Introduction

One of the main challenges associated with mining activities is to achieve sustainable growth without causing environmental problems, such as land degradation or changes in surface and groundwater hydrology (Ochieng et al., 2010). One of the main environmental problems of mining activities is acid mine drainage (AMD), which can cause severe environmental damage due to the low pH, high sulfur content, and metals contained in AMD (e.g., Fe, Cu, Mg, Mn, Ni, Zn, As, Se La, Pr, Nd, and Sm) (Kocaman et al., 2016; Van Geen et al., 1999).

In the Iberian Pyrite Belt (Southwestern Spain), there are many old mining installations which produce AMD, and it is one of the main metallogenic provinces in the world due to the high of massive polymetallic sulphide deposits around the Tinto and Odiel rivers which cause metallic pollution (Nieto et al., 2013; Olías et al., 2006; Cánovas et al., 2007; Martínez et al., 2019). Although the composition of AMD depends on geological and environmental conditions, its management poses a challenge in most of the cases; although sometimes it can be considered a resource of valuable metals and water (Kocaman et al., 2016). In recent years, many researchers have focused their efforts on characterizing the typical metal content of mines in the Iberian Pyrite Belt; in most samples, the main metals contained are Al, Cu, Fe, Mg, Mn, Zn and Ca (León et al., 2021; Olías et al., 2016; Nieto et al., 2013; Sánchez España et al., 2008). León et al. (2021) have studied a total of 339

samples from a variety of AMD sources from different sites such as the Perrunal mine, Esperanza mine, Poderosa mine and San Platón mine with seasonal variations from 2010 to 2018 (Figure 1) (León et al., 2021).

There are two types of treatment techniques: passive (e.g., aerobic wetlands compost/anaerobic wetlands, vertical flow rectors) and active processes (eg, precipitation, sedimentation, sulphidisation, reverse osmosis, nanofiltration) (Rodríguez-Galán et al., 2019). Normally, passive treatments focus on protecting against associated environmental and health risks (Kefeni et al., 2017; Pozo-Antonio et al., 2014; Park et al., 2019); while active processes allow for the valorization of AMD, since they can provide high quality water or/and metals (Rodríguez-Galán et al., 2019). Therefore, active treatments are effective when the aim is to valorize AMD in terms of the recovery of water and/or metal, the objective of this work.

One of the treatments frequently employed for the recovery of metals from AMD is selective precipitation (Vecino et al. 2021; Passos et al. 2021; Park et al. 2015). Some researchers have studied the pH of precipitation for the selective recovery of metals using simulation or experimental tests employing simulated or real AMD based on the different solubility of the dissolved metals (Passos et al., 2021; Vecino et al., 2021; Seo et al. 2017; Flores et al., 2012). Previously published articles showed that Fe precipitated at pH above 2.2 as hematite, Al as diaspore at pH=4,6, Cu between pH=5-6 and Zn and Ni precipitated

simultaneously around pH=8,5 (Park et al., 2015; Rodríguez-Galán et al., 2019). In most cases, a previous oxidation step is recommended to improve separation efficiency and increase purity of precipitate (Vecino et al., 2021; Seo et al., 2017). Seo et al. (2017) studied two processes of precipitation based on neutralization, one of them using hydrogen peroxide to oxidize the solution to obtain better selectivity and purity of the recovered metals (Seo et al., 2017). In recent studies, Passos et al. (2021) demonstrated the feasibility of a novel selective sequential recovery process to recover strategic metals from a real AMD using an aqueous biphasic system composed of different ionic-liquids and Na_2SO_4 (Passos et al. 2021). Furthermore, Vecino et al. (2021) proposed a mixed process consisting of selective metal precipitation and an adsorption process to recover valuable metal ions using NaOH to control pH. They recovered Fe and Al with selective metal precipitation, and Cu and Zn with two ion exchangers (Vecino et al. 2021).

Other active treatments applied to AMD and wastewater effluents and to recover water are based on the use of membranes. Membrane technologies have significant advantages; their operation is simple; they can be integrated with other processes to improve the yield of the recovery; and they presents low energy consumption (Cho et al., 2012; Rodríguez-Galán et al., 2019; Baena-Moreno et al., 2020). In addition, membranes allow for obtaining high-quality water recovery. In contrast, there are many challenges, such as membrane fouling, and the price of membranes (Mi et al. 2010). The most promising membrane processes used for AMD valorization are reverse osmosis, forward osmosis, distillation (Asif et al., 2021), electrodialysis, and nanofiltration (López et al., 2021). Within concentration-driven membrane processes, forward osmosis presents lower energy consumption due to the use of the osmotic pressure difference between the two-faced solutions: the less concentrated feed solution and the highly concentrated one, known as the draw solution as the driving force (Naidu et al., 2019). An important challenge of the FO technique is that after use, the draw solution must be regenerated to obtain pure water and a regenerated draw solution to reuse in the process (Ge et al. 2013). Selection of the draw solute is one of the most important factors in the regeneration process (López et al., 2021; Chekli et al., 2012; Ge et al., 2013; Achilli et al., 2010; Hamdan et al., 2015). Baena-Moreno et al. (2020) have studied the use of

different inorganic salts with ultrapure water and acid mine drainage as feed solution (Baena-Moreno et al., 2020). Through experimental tests, they have demonstrated that magnesium chloride and calcium chloride afford the highest water fluxes and thus the highest water recovery per unit of area with the same molarity. However, the connection between water flux, DS regeneration process, and metal rejection should be considered to determine the best draw solution to use. NaCl can be a good option due to the osmotic pressure it can generate, its cost, and its availability on the market and according to Achilli et al. (2010) the lower water flux obtained by Baena-Moreno et al. (2020) can be balanced by cost (Achilli et al., 2010; Baena-Moreno et al., 2020). Furthermore, as other inorganic salts, the NaCl-based draw solution can be regenerated by a conventional reverse osmosis process when it is in low concentrations (<90 g•L^{-1}) or with a modified reverse osmosis process for highly concentrated draw solutions with lower energy consumption than traditional evaporation processes (Martínez et al., 2020; Bartholomew et al. 2018).

Few detailed scientific studies are available for acid mine drainage using forward osmosis. Vital et al. (2018) studied two alternatives for the DS: NaCl and NH_4HCO_3 to treat real AMD. They obtained an average water flux of 12 L•m^{-2}•h^{-1} by employing a 1M NaCl solution as draw solution (Vital et al., 2018). One year later, Pramanik et al. (2019) published the recovery of rare earth elements from AMD using 279 g/L NaCl as a draw solution with average fluxes between 9 and 12 L•m^{-2}•h^{-1} (Pramanik et al., 2019) and Choi et al. (2019) used aqueous solutions of tetrasodium ethylenediaminetetraaceticacid and poly sodium-4-styrenesulfonate and achieved average fluxes of 8 L•m^{-2}•h^{-1} (Choi et al., 2019). The most recent study was developed by Cabrera-Castillo et al. (2021) where AMD was treated using a 1M NaCl solution for continuous assays at 60°C until 50% water recovery was achieved, obtaining a water flux = 25 L•m^{-2}•h^{-1} (Cabrera-Castillo et al., 2021). In these studies, the draw solutions used had reduced osmotic pressure, which limits the feed concentration and water recovery (NaCl 0.5M and 1M), or were high-priced solutes (tetrasodium ethylenediaminetetra-aceticacid and poly sodium-4-styrenesulfonate), or their regeneration involved high energy consumption (NH4HCO3).

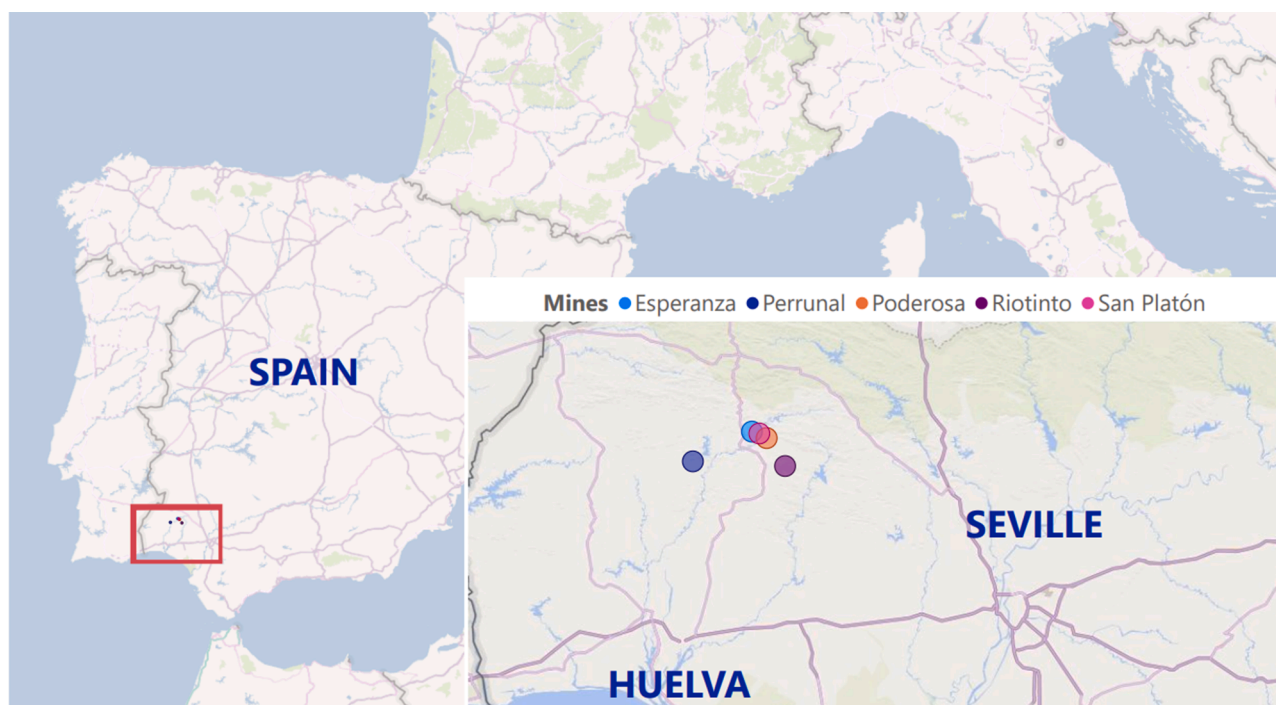The osmotically assisted reverse osmosis process is a modification of

Figure 1. Iberian Pyrite Belt and mine locations

the conventional reverse osmosis studied in recent years which allows the regeneration of highly concentrated draw inorganic solutions (Atia et al. 2021; Beni et al 2022). The characteristics of the process make it suitable for treating highly-concentrated brines with lower cost and specific energy consumption than traditional thermal evaporators (Atia et al. 2021; Beni et al 2022). Reports have been published mainly concerning the use of the OARO technique for desalination, and more recently they have included the possibility of regenerating the draw solution from the FO technique (Martínez et al. 2020), thus making it possible to treat more highly concentrated solutions. Considering that membrane processes can be used to retain an added value solute for its concentration and water recovery, they could facilitate the selective metal precipitation process by reducing the amount of sludge (López et al., 2021; Brewster et al., 2020).

In recent years, new methodologies have been tested to recover metals and water from AMD (Johnson et al., 2005; Sheoran et al., 2006; Bejan et al., 2015; Rodríguez-Galán et al., 2019). One of the most promising studies was developed by López et al. (2021) who they present the potential of the membrane technologies combined with other technologies such as electrowinning, ion-exchange, solvent extraction, precipitation, etc. for the valorization of acid mine waters and to obtain three products: metal-enriched stream, water, and acid stream (López et al., 2021). The benefit of recovering water prior to selective metal precipitation is that it increases precipitation efficiency (López et al. 2021). But although the fouling propensity in the FO process is lower than in other membrane technologies such as reverse osmosis, the feasibility of the FO is affected by the possible layer of precipitates (e.g. gypsum) on the membrane in terms of water flux decline (Cabrera-Castillo et al., 2021; Xie et al., 2016). For this reason, in order to obtain high levels of metals and water recovery in a combined process, it is ideal to combine both types of technology by alternating concentration steps (water recovery) with the precipitation steps, where possible solids are eliminated.

The focus of this work is to demonstrate the feasibility of a process for the valorization of AMD by recovering water and metals, using membrane technologies and selective metal precipitation (Figure 2) by means of experimental tests of FO and a model for the selective metal precipitation process. The process consists of different forward osmosis steps to recover water and selective metal precipitation steps to obtain concentrated sludges. Furthermore, a new configuration based on osmotically-assisted reverse osmosis plus conventional RO to regenerate the draw solution is proposed. Finally, the cost of water production and the specific energy consumption of the applied membrane technology were estimated to analyze the economic feasibility of the process. In relation to the FO studies to treat AMD presented above, in this study draw solutions with concentrations of NaCl of up to 2.5M were used. They allow high water recovery from highly concentrated AMD without high economic costs and energy consumption using membrane technologies.

To achieve this objective; first, a brief overview of the AMD of the
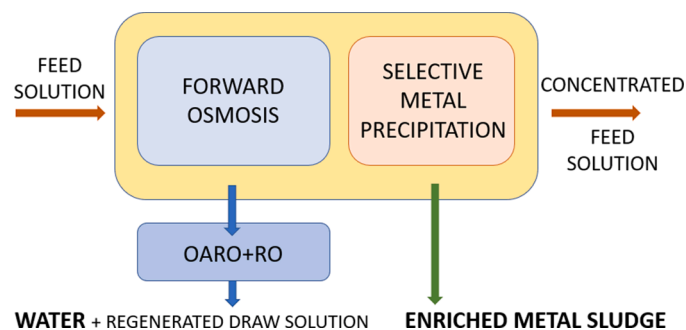
Iberian Pyrite Belt is presented. Subsequently, experimental FO tests were developed to treat AMD with the objective of determining water flux and water recovery. Considering the experimental results, different alternatives of the combined process of FO and selective metal precipitation were modelled in the PHREEQC software (PH REdox EQuilibrium in C language). Furthermore, the best alternative related to the draw solution regeneration stage was optimized in terms of water and metal recovery. Finally, the cost of water production and the specific energy consumption of the applied membrane technology have been estimated.

In this work, a process that allows the valorisation of AMD has been proposed. The combination of membrane technologies with selective precipitation enables high water and metal recovery. In addition, the incorporation of osmotically assisted reverse osmosis as regeneration technology for the forward osmosis stage allows this technique to be applied with a cost and energy consumption lower than those of conventional techniques.

2. Materials and methods

2.1. AMD and draw solution characterization

An exhaustive review of the typical metals and their concentrations contained in acid mine drainages was carried out to select a representative concentration of AMD with the objective of proposing a new and more efficient and economical treatment to obtain water and metals. In this work, the concentration of the feed solution of the FO process was considered as the maximum value of all samples from the Iberian Pyrite Belt studied in the last few years and are listed in Section 1. The composition of AMD is shown in Table 1 and was elaborated by dissolving reagents with a purity $\geq$95% in deionized water obtaining an initial pH = 2.65.

The concentration of the DS, among other operating conditions such as linear velocity and temperature used in the forward osmosis process, is one of the most important parameters to determine; since they affect the water flux (J_w) through the membrane and the regeneration of the draw solution, and hence affected the process costs. The inorganic salt used in this work was NaCl at different concentrations.

2.2. Membrane Technologies

2.2.1. Mathematical modelling

To estimate the membrane area of the proposed process to regenerate the draw solution, the water and salt theoretic flux through the membranes was calculated using the model proposed by Bartholomew et al. (2019) for pressure-driven membrane processes (Bartholomew et al., 2019). The fluxes of water and salt are defined by Equations 1 and 2:

$$J_w = A \cdot \sigma \cdot (\Delta P - \Delta \pi) \tag{1}$$

$$J_s = B \cdot \Delta C \tag{2}$$

where Jw is the water flux [m$^3 \bullet$m$^{-2} \bullet$h^{-1}]; A is the water permeability coefficient [m$\bullet$bar$^{-1} \bullet$h^{-1}]; ΔP is the hydraulic pressure difference

Figure 2. Proposal for a hybrid process to treat AMD and obtain high-quality water and metal sludge

Table 1
Chemical characterization of AMD

Element	Content (mg L^{-1})	Element	Content (mg L^{-1})
Al	700	**Mn**	60
As	25	**Na**	140
Cl$^-$	180	**Ni**	1.5
Co	4.5	**Sb**	3
Cu	100	**Si**	35
Fe	3900	**Zn**	200
K	4	**SO$_4^{-2}$**	17970
Mg	600	**HPO$_4^{-2}$**	8
Ca	155	**HCO$_3^-$**	30

[bar]; $\Delta\pi$ is the osmotic pressure difference [bar], σ is the reflection coefficient [-], Js is the salt flux [kg•m^{-2}•h^{-1}], B is the salt permeability coefficient [m•h^{-1}], and ΔC is the salt concentration difference [kg•m^{-3} or g•L^{-1}]. The reflection coefficient is assumed to be 1, assuming high salt rejection and low salt permeability in the membrane.

Some solution properties are necessary to calculate the water and salt theoretic flux. The osmotic pressure is calculated by Equation 3.

$$\pi = i \cdot \phi \cdot C \cdot \frac{R \cdot T}{MW} \tag{3}$$

where π is the osmotic pressure [bar]; i is the number of dissociating ions, 2 for NaCl [-]; φ is the osmotic coefficient [-]; C is the salt concentration [g•L^{-1}]; M_W is the molecular weight [g•mol^{-1}]; R is the gas constant; and T is the temperature [K]. The osmotic coefficient depends on the salt concentration and was calculated using Equation 4 (Bartholomew et al. 2019).

$$\phi = 3.14E - 6 \cdot C^2 + 2.13E - 4 \cdot C + 0.917 \tag{4}$$

Density, viscosity, and diffusivity were calculated according to Equations 5-7 (Bartholomew et al. 2019).

$$\rho = 756 \cdot x + 995 \tag{5}$$

$$\mu = 2.15E - 3 \cdot x + 9.80E - 4 \tag{6}$$

$$D = 153 \cdot x^4 - 122 \cdot x^3 + 30.1 \cdot x^2 - 2.00 \cdot x + 1.51 \tag{7}$$

where x is the mass fraction. Dimensionless parameters are calculated using Equations 8-10. Equation 10 allows us to calculate the Sherwood number when the Reynolds number is between 10 and 400.

$$Re = \frac{\rho \cdot v \cdot dh}{\mu} \tag{8}$$

$$Sc = \frac{\pi}{\rho \cdot D} \tag{9}$$

$$Sh = 0.45 \cdot (Re \cdot Sc)^{0.36} \tag{10}$$

where ρ is the density [kg•L^{-1}], v is the linear velocity [m•s^{-1}], μ is the viscosity [Pa•s], D is the diffusivity [1.5E-9 m^2•s^{-1}] and d_h is the hydraulic diameter [m]. The hydraulic diameter is calculated using Equation 11:

$$d_h = \frac{4 \cdot flowarea}{wetted\ perimeter} \tag{11}$$

To calculate the driving force through the membrane, the internal and external concentration polarizations must be known. Bartholomew et al. (2019) proposed a way to calculate the concentration of the FS and DS at the membrane interface and in bulk considering the steady state film theory. Other factors to determine the real out-pressure in each channel are the pressure drop across the membrane and the friction factor (Bartholomew et al., 2019). In this work, the average of water and salt flux, as well as the pressure drop, was approximated by the logarithmic mean according to Equation 12 (Bartholomew et al., 2019).

$$f_{avg}(Y_1,\ Y_2) = \frac{Y_1 - Y_2}{ln\left(\frac{Y_1}{Y_2}\right)} \approx \left(Y_1 \cdot Y_2 \cdot \frac{(Y_1 + Y_2)}{2}\right)^{\frac{1}{3}} \tag{12}$$

2.2.2. Experimental setup

Experimental tests were carried out in the laboratory-scale FO plant with different NaCl aqueous solutions as the draw solution (Figure 3). The experimental results provided water fluxes and water recoveries for each draw solution.

FO experiments were carried out in a membrane module, the main part of the plant, made up of two identical cells of white polytetrafluoroethylene commonly known as Teflon with a cross-flow configuration working at atmospheric pressure and room temperature, where the membrane has an active membrane area of 42 cm^2. The treatment solution was contained in a vessel (V-1) and driven by a peristaltic pump (P-1, Watson Marlow 520S) to cross the module at 25 cm•s^{-1}, after which the solution was recirculated in the tank, V-1. Furthermore, the DS was contained in a vessel (V-2) and pumped similarly to the FS toward the membrane module at 25 cm•s^{-1}. Once the draw solution passed through the module, it was recirculated to V-2. The velocity suggestions of the FO-standardized studies (Cath et al., 2013) were followed. The initial volumes were 0.6 L for FS and 3.5 L for DS, keeping the concentration of DS as constant as possible by replenishing the salt and controlling the pH with a WTW conductivity meter (Profiline Cond 3310 model). The OHAUS scale (AX5202 model) was located under the V-2 vessel and recorded the weight change in the DS, indicating the water permeability from the FS to the DS. The membranes used were of the FOMEM type, supplied by Porifera, Inc. (USA), and were soaked prior to the test for 15 minutes with deionized water. The active layer of the membrane was oriented toward the feed solution.
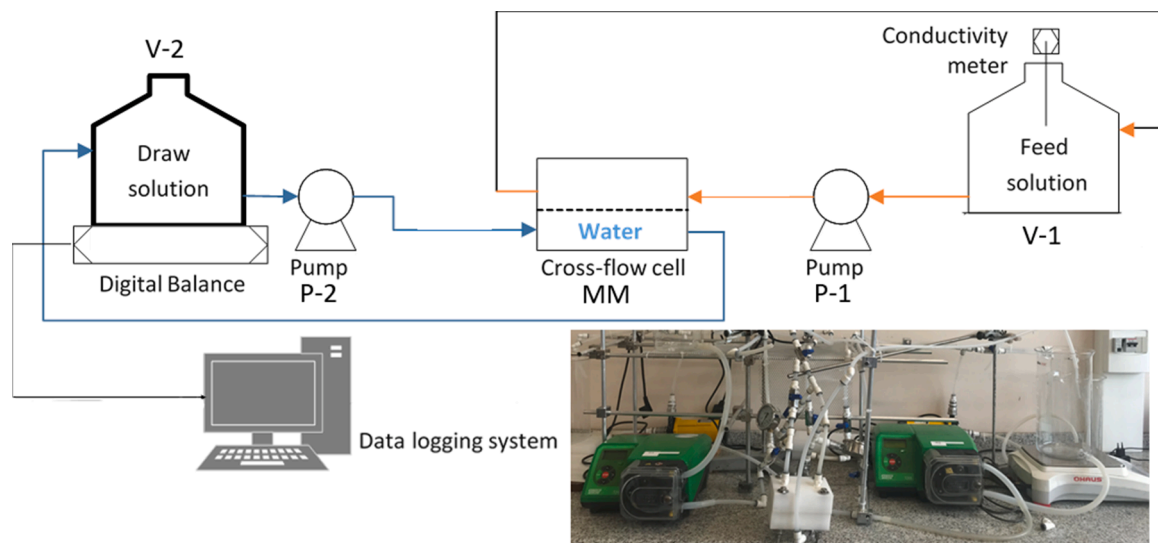

Figure 3. Lab-scale pilot plant experimental setup

2.2.3. Experimental design

All experiments were carried out under the same operating conditions, at room temperature and atmospheric pressure with a linear velocity of 25 cm/s, while modifying the concentration of DS to know the osmotic pressure necessary to achieve the maximum water recovery from acid mine drainage with a water flux greater than 5 L•m^{-2}•h^{-1}.

Before each test run, fresh membranes were compacted using deionized water as feed solution and the same draw solution used in the subsequent test for at least 1 h (Mi et al., 2010, 2013). Assays were carried out until the water flux was greater than 5 L•m-^{2}•h^{-1} or until the volume of the feed solution was the minimum possible in the system, 100 ml. The NaCl concentration of the DS used was 0.5, 1, 1.5, 2 and 2.5M, and the FS was the AMD mentioned above.

2.2.4. Experimental calculations

The flux of water through the membrane (Jw) is the amount of water that crosses the membrane surface in a unit of time, depending on both the DS and the FS, and the membrane characteristics. It was quantified by the weight changes in the DS reservoir with the scale mentioned connected to a computer data logging system according to Equation 13.

$$Jw = \frac{\Delta weight\ of\ DS}{Membrane\ area \cdot \Delta time} \quad (13)$$

where J_w is the flux of water through the membrane (L•m^{-2}•h^{-1}); M_i is the mass of DS at time t_i (kg); M_{i-1} is the mass of DS at time t_i (kg); t_i is the time in i (h); t_{i-1} is the time in i-1 (h); A_m is the membrane area (m^2); and ρ_w is the density of the water (kg•L^{-1}).

At each time, the recovery of water in the process was calculated using the weight changes in DS.

2.3. Modelling of Forward Osmosis and Selective Metal Precipitation

PHREEQC is a software written in the C++ programming language by the United States Geological Survey (USGS), which, among other software, like Visual MINTEQ, is used in engineering processes to analyze the speciation of dissolved compounds and to simulate acid-base and redox equilibrium, dissolution, precipitation processes and other physical and chemical processes, such as evaporation using equilibrium constants (Park et al., 2015). In this work, PHREEQC was used to model forward osmosis and selective metal precipitation processes, allowing the determination of the maximum amount of water that can be recovered without mineral precipitations and the pH values for the precipitation of each metal with a certain purity. The main operating conditions, pH, and temperature allowed by the membranes, are limitations to the recovery of water and possible minerals formed and contained in the treated solution. PHREEQC shows the saturation index of possible mineral phases and when the saturation index is above 0 indicates that this mineral phase could precipitate. The study was carried out with the following considerations:

- Possible precipitates have adverse effects on membrane operation due to internal and external fouling, mainly due to calcium precipitate in the form of gypsum.
- The operating pH range in forward osmosis of TFC membranes is between 2 and 11. It is not recommended to work at the lowest or highest pH.

The neutralizing agent selected for this work was NaOH.

The Thermoddem data base from the Geological National Service of France, BRGM, including thermodynamic data and equilibrium reactions involving mineral, gas, and aqueous complexes, was used (Blanc et al., 2012). Different options were modelled according to the recovery of water or metals.

3. Results

The combined processes to recover water and enrich sludges in different metals were designed once the AMD feed solution was characterized. The first experimental stage was to determine the water flux (L•m^{-2}•h^{-1}) and the water recovery (%) using different concentrations of draw solution with simulated AMD. In the second stage, different process alternatives were modelled in PHREEQC by estimating the pH values for the precipitation of each metal and the maximum amount of water that forward osmosis is able to recover without mineral precipitation. Finally, the results obtained in the first two stages were applied to the mass balance of the selected combined process.

3.1. Water recovery using forward osmosis

With 0.5 M NaCl, 50% water recovery from AMD can be achieved with a flux greater than 5 L•m^{-2}•h^{-1} (Figure 4). Nevertheless, there are significant differences at high concentrations, ranging from 1 M to 2.5 M NaCl, resulting in a water recovery of more than 50% and nearly 80% with 2.5 M of NaCl. The membrane area needed for FO could be calculated using an average flux for each feed solution concentration at the input and outlet of the module. In this work, the lowest possible concentration was used for each stage of FO in the combined process, but this decision was balanced with the required membrane area and regeneration technology. An increase in DS concentration means an increase in the osmotic pressure difference between FS and DS, allowing higher water fluxes through the membrane by theoretical calculations. The experimental results are similar to those obtained by Baena et al. (2020) showing higher fluxes for higher concentrations (Baena-Moreno et al., 2020). Furthermore, the water fluxes obtained using NaCl and AMD as extractive solute and FS, respectively, are comparable to some of the results shown by Cabrera-Castillo et al. (2021) and Vital et al. (2018) (Cabrera-Castillo et al., 2021; Vital et al., 2018), initially close to 10 L•m^{-2}•h^{-1} with 0.5M and around 25 L•m^{-2}•h^{-1} for the highest concentrations tested. Using the lowest concentration, 0.5M NaCl, it could be possible to recover nearly 50% of the initial water. The higher water recovery, the higher the concentration of the required draw solution (for example, for WR > 60%, > 1M NaCl). Another possibility could be to use a different draw solution concentration in different FO stages. Since the objective of the study is to achieve high water recovery, a water recovery of 75% (near maximum) was established for the following modeling calculations (see Section 3.2).

3.2. Combined processes to recover water and metal sludges

Four different theoretical alternatives for water and metal recovery were modelled in PHREEQC. Due to the characteristics of AMD, the simulations show that the only possible metal precipitated during the forward osmosis process is Ca in the form of CaSO$_4$ (gypsum). For this reason, two main study lines were developed: 1) considering the real Ca content in the feed solution (155 mg•L^{-1}) and 2) adding a previous process to decrease the amount of Ca (1.55 mg•L^{-1}).

To ensure that iron exists as Fe^{3+}, a process of oxidation with hydrogen peroxide (H$_2$O$_2$) was included. Considering that AMD pH is 2.5-3 and knowing the pH range for precipitating metals, Fe and Si are the first metals that precipitated. The reason for precipitating these metals before the FO process is to avoid fouling in the membrane and to increase the pH to improve the operating conditions. For the two lines of simulations at pH=3.3, iron exists as a solid phase as Fe$_2$O$_3$, and the theoretical recovery yield of Fe was greater than 98%.

Figure 5 shows the first line of the study that maintained the initial calcium concentration of the feed solution after Fe was precipitated and eliminated. In this context, the maximum value of water recovery without the formation of solid phases was 60% at pH 3, with gypsum being the first mineral phase formed from that moment. The rejection of the process is concentrated in Al, Cu, Zn, and Mn, and enriching sludges
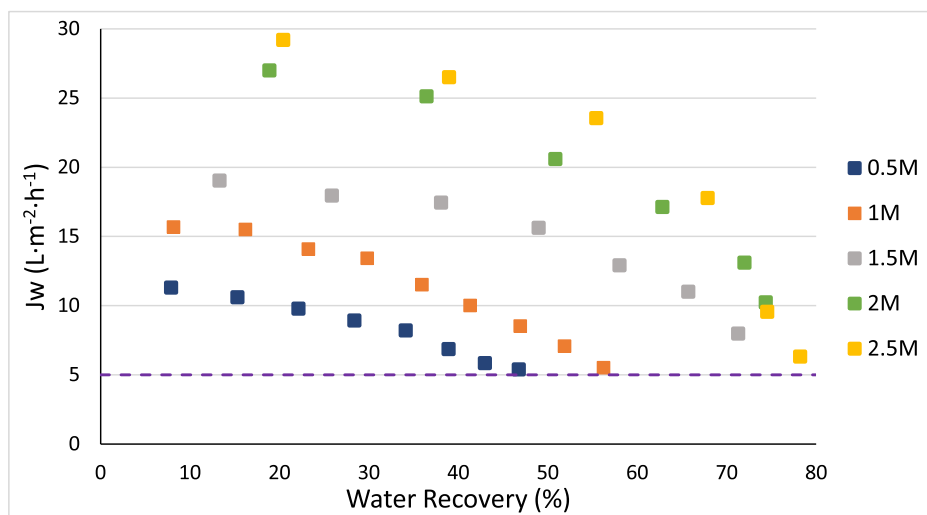
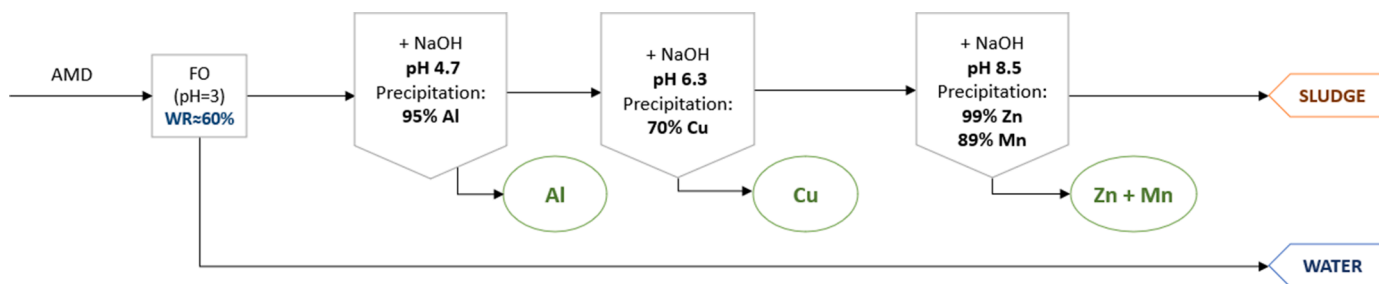**Figure 4.** Flux of water and water recovery at different concentrations

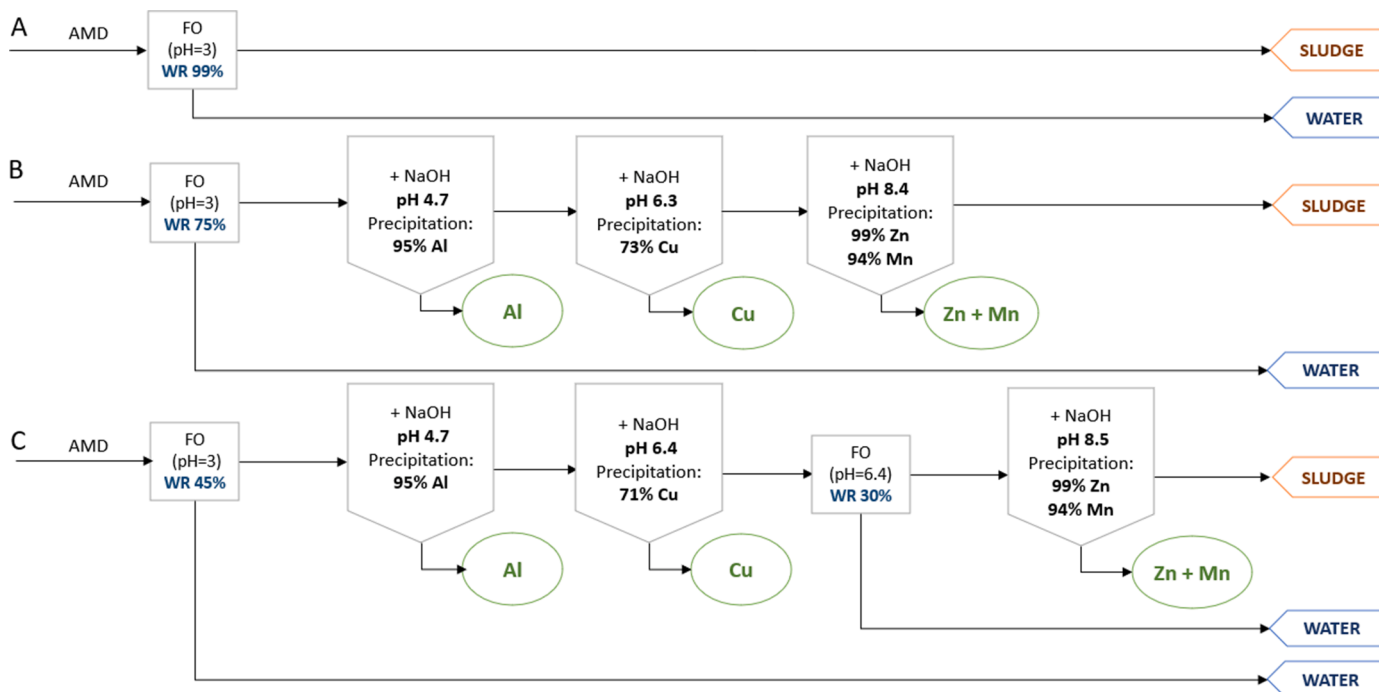**Figure 5.** PHREEQC modelled with initial Ca concentration

Figure 6. Simulations in PHREEQC decrease the amount of Ca. A: 99% water recovery. B: 75% water recovery and selective metal precipitation. C: 45% water recovery, selective precipitation of Al and Cu, 30% water recovery, and precipitation of Zn and Mn.

could be formed by selective metal precipitation. At pH = 4.6, the solid aluminium form was Diaspore (AlO(OH)), at pH=6.4, Cu can precipitate as copper hydroxide (Cu(OH)$_2$) and finally Zn and Mn were simultaneously precipitated at pH=8.5 as hydroxides. The theoretical recovery yields obtained for Al, Cu, Zn, and Mn were 95, 70, 99, and 89%, respectively.

When decreasing the amount of Ca to 1.55%, three different alternatives are shown in Figure 6. Alternative A shows that it is possible to recover almost all the water with ideal performance, obtaining an enriching metal sludge in all metal compounds, but it is impossible to separate the different minerals with selective metal precipitation. However, in the experimental FO tests, it was observed that 75% water recovery was the maximum possible through forward osmosis from AMD, verifying this possibility with simulations in PHREEQC without the formation of solid phases. For this reason, alternative B shows a configuration of the process that works with the membrane process at pH=3, setting the water recovery at 75%. With the objective of improving operating conditions, alternative C was proposed, where in the first stage of FO water recovery was set at 45% and pH=3 because this is the limitation when the lowest NaCl concentration tested, 0.5M, is used. Cu and Al were precipitated before the pH increased with NaOH, and then the remaining percentage was recovered until 75% at pH=6.3, improving the operating conditions. The recovery yield of all metals was similar regardless of the recovery of water and the percentage of Ca in the feed solution, approximately 95% for Al, 70% for Cu, and more than 94% for Mn and Zn.

To achieve 75% water recovery, the best option, knowing the operating conditions recommended by the manufacturer in terms of pH in FO, is option C. Although option B could be another alternative, the service life of the membrane could be improved by working at higher pH values. For this reason, the mass balance of a global process was resolved considering two steps of FO, as the presented option C, including a proposal methodology for the regeneration of both DS used, as shown in Figure 7.

3.3. Mass balance of the combined process

Once the capacity of the membrane technology and the recovery yield of the main metals are known, Figure 8 shows a proposal methodology scheme that covers both the FO and the regeneration of the draw solution. Depending on the objectives in terms of valuable products, water, or metals, the configuration of the FO and the selective metal precipitation process could be different. In the proposal scheme, the precipitation process could be modified using the forward osmosis stages due to the scenery presented is the worst case, high concentration of metals in AMD, 75% of all water recovery, and the lowest concentration of NaCl in the first stage of FO considering a minimum flux of 5 L•m^{-2}•h^{-1}.

An AMD feed volumetric flow of 17 m^3•h^{-1} was considered as FS to resolve the mass balance of the combined process and characterize all currents in the system. The values given in the literature of 1.5

L•m^{-2}•h^{-1}•bar^{-1} and 4.46E-2 L•m^{-2}•h^{-1} were considered for the water permeability coefficient, A, and salt permeability coefficient, B, respectively, characteristic of bilateral counter current membranes (Atia et al., 2021). The last stage of the conventional reverse osmosis process allows the use of a low-salt rejection membrane in the OARO stage, although the salt rejection decreases. The mass balance was modelled and calculated using Engineering Equation Solver software to characterize both the flux of water (H) and salt (S) for each current considering the following assumptions:

- In the FO and RO modules, salt flux and reverse flux were considered insignificant but not in the OARO process (Bartholomew et al., 2018). In this case, adjustment or recirculation of salt in the system by adding or purging was not considered, as is necessary in industrial processes.
- The water recovery was set at 75%, which is on the conservative side considering the fluxes of water from the experimental forward osmosis tests explained in Section 2.2.
- By analysis of the number of degrees of freedom, the process was defined with nine specifications of the currents and three variables associated with the fluxes of water and salt (J$_s$) in the osmotically-assisted reverse osmosis (OARO) process and the water flux in conventional reverse osmosis. It was taken for granted that:
- J$_w$ and J$_s$ in the OARO process and J$_w$ in conventional RO were defined by the model proposed by Bartholomew and Mateur (2019) (Bartholomew et al., 2019).
- The percentage of salt mass flux in the FO stages (WFO1 and WFO2) was considered negligible.
- According to the osmotic pressure needed in the FO stages, the input and output concentrations of the second stage of forward osmosis (W1 and W2) as well as the input of the first stage (W8), were set. 0.5M NaCl was set for the first stage of FO and 2.5M NaCl for the second stage, taking into account the water recovery achieved in the experimental tests.
- To use conventional pumps and energy recovery devices typical of membrane processes for desalination, the inlet concentration of the feed solution (W3) and the outlet concentration of the draw solution (W6) in the OARO stage were fixed with a difference in osmotic pressure of less than 45 bar (π_3- π_6 = 15 bar).
- Taking into account the objective of set water recovery, half of the total water passes through each FO module, and all of the water leaves the system by the RO module.

Table 2 shows the concentration, the flux of water and salt for each current, and the required membrane area for each module. The membrane area for both RO and OARO was calculated once the fluxes of water and salt were known by the explanation mentioned above, Section 2.2.1. To estimate the membrane area for forward osmosis, the logarithmic mean flux using the experimental values obtained in Section 3.1 was considered. The theoretical results of the water fluxes and required membrane areas were optimized by modifying the inlet
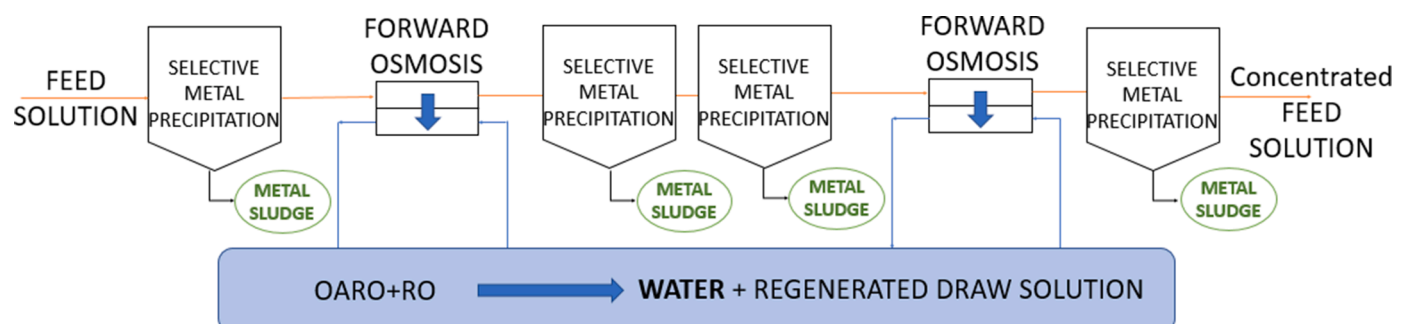

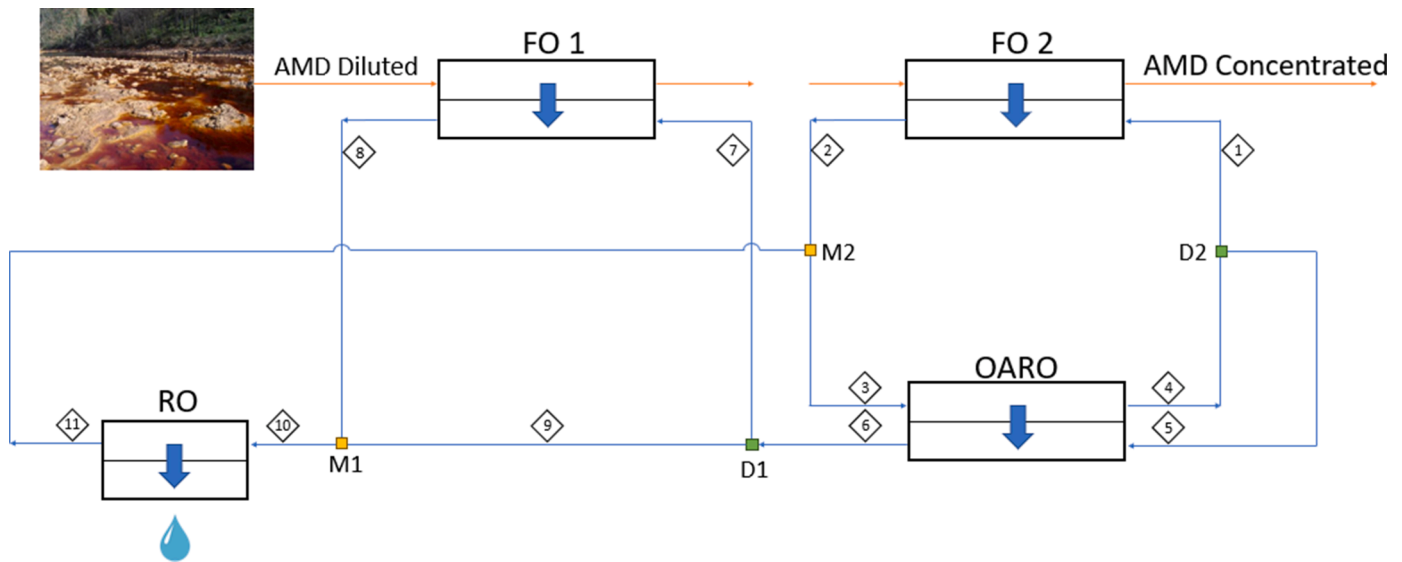**Figure 7.** Schematic configuration of the selected hybrid process

Figure 8. Integration of FO and Regeneration Process

Table 2
Mass balance results. Mass percentage, water and salt fluxes in each stream, water and salt fluxes through the membranes, and membrane area for each module.

W (mass % weight)				
W1 = 10.9	W2 = 7.2	W3 = 5.5	W4 = 10.9%	W5 = 10.9
W6 = 3.7	W7 = 3.7	W8 = 2.8	W9 = 3.7	W10 = 3.2
W11 = 4.5	WFO1 < 0.01	WFO2 < 0.01	WOARO = 0.03	WRO < 0.01
H, water flux (kg•h⁻¹)				
H1 = 11142	H2 = 17517	H3 = 47623	H4 = 22693	H5 = 11551
H6 = 36481	H7 = 18438	H8 = 24831	H9 = 18043	H10 = 42856
H11 = 30106	HFO1 = 6375	HFO2 = 6375	HOARO = 24930	HRO = 12750
S, NaCl flux (kg•h⁻¹)				
S1 = 1357	S2 = 1357	S3 = 2772	S4 = 2769	S5 = 1407
S6 = 1414	S7 = 714.8	S8 = 714.8	S9 = 699.5	S10 = 1414
S11 = 1414	SFO1 ~ 0	SFO2 ~ 0	SOARO = 6.95	SRO ~ 0
A (m²)				
AFO1 = 720	AFO2 = 386	ARO = 607	AOARO = 2043	
Water and salt membrane fluxes (kg•m⁻²•h⁻¹)				
JwFO1 = 8.86	JwFO2 = 16.55	JWRO = 21	JWOARO = 12.2	
JsOARO = 0.003				

The equations for the W (mass % weight), H (water flux, $kg \cdot h^{-1}$), S (NaCl flux, $kg \cdot h^{-1}$), A (m^2), and water and salt membrane fluxes ($kg \cdot m^{-2} \cdot h^{-1}$) are shown in Table 2.

concentration of FS, the outlet concentration of DS, and the applied pressure in the OARO stage.

The results showed the feasibility of the combined process compared to the results obtained by Martínez et al. (2020) to achieve the same water recovery and showed that it could be possible to improve the cost of the process, FO, and regeneration, reducing the concentration of the DS and consequently the required membrane area (Martínez et al. 2020).

The FO was designed for the combined process using the results obtained from the experimental assays. The desired water recovery from each FO module and the concentration in the draw solution channel required limit the technology and the configuration of the system to regenerate the DS. This process is promoted by employing the lowest possible concentration of DS with the ability to use conventional technology, such as reverse osmosis, to recover water. For this reason, the process was optimized using the minimum concentration of DS possible to reduce the cost of the regeneration step. In addition, the amount of water that is recoverable in each stage of forward osmosis is determined by the first possible precipitated minerals shown with the simulations in PHREEQC. To improve the operating conditions of membrane

technology in terms of pH, close to the neutral value, the third alternative showed, C, to the best of the author's knowledge, could be better for the balance between the pH condition in FO and the recovery of the metals. The selective metal precipitation process could be configured between forward osmosis stages according to the results of the simulations. The yields obtained for Fe and Zn are very similar to those shown by Park. et al. 2015 for actual acid mine drainage, otherwise for Al, Zn and Mn, the yield was slightly higher than theirs (Park et al., 2015).

In summary, a combined process was proposed (Figure 9) according to the alternatives presented in Section 3.2. and the water fluxes previously obtained with the simulated acid mine waters in FO. In addition, a mass balance of the proposal process was resolved using a numerical example with a specific goal for water recovery. The numerical example indicates the feasibility of eliminating water from high concentration AMD, simplifying the methodology for regenerating the draw solution compared to the treatment proposed by Martínez et al. (2020) (Martínez et al., 2020). The innovation of this process is the high water recovery achieved from acid mine drainage and a modification of the low-cost methodology to regenerate the draw solution.

Taking into account the same methodology to estimate the water production cost (WPC) and the specific energy consumption (SEC) as Martínez et al. (2020), the WPC could be reduced from 6.05 $/m³ to 2.01 $/m³, and the SEC was 8.03 kWh$_e$/m³ close to the value obtained by them, 7.4 kWh$_e$/m³ and lower than other combined processes made up of FO and membrane distillation or mechanical vapor compression brine concentrator (Martínez et al., 2020; Tong et al., 2016). The decrease in the cost of producing water is mainly due to the smaller membrane area required. The methodology used for the economic estimation can be seen in the Supplementary Information.

4. Conclusions

In this work, a methodology based on membrane technologies, forward osmosis, reverse osmosis, and osmotically-assisted reverse osmosis mixed with selective metal precipitation has been presented to treat concentrated acid mine drainage, obtaining high water recovery and enriched metal sludge.

On the one hand, the results show that it is possible to recover nearly 80% of the water from AMD using two steps of FO with draw solutions based on sodium chloride. On the other hand, rich sludges in Fe, Al, Cu, Zn, and Mn can be obtained from AMD using selective metal precipitation. At pH=3, the model shows that the recovery yield of Fe was more than 97% as hematite (Fe_2O_3), around pH=4.7 95% of Al can be
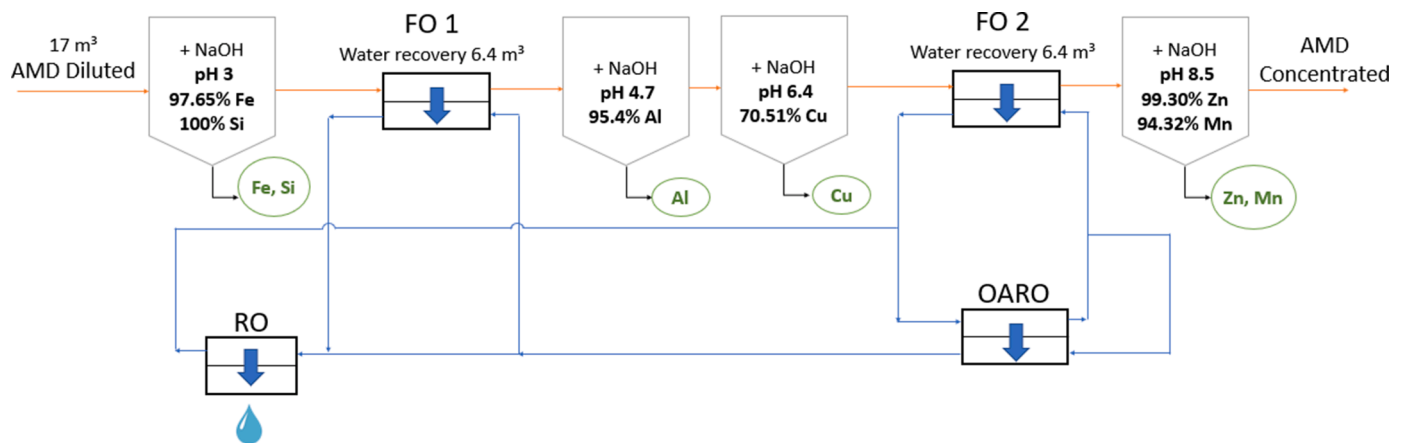
Figure 9. Combined processes to recover water and metal sludges

precipitated as diaspore (AlOOH), 70% of the initial copper is transformed into a solid phase at pH=6.3 as Cu(OH)$_2$ and finally Zn and Mn can be precipitated at pH=8.5, with a recovery of 99% for Zn and 94% for Mn in the form of hydroxides. In addition, a process has been designed to regenerate the draw solution of the FO process. The specific energy consumption of the combined membrane process, FO and regeneration stage, was 8.03 kWh$_e$/m^3 and the cost of producing water was 2.01 \$/m^3.

This research demonstrates the viability of a promising technology, forward osmosis, for the management of industrial effluents or to desalinate high concentration brines with high water recovery, as well as a combined process to obtain both water and valuable metal products using forward osmosis and selective precipitation, respectively.

Future works will consist of recovering the water from real AMD and optimizing the operating conditions to achieve lower energy consumption, as well as obtaining metal-concentrated sludge from real AMD in the laboratory.

Author Contributions

Elena León-Venegas was responsible of the Methodology, Data curation, Formal analysis, Investigation, Software, Visualization, Resources, Supervision, Validation, Writing – original draft, Writing – review & editing.

Fátima Arroyo-Torralvo was responsible of the Conceptualization, Formal analysis, Funding acquisition, Investigation, Project administration, Resources, Supervision, Validation, Writing – review & editing.

Luis F. Vilches-Arenas was responsible of the Conceptualization, Formal analysis, Funding acquisition, Investigation, Software, Project administration, Supervision, Validation.

Custodia Fernández-Baco was responsible of the Writing – original draft, Visualization, Investigation, Software.

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Declaration of Competing Interest

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.

Data Availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2022.106629.

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