

Recovery of sulphuric acid and valuable metals (Zn, Cu and REE) from acidic mine waters using nanofiltration

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Abstract

Acidic mine waters (AMWs) contains moderate concentrations of sulphuric acid, relatively high concentrations of metals (Al, Fe, Cu and Zn) and minor amounts or rare earth elements (REE). The established management routes for AMW treatment include a neutralization-precipitation step, which implies a high cost due to the reagents consumption. Nanofiltration (NF) membranes are emerging as an alternative to conventional methods to treat AMW due to a good passage of mono-charged ions (e.g. hydrogen sulphate, proton) for further recovery of sulphuric acid and high rejection of multi-charged ions, such as transition metals and REE. The behavior of one typical NF membrane (NF270, poly(piperazinamide)) was tested in a cross-flow experimental set-up with model solutions at pH 1.0. Moreover, experimental results were modelled according to Solution-Electro-Diffusion Model coupled with reactive transport to characterize the transport of species across the membrane, by means of the membrane permeances. Finally, the performance of NF270 working at batch mode was predicted with the obtained membrane permeances.

Keywords: Acidic mine waters, rare earth elements, nanofiltration, NF270, membrane permeances

1. Introduction

The European Union has identified a list of critical materials based on their high importance to its economy and the high risk associated with their supply. This list includes (REEs), which comprise in turn lanthanides, scandium and yttrium to name a few (European Commission, 2018).

Acidic mine waters (AMWs) are a by-product of the mining industry that occurs when sulphide minerals, such as pyrite (FeS₂), are oxidised when entering in contact with water and oxygen. The oxidation of sulphide minerals leads to sulphuric acid production, which can dissolve the surrounding soil minerals and a stream containing a high content of iron, aluminium, zinc and copper, and a minor presence of REEs (the so-called AMW) is released to the environment (Simate G.S. and Ndlovu S, 2014). AMWs from the Iberian Pyrite Belt can present concentrations from 0.3 to 11.7 mg/L of REE, so they can be considered as an

alternative source for REEs recovery (Ayora C. et al., 2016).

However, it may be desirable to concentrate REEs before the acid neutralisation and solvent extraction steps before their recovery. This can be accomplished by membrane technologies, such as nanofiltration (NF). NF membranes have demonstrated to offer two-fold benefits when treating AMWs: on the one hand, they can concentrate multi-charged ions (and hence REEs) in the retentate side while, on the other hand they allow permeation of mono-charged ions (e.g. H⁺) (López J. et al., 2018).

Nevertheless, and contrarily to reverse osmosis processes, there is still a lack of mathematical models to scale and predict the behaviour of NF membranes for treating AMWs. Mathematical models such as the Solution-Electro-Diffusion (SED) can describe the transport of species across NF membranes using membrane permeances, but most of the efforts are centred in the description of single solutions containing strong electrolytes (Yaroshchuk A. et al., 2011). A step forward has been done by a recent study on the rejection of species in acidic waters by NF considering the formation of chemical species between weak electrolytes (e.g. SO₄²⁻/HSO₄⁻) and metallic ions in solution (Mⁿ⁺) (López J. et al., 2018). The incorporation of the reactive transport concept of species in the SED model has originated a database of NF membrane permeances to species as a potential tool for the design of NF processes for the recovery of valuable metals (e.g. REEs) from acidic waters.

2. Materials and methods

A commercial semi-aromatic poly(piperazine amide) NF membrane was tested (NF270 from Dow Chemical). This membrane presents ionisable amine (R-NH₂/R-NH₃⁺) and carboxylic (R-COOH/R-COO⁻) groups, which are responsible for the membrane charge. Its isoelectric point (IEP) is 2.5. This membrane was tested in a flat-sheet (140 cm²) cross-flow set-up equipped with a test cell (GE SEPATM CF II) with a spacer-filled feed channel. Two kinds of experiments were performed with the membrane test cell. In first one, the trans-membrane pressure (TMP) was varied from the

osmotic pressure to 20 bar to study the ion fluxes and rejections of each species and to determine their membrane permeances. From them, it was possible to predict the concentration factor of the different species in solution with the permeate recovery. Finally, an experiment was performed to validate the model prediction.

The synthetic solution mimicked an AMW from La Poderosa Mine at the Iberian Pyrite Belt (Huelva, Spain). This solution contained a sulphuric media (pH around 1.0 ± 0.1) and Al(III) (600 mg/L), Ca(II) and Zn(II) (40 mg/L each), Cu (25 mg/L) and REE such as La, Dy, Nd, Pr, Sm and Yb (10 mg/L each one).

3. Results and discussion

NF270 showed high metal rejection (>98 %) and low hydrogen (from -10 to 10% for NF270) and sulphate rejections (from 40 to 50% for NF270). These results can be explained with the basis of the main exclusion phenomena: Donnan and dielectric exclusion (Yaroshchuk A., 2001). According to the IEP membrane (2.5), at pH 1 free carboxylic groups are fully protonated (R-COOH) and amine groups are partially protonated (R-NH₂⁺). This led to a high rejection of metals while it favoured the transport of sulphate across the membrane. The fact that cations were rejected led to H⁺, which was the more mobile ion and the one with the highest concentration in solution, to permeate easily. On the other side, the dielectric exclusion can be used to explain the low rejections of sulphate. At pH 1, the main sulphate specie in solution is a monovalent anion (HSO₄⁻) (pKa = 1.92), which is less affected by dielectric exclusion and then responsible for low sulphate rejections. Moreover, as explained, its transport was also favoured by the presence of a positively charged surface.

Calculated membrane permeance values were in agreement with dielectric and Donnan exclusion. For instance, membrane permeance to HSO₄⁻ was higher than the one to SO₄²⁻ (114 and 0.2 μm/s, respectively). The fact that metals were highly rejected by the membrane implied lower membrane permeance values than for H⁺. For example, membrane permeance to H⁺ was 86.04 μm/s, while the one for Zn²⁺ was 0.01 μm/s.

After that, membrane permeances were used to predict the concentration factors and rejections at different permeate recoveries ratios. The calculated concentrations matched consistently the experimentally measured values for both dominant and minor species in solution. With regard to the permeate stream, a good matching was generally obtained, although significant discrepancies were observed for H⁺ and aluminium for the NF270 membrane.

4. Conclusions

NF270 membrane has shown its potential for treating AMWs since allows the recovery of sulphuric acid as permeate and concentrate the metals and REEs in the solution. Results showed that the electric fields govern the separation originated between the membrane and dissolved species (Donnan and dielectric exclusion). Therefore, metallic ions were effectively rejected by the membrane (>98%) whereas sulphuric acid was transported (H⁺ rejections below 10%). The developed algorithm integrating the SED model and reactive transport has proven its applicability to determine the REE recovery factors and the sulphuric acid recovery at different % permeate recovery ratios

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