Separation and Purification Technology

Integration of membrane technologies to enhance the sustainability in the treatment of metal-containing acidic liquid wastes. An overview

--Manuscript Draft--

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Abstract:	The mining and hydrometallurgical industries generate effluents characterised by a high acidity (pH < 3) and a high content of metals (e.g. Fe, Al, Cu and Zn, among others) and non-metals (e.g. As, Sb, Bi), which confers them toxicity that makes necessary their treatment. The conventional treatments of such streams mainly rely on neutralisation/precipitation, solvent extraction, ion-exchange and adsorption. However, these options are often not feasible because of their high consumption of chemicals and the generation of large volumes of sludge. On the other hand, due to the exhaustion of natural resources, circular economy schemes are increasingly promoted for the recovery of valuable elements (e.g. Cu, Zn, rare earth elements) from waste effluents as an alternative to mining the already over-exploited mine sites. Within this new paradigm, the integration of membrane technologies are gaining importance for the valorisation of such effluents since they provide the possibility of: i) reducing the volume of the streams to be treated, ii) favour the selective separation of metal ions from acids, and, iii) the concentration of metals in acidic streams. Membrane technologies are promoting the recovery of valuable dissolved components and the reuse of the acid, reducing the generation and disposal of sludge. Among the different membrane technologies, nanofiltration (NF), diffusion dialysis (DD), reverse osmosis (RO), electrodialysis (ED), forward osmosis (FO) and membrane distillation (MD) are the most promising ones to tackle these challenges and promote circularity.
Suggested Reviewers:	Karin Soldenhoff Australian Nuclear Science and Technology Organisation khs@ansto.gov.au Expert in the treatment of acidic waters, including their processing with membranes
	Mìriam C.S. Amaral Federal University of Minas Gerais miriam@desa.ufmg.br Experience on the treatment of acidic waters with nanofiltration and reverse osmosis
	Andrea Cipollina Università degli Studi di Palermo andrea.cipollina@unipa.it Experience on the treatment of acidic waters with diffusion dialysis
	Gerardo Cifuentes Universidad de Santiago de Chile gerardo.cifuentes@usach.cl Experience on the treatment of acidic waters with electrodialysis
	Marek Gryta West Pomeranian University of Technology

	marek.gryta@zut.edu.pl Experience on the treatment of acidic waters with membrane distillation
	Francisco Baena-Moreno Universidad de Sevilla fbaena2@us.es Experience on the treatment of acidic waters with forward osmosis
Response to Reviewers:	Reviewers' comments: Reviewer #1: The manuscript entitled, "Integration of membrane technologies to enhance the sustainability in the treatment of metal-containing acidic liquid wastes. An overview", looks interesting for the readers. It deals with the state of the art of membrane technologies on treatment of heavy metal ions in acidic liquid wastes. In general, the paper provides good overview and insights in the field, however, the reviewer (expert in different membrane technologies and applications) has some comments to be addressed by the authors. The manuscript can be accepted for publication after carefully attending some suggestions: We are grateful to the reviewer for her/his comments and useful suggestions that have helped us improve our paper. As indicated in the responses that follow, we have taken all these comments and suggestions into account in the revised version of our paper. •Regarding the pressure driven membrane technologies (MF, UF and NF). The authors are providing the current development work when using these technologies in acidic liquid wastes processing, but the article still lack in the following issues that should be addressed in the revised manuscript. i.Key factors influencing the performance of membrane processes, e.g. feed concentration, pH, temperature, pressure influence, and metal type ions, among others. Key factors, such as the feed concentration, pH and metal type ions are presented in the manuscript. RO membranes are only dependent on operation parameters (e.g. pressure), with little effect of the solution properties. However, those parameters have an important influence on the performance of NF membranes as follows: a.Feed concentration. Feed concentration has a direct effect on solvent flux (i.e. osmotic pressure). Besides, the transport of species in NF membranes is due to a combination of diffusion and electromigration with a small contribution of convection (<5%). The higher feed concentration, the higher species passage. b.Metal type ions. Dielectric exclusion mechanisms are caused by interaction between ions and bound electric charges induced in the membrane at the interface solution/membrane with different dielectric constants. The effect of dielectric exclusion is proportional to the square of the ion charge. For that reason, multi-charged ions are better rejected than single-charged ones. Other parameter of importance regarding the metal type is their speciation in water. c.pH. The pH is correlated with the membrane surface charge. Depending on the pH the membrane will exhibit a positive or negative charge due to the ionisation of membrane functional groups. Besides, the pH highly influences solution speciation. This is aligned with sulphate rejections. For example, at neutral pHs, NF rejects more than 99% sulphate, whereas at pH<1.9 (=pKa) sulphate rejections can drop to 20%. d.Temperature, additionally to the influence on fluids viscosity, can impact on physicochemical properties of membrane and fluid streams and solution speciation. Then, it is affecting for example scaling events as the solubility constants are directly dependent on temperature. It should be mentioned that scarce efforts are found in the literature. e.In the case of NF membranes, pressure directly affects solvent flux. It is assumed that the transport of water and species across the membrane is not coupled. ii.Weakness/limitations of pressure membrane-based technologies, fouling (https://doi.org/10.3390/pr8020182) etc., As indicated by the reviewer, weaknesses and limitations of pressure membrane-based technologies have been added. One of their main limitations is their stability under acidic media, especially for polyamide-based membranes. Nowadays, efforts are being towards this direction, in order to improve membrane stability at acidic media. Concerning the fouling, due to the high acidity of acidic wastewaters (industrial or natural occurrence, pH <3) it is quite unlikely to have organic fouling due to the accumulation of algae, colloids or biofouling. Under the operation in this media, pressure-driven membrane processes face scaling (i.e. precipitation of inorganic

minerals), typically of iron, calcium, barium and strontium sulphates.
iii.Relation to separation technologies, molecule properties, membrane characteristics and other interesting phenomena that occur during their recovery/separation.
As indicated by the reviewer, the relation to the separation technologies has been added to the manuscript.
In relation to the interesting phenomena that occur during their recovery/separation, the manuscript refers to the functional groups of NF membranes. Contrary to RO or UF membranes, the active layer of NF membranes has ionisable groups, which depending on the pH confer the membrane a superficial charge. This has a noticeable impact on the separation performance, e.g. those ions with the opposite charge to the one of the membrane will be transported, whereas those with the same charge will be rejected.
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As indicated by the reviewer, information about the post separation was added in Section 6 (see Figure 5). Most of the information reviewed refers to research level at laboratory scale and more limited information is found on full scale applications. The more reported cases describe projects devoted to water reuse applications (see Section 7).
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No information regarding the economic feasibility of membrane technology for the treatment of acidic liquid wastes was found. We have found information comparing membrane technology and the current management options (See Section 6).
The following paragraph was added: “In relation to an economic point of view, no data about the comparison of operational expenditure (OPEX) and the capital expenditure (CAPEX) among the different membrane technologies for the treatment of acidic liquid effluents have been reported. However, it is estimated that membrane treatment can imply a CAPEX of 500-1000 US $/m3 and an OPEX of 0.5-1.0 US $/m3. Instead, the current management options, such as chemical precipitation has a CAPEX of 300-1250 US $/m3 and an OPEX of 0.2-1.5 US $/m3, whereas biological sulphate removal has a CAPEX of 800-1500 US $/m3 and an OPEX of 0.7-1.5 US $/m3.”
Additionally, a section devoted to the market perspective for mining and hydrometallurgical industries was added (Section 8).
vi.What is the current status for large-scale application in these types of applications?
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Please, all those issue must be included and check and reference the following contributions (https://doi.org/10.1016/j.foodchem.2016.07.030; https://doi.org/10.1080/10408398.2020.1772717; https://doi.org/10.3390/pr8020182; https://doi.org/10.1002/apj.2332), that will help for the feedback.

•It is surprising by the reviewer that authors did not talk deeply about the role of new nanocomposite in heavy metals separation from water. This is a hot topic in the field since new composite material provide synergistic removal efficiencies supported by different metal uptake mechanisms. There are recent published articles reviewing the new concepts of composite membranes for heavy metal ions that are not cited by the authors (https://doi.org/10.3390/membranes10050101; https://doi.org/10.1016/j.chemosphere.2020.129421; 10.1016/B978-0-12-816778-6.00007-2). The reviewer encourages to the authors to address such contributions in the revised version of the paper.
As indicated by the reviewer, nanocomposite membranes can provide good heavy metal rejections in water (mostly neutral). However, the nanoparticles have proven not to be stable at acidic media (see the references below). Most of them are unstable at pH lower than 5. Therefore, it is not worth to use nanocomposite membranes in acidic media.
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M. Smiljanić, U. Petek, M. Bele, F. Ruiz-Zepeda, M. Šala, P. Jovanovič, M. Gaberščček, N. Hodnik, Electrochemical Stability and Degradation Mechanisms of Commercial Carbon-Supported Gold Nanoparticles in Acidic Media, J. Phys. Chem. C. 0 (2021). doi:10.1021/acs.jpcc.0c10033.

•I did not see the weakness and advantages of concentrating these wastewaters via RO. An info should be provided.

As requested by the reviewer, the advantages and weakness of treating Acidic Liquid Wastes have been added. RO membranes are not suitable for this application because of:

a.Need of a high hydraulic pressure due to the solution composition because of the presence of metals and acids.

b.Low chemical stability at acidic media. RO membranes are usually made of polyamide, which makes them unstable at acidic media.

c.Scaling. The high metal rejections can cause a sever scaling at the membrane surface.

In mining and hydrometallurgical industries, RO membranes are usually to produce water for internal re-use or some polishing stage, and its direct application to acidic effluents is very limited.

•Regarding the thermal processes (like MD), a brief feedback on fundamentals is needed together with advantages and drawbacks on the technologies. To address such points over the paper will guarantee that you papers will be different from others. Importantly, within the selective membrane technologies and solvent separation, it should be mentioned pervaporation. Please, a brief section must be included and the potentialities of these technologies for the removal of organics, salts, etc. Check these references and use them if possible (https://doi.org/10.1016/j.watres.2020.116428; https://doi.org/10.1016/j.cherd.2020.09.028; https://doi.org/10.1016/j.seppur.2018.01.045; https://doi.org/10.1016/j.memsci.2019.03.076 ; https://doi.org/10.1007/s13197-019-03751-4).

As indicated by the reviewer, more information concerning the fundamentals, advantages and drawbacks of MD has been added.

Regarding to the pervaporation, this technology has been successfully applied for separating different types of multicomponent azeotropic mixtures by partial vaporization. Most of the works published refers to water/organic (ethanol, acetic acid) mixtures, which are out of the scope of the present review. By the date, most of the works published are addressed for solutions at neutral pH containing only NaCl. In addition, only a couple of works studying complex mixtures (e.g. seawater) have been published, and its application has not been studied yet to the treatment of acidic liquid wastes. It may be potentially postulated, but there is still no information on pervaporation membrane stability in acidic solutions.

•Importantly, the authors also should pay attention of the type of membranes used in these applications. Most probably, polymeric membranes are preferred for this separation due to their chemical and thermal stability. But it is important also to address some applications by using other concepts of membranes, such as mixed matrix membranes, composite membranes, and ultrathin membranes, due to they offer the enhanced separation performance (DOI: 10.1039/D0RA02254C ; doi: 10.3389/fchem.2019.00897).

As indicated by the reviewer, information regarding the performance of other concepts of membranes was provided in the manuscript. Only data for composite membranes for DD purposes was found in the literature.

•Conclusions: more than providing the concluding remarks and findings of the contributions, the authors may provide some suggestion or new research gaps for the new scientists in the field, in such a way, the membrane field will be further studied and explored.

As requested by the reviewer, the conclusions section has been reformulated to cover the recommendations provided (e.g. research needs and application challenges).

Reviewer #2: I consider that a complete revision on the subject was presented, only a spell check would be necessary.

We are grateful to the reviewer for her/his positive feedback.

Departament d'Enginyeria Química
UNIVERSITAT POLITÈCNICA DE CATALUNYA

Barcelona, 11/02/2020

Dear Prof. Bart Van der Bruggen ,

Editor-in-Chief of Separation and Purification Technology,

Please find enclosed the revised version of our manuscript "*Integration of membrane technologies to enhance the sustainability in the treatment of metal-containing acidic liquid wastes. An overview*" by: Julio López, Oriol Gibert and José Luis Cortina (**Reference SEPPUR-D-20-04538**)

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 **Separation and Purification Technology**.

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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Universitat Politècnica de Catalunya-BarcelonaTech
Av. D'Eduard Maristany 10-14, 08019 Barcelona, Spain
Phone: (+34) 93 401 6997
e-mail: julio.lopez.rodriguez@upc.edu

Ref. No.: SEPPUR-D-20-04538

Title: *Integration of membrane technologies to enhance the sustainability in the treatment of metal-containing acidic liquid wastes. An overview*

Journal: Separation and Purification Technology

Dear Prof. Bart Van der Bruggen,

Thank you for your invitation to resubmit our manuscript after addressing all reviewer comments. We have completed the review of our manuscript, and a summary of the raised comments and the comments and changes made can 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

Reviewers' comments:

Reviewer #1:

The manuscript entitled, "Integration of membrane technologies to enhance the sustainability in the treatment of metal-containing acidic liquid wastes. An overview", looks interesting for the readers. It deals with the state of the art of membrane technologies on treatment of heavy metal ions in acidic liquid wastes. In general, the paper provides good overview and insights in the field, however, the reviewer (expert in different membrane technologies and applications) has some comments to be addressed by the authors. The manuscript can be accepted for publication after carefully attending some suggestions:

We are grateful to the reviewer for her/his comments and useful suggestions that have helped us improve our paper. As indicated in the responses that follow, we have taken all these comments and suggestions into account in the revised version of our paper.

- Regarding the pressure driven membrane technologies (MF, UF and NF). The authors are providing the current development work when using these technologies in acidic liquid wastes processing, but the article still lack in the following issues that should be addressed in the revised manuscript.

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c. pH. The pH is correlated with the membrane surface charge. Depending on the pH the membrane will exhibit a positive or negative charge due to the ionisation of membrane functional groups. Besides, the pH highly influences solution speciation. This is aligned with sulphate rejections. For example, at neutral pHs, NF rejects more than 99% sulphate, whereas at pH<1.9 (=pK_a) sulphate rejections can drop to 20%.
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ii. Weakness/limitations of pressure membrane-based technologies, fouling (https://doi.org/10.3390/pr8020182) etc.,

As indicated by the reviewer, weaknesses and limitations of pressure membrane-based technologies have been added.

One of their main limitations is their stability under acidic media, especially for polyamide-based membranes. Nowadays, efforts are being towards this direction, in order to improve membrane stability at acidic media.

Concerning the fouling, due to the high acidity of acidic wastewaters (industrial or natural occurrence, pH <3) it is quite unlikely to have organic fouling due to the accumulation of algae, colloids or biofouling. Under the operation in this media, pressure-driven membrane processes face scaling (i.e. precipitation of inorganic minerals), typically of iron, calcium, barium and strontium sulphates.

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Integration of membrane technologies to enhance the sustainability in the treatment of metal-containing acidic liquid wastes. An overview

J. López[a,*], O. Gibert[a], J. L. Cortina[a,b]

[a] Chemical Engineering Department and Barcelona Research Center for Multiscale Science and Engineering, UPC-BarcelonaTECH, C/ Eduard Maristany, 10-14 (Campus Diagonal-Besòs), 08930 Barcelona, Spain

[b] Water Technology Center CETaqua, Carretera d'Esplugues 75, 08940 Cornellà de Llobregat, Spain

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Abstract

The mining and hydrometallurgical industries generate effluents characterised by a high acidity (pH < 3) and a high content of metals (e.g. Fe, Al, Cu and Zn, among others) and non-metals (e.g. As, Sb, Bi), which confers them toxicity that makes necessary their treatment. The conventional treatments of such streams mainly rely on neutralisation/precipitation, solvent extraction, ion-exchange and adsorption. However, these options are often not feasible because of their high consumption of chemicals and the generation of large volumes of sludge. On the other hand, due to the exhaustion of natural resources, circular economy schemes are increasingly promoted for the recovery of valuable elements (e.g. Cu, Zn, rare earth elements) from waste effluents as an alternative to mining the already over-exploited mine sites. Within this new paradigm, the integration of membrane technologies are gaining importance for the valorisation of such effluents since they provide the possibility of: i) reducing the volume of the streams to be treated, ii) favour the selective separation of metal ions from acids, and, iii) the concentration of metals in acidic streams. Membrane technologies are promoting the recovery of valuable dissolved components and the reuse of the acid, reducing the generation and disposal of sludge. Among the different membrane technologies, nanofiltration (NF), diffusion dialysis (DD), reverse osmosis (RO), electrodialysis (ED), forward osmosis (FO) and membrane distillation (MD) are the most promising ones to tackle these challenges and promote circularity.

Keywords: acidic effluents; membrane technology; valorisation; circular economy; resource recovery

Table of contents

Symbols and abbreviations

AEM	Anion Exchange Membrane
AGMD	Air Gap Membrane Distillation
AL-DS	Active layer facing the draw solution
AL-FS	Active layer facing the feed solution
ALW	Acidic Liquid Waste
AMD	Acid Mine Drainage
BMED	Bipolar Membrane Electrodialysis
BPPO	Brominated poly (2,6-dimethyl-1,4-phenylene oxide)
CAGR	Compound Annual Growth Rate
CAPEX	Capital expenditure
CEM	Cation Exchange Membrane
CVD	Chemical Vapour Deposition
DCMD	Direct Contact Membrane Distillation
DD	Diffusion Dialysis
DMAEMA	2-(dimethylamino) ethyl methacrylate
DMSO	Dimethyl Sulfoxide
ED	Electrodialysis
EU	European Union
FO	Forward Osmosis
IEP	Iso-Electric Point
MD	Membrane Distillation
MF	Microfiltration

MP	4-methylpyridine
MVC	Monovalent Selective Cation Membrane
MWCO	Molecular Weight Cut-Off
NF	Nanofiltration
OPEX	Operational expenditure
PGM	Platinum Group Metals
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
RED	Reactive Electrodialysis
REEs	Rare Earth Elements
RO	Reverse Osmosis
SBR	Sulphate-reducing Bacteria
SED	Selectrodialysis
SPIRE	Sustainable Process Industry through Resource and Energy Efficiency
TDA	Tris(2-(2-methoxyethoxy) ethyl) amine
UF	Ultrafiltration
ULPRO	Ultra-low Pressure Reverse Osmosis
VMD	Vacuum Membrane Distillation
WGMD	Water Gap Membrane Distillation

1. Introduction: management of metal-polluted acidic liquid wastes

1.1. Linear and circular management options

Mining, metallurgical and hydrometallurgical industries generate acidic liquid wastes (ALWs) that are characterised by their low pH and high content in transition metals. The generation of these ALWs may suppose an environmental issued, especially if they are not treated properly and these contaminants (e.g. acid and transition metals) are released to the environment, the destruction of ecosystems, corrosion of infrastructures as well as the water staining can take place. Typical compositions of these waters are collected in **Table 1**. The origin of ALWs can be natural, such as Acid Mine Drainage (AMD) due to the infiltration of water in mines, or industrial, during leaching, electrorefining, pickling or gas scrubbing processes. Such toxicity makes necessary to implement an appropriate treatment to avoid the contamination of ecosystems. Nevertheless, the current management options are not focused on the recovery of added-value products. In this case, circular economic approaches can be implemented for resource recovery.

Table 1. *Mean composition of acidic mining and hydrometallurgical wastewaters*

Origin	Generation	Composition	Ref.
AMD	Oxidation of sulphide minerals	$1<pH<3$ <85 g/L SO_4 <3.5 g/L Fe <3.5 g/L Al <675 mg/L Cu <800 mg/L Zn 80 mM REEs	[1–5]
Leaching	Leaching spent solution, after recovering the elements of interest	<100 g/L H_2SO_4 or HCl <15 g/L Fe < 1g/L Zn, Cu and Ni	[6–9]

Electrorefining	Electrolytic bath to produce Cu 99.99%	140-200 g/L H_2SO_4 40-60 g/L Cu 1-4 g/L Fe	[7,10]
Pickling	Removal of impurities from ferrous and non-ferrous materials	40-200 g/L H_2SO_4 or 80-150 g/L HCl <150 g/L Fe <150 g/LZn	[7,11]
Gas scrubbing	Removal of $SO_2(g)$ and dust	10-500 g/L H_2SO_4 <10 g/L As <2.5 g/L Cu, Zn and Fe <0.05 g/L Hg and Pb <50 mg/L Al, Ni, Cr, Cd, Bi and Sb 0.2-2 g/L HCl 0.1-1g/L HF	[7,12]

One example of ALWs is the AMD, which is generated in the mining industry when sulphide minerals (especially pyrite, FeS_2) are exposed to contact with water and oxygen and then oxidized. AMDs can be generated naturally, but the process can be accelerated because of human activity. Therefore, AMDs can be found in both operating and abandoned poly-sulphide mining sites, including galleries, open pits and mill tailings [13–15]. The oxidation of sulphide minerals produces H_2SO_4, which can dissolve the soil minerals, and finally, an effluent containing mainly metal sulphates (e.g. Fe, Al, Cu and Zn), a low amount of non-metals (e.g. As, Se) and a minor amount of rare earth elements (REEs) is released to the environment [16,17]. REEs, which are included within the list of critical raw materials of the EU, can be found in AMDs, and its recovery is pursued because of their applications in the high-tech industry [18].

Iberian Pyrite Belt is one of the major sources of pyrite worldwide and has been mined from more than 5000 years. Such activity has led to the generation of AMDs, and up to 150 different types of effluents can be found in the Odiel and Tinto basins [1–5]. Usually, REEs are obtained by acidic leaching (mainly with H_2SO_4) of different minerals (bastnaesite, monazite and xenotime), with successive acid neutralisation and solvent extraction stages [19–22]. Nevertheless, the high need for REEs has made necessary to evaluate other secondary resources such as AMDs. For instance, effluents from the Iberian Pyrite Belt discharge watersheds around 1 m^3/s in the dry season, with a mean composition on REEs of 1 mg/L, but it can vary from 0.3 to 11.7 mg/L [3,23,24]. Then AMD can be used for REEs recovery.

The current management option for AMD is the neutralisation/precipitation using an alkali (e.g. lime, caustic lime or limestone). Therefore, acidity is neutralised, and metals precipitate as hydroxides [25,26]. This kind of treatment implies the generation of a voluminous sludge, which is rich in water with a solid content ranging from 2 to 4% and mainly composed of Fe and Al hydroxides, oxyhydroxides and hydroxysulphates (e.g. schwertmannite ($Fe_8O_8(OH)_6SO_4$) at pH>4 or ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) at pH<4) with minor amounts of other metals (e.g. Zn, Cu, Mn, REEs), which can be adsorbed on or co-precipitate with the precipitated phases. In addition, the sludge should be properly treated in solid-liquid separation units, which can increase the cost of the treatment [16,25–27]. Despite these disadvantages, this method presents a potential recovery of metals by selective precipitation caused by differences in solubilities. For example, Wei et al. [28] evaluated the selective precipitation of Fe and Al using different alkaline reagents (NaOH, Na_2CO_3, NH_4OH, CaO and $Ca(OH)_2$). They were able to recover Fe (98%, purity >93%) at pH 3.5-4.0 and, subsequently, by a further increase of pH to 6.0-7.0, Al precipitated (recovery of 97% with a purity >92%).

Besides, the effectiveness of this method is relatively low with H_2SO_4-rich effluents (10-25%) due to the high alkali consumption. In addition, the presence of non-metals such as As or Se may require a pre-treatment, which usually rely on the use of strong oxidants (O_3, H_2O_2) to oxidise As to As(V) and Se to Se(VI), and their removal by coagulation-precipitation with Al or Fe, ion exchange or electrochemical treatments (for AsH_3 removal) [29–31].

Due to the generation of a water-rich hazardous sludge, which is composed by gypsum, transition metals as hydroxides as well as other impurities (e.g. iron arsenates, Se, Sb, and Bi) [7], that requires an appropriate treatment in addition to the high and continuous consumption of alkalis makes this process not economically viable [16,32]. However, a potential recovery of the acid, although its value is marginal, may imply lower alkali consumption and sludge management costs for its disposal.

For the case of waters with the presence of sulphate, another alternative is the use of Sulphate-reducing bacteria (SBR) under anaerobic for the precipitation of metallic sulphides [33,34]. For example, *Desulfovibrio* and *Desulfotomaculum* are used for such purpose. These bacteria generate sulphide which can precipitate metals, but also at the same time, they lead to an increase in the water alkalinity. Several specific conditions must be present to treat AMDs with SRB, such as: i) pH>5; ii) the presence of an anaerobic media (-200 mV ORP), and; iii) an energy source (organic substrate). SRBs have been mainly studied for in-situ passive remediation of typically small flows of acidic waters for ground-water remediation in the form of permeable reactive barriers [33] or surface bioreactors in wetlands [34].

A reliable management option should consider the subsequent treatment and/or disposal of the generated wastes. The proper management of the generated sludge is, however, one of the main barriers and challenges that require specific consideration and planning. Therefore, a paradigm displacement on the further processing of such hazardous wastes for safe disposal is needed. Efforts could not be allocated to acidity neutralization and should be directed to the development of near-zero liquid and solid waste processes promoting the recovery of water with enough quality for on-site reuse and potential recovery of exploitable by-products from both the ALWs and the resulting residues. In other words, it is necessary to integrate and develop hybrid processes promoting the recovery of industrially profitable by-products.

1.2. The new paradigm of circular management options: the need of integration of concentration and separation technologies

The well-established linear economy model based on a “take-make, consume and dispose of” arrangement in the industry has assumed that there is an unlimited stock of raw materials, which are easy and cheap to obtain and dispose of. Nevertheless, the continuously increasing demand and scarcity of resources, and the consequent environmental degradation, have forced the search for alternative sources of raw materials sought [35].

In the last years, the European Union (EU) has promoted action policies to improve resource efficiency, all of them relying on circular economy models. In comparison to linear economy model, the circular one maintains the added value of products for as long as possible, reducing the need for raw materials and minimising or avoiding the generation of wastes. Nevertheless, in order to implement them is necessary to re-design the value chain, starting from the production until reaching the waste management so the product can be used to create further value at the end of its lifetime. If circular economy schemes are implemented, it is estimated they can bring an economic saving of 630 billion € in the EU industries, by reducing the need for input materials by 17-24% [18,35]. Recently, the EU is promoting circularity through several initiatives, such as the Sustainable Process Industry through Resource and Energy Efficiency (SPIRE) [36]. Furthermore, the EU has identified critical raw materials in terms of their supply risk and economic importance. This first list contained 14 critical raw elements and was enlarged up to 27 in 2017, and it includes REEs, phosphate rock, platinum group metals (PGM) and other elements (e.g. Sb, Bi, Co, In and Mg among others). Mostly, these are important for high-tech products and emerging innovations, and the EU has a lack of primary sources so are mainly imported from China, USA, Russia and Mexico [18]. Therefore, other alternative routes should be found to ensure the supply of critical raw materials.

Despite the application of traditional technologies for the valorisation of ALWs, any of them have not provided solutions regarding the recovery of valuable elements. Nowadays, with the promotion of circular economy and stringent environmental regulations, the recovery of valuable (e.g. Zn, Cu and REEs) and un-valuable (e.g. acid) components from Awls is being pursued.

Ion exchange and adsorption technologies have been applied to treat AMDs by using low-cost sorbents (e.g. natural zeolites) [37–39]. For example, zeolites, with a net negative charge, can be used for the removal of metallic cations from waters. One of the most widely used is the clinoptilolite, which is stable in moderate acidic solutions, but it can suffer degradation ad pH values below 2.0. Blanchard et al. [38] and Zamzow et al. [39] have evaluated the selectivity of zeolites for metal recovery. However, although a large number of studies can be found on the characterization of the equilibrium and kinetics of the metal sorption, there are concerns about the zeolite dissolution along with the sorption and desorption cycles, which limited their study at full scale. In general, most of the developed applications devoted to the treatment of medium to low flow-rate capacities (up to 100 m^3/d) are based on the use of synthetic polymeric ion-exchange resins. Examples of such applications are focused in the metallurgical industry for the recovery of hazardous and/or added-value compounds (e.g. As, Sb, Bi, Se) from strongly acidic solutions. It is worth mentioning the use of highly specific sorbents based on molecular recognition technology and commercialized by IBC (Superlig) [40] for the recovery of Sb and Bi from H_2SO_4 solutions from copper tank house electrolytes, or the use of ion-exchange resins for the same applications commercialized by Koch (BARS, AsRU and SSU) [41].

Acid retardation, based on the sorption of the un-dissociated acid on polymeric ion-exchange resins and its further recovery after water backwashing has been postulated for specific applications in metallurgical and surface treatment industries [12,42,43]. Anion exchange resins (Dowex 1 X8 and Retardation 550WQ2) have been employed for the purification of different acids (e.g. H_2SO_4 and $NiSO_4$, HCl and $FeCl_2$) by Hatch and Dillon [42]. They observed that differences in elution times allowed the separation of the acid and salt. For example, with a mixture containing 176 g/L H_2SO_4 and 38 g/L $NiSO_4$, they were able to recover H_2SO_4 (137 g/L) free of $NiSO_4$. Petkova et al. [43] tested the Wofatit SBW resin for acid recovery from waste plating solutions (H_2SO_4 250-270 g/L, 6-13 g/L Ni, <1 g/L Cu and Fe, <0.5 g/L Zn). They achieved 80% of acid recovery with a low presence of impurities (<2 g/L). Despite the advantages of acid retardation, two disadvantages should be considered: one stage for purifying the acids may be needed, and the regeneration of the resin can increase the cost of the process.

Solvent extraction, typically used in large hydrometallurgical processing stages, is used in specific applications to recover expensive acids and added value metallic ions [44–46]. For example, the extractant Cyanex923 dissolved in toluene can be used for acid recovery (e.g. H_2SO_4, HCl) [44] and its extraction (H^+X^-) by solvating reagents (S_{org}) is explained as a solvation reaction described by equation 1:

$$mH^+_{aq} + X^{m-}_{aq} + S_{org} \rightleftarrows HXLS_{org} \qquad (1)$$

Solvent extraction has been applied for treating pickling solutions (10-80 g/L HCl, 80-150 g/L Fe and 5-150 g/L Zn) for the recovery of Zn using tri-octyl-amine or tri-butyl-phosphate extractants [45]. They found that the presence of Fe and pH affected the Zn extraction capacity using solvating extractants. Wisniewski [46] studied the performance of Cyanex 923 (50% diluted in kerosene) for the removal of As from 50-200 g/L H_2SO_4 solutions. The removal of As species (both As(III) and As(V)) was attained, but part of the H_2SO_4 was co-extracted at high acidity levels. As in the previous case, acid can be recovered, but an acid purification unit, as well as regeneration unit for the organic phase, are needed.

1.3. Integration of membrane-based technologies for the recovery of valuable elements from Acidic Liquid Wastes

In the last years, membrane technologies are being preferred in the industry over conventional methods because they can attain similar results as current management options but saving costs. A membrane is a semi-permeable barrier that can separate particles, molecules, solutes or ions regarding their size, charge or diffusivity. As a result, for cross-flow configurations, a permeate (i.e. the stream containing the compounds that have permeated across the membrane) and a concentrate (i.e. the stream containing the compounds that are rejected by the membrane) streams are obtained. Nowadays, membranes are widely applied in many fields, especially for the removal of undesirable compounds from the feed solution such as CO_2(g) from natural gas and salts from seawater for drinking water production. The advantages of membrane processes comprise low to medium energy consumption, medium to high concentration factors, working at mild conditions (pressure and temperature), no need for additives and the easiness to be combined with other separation units. However, membrane fouling, the low lifetime (especially at extreme conditions) and limited selectivity are their main drawbacks [45].

In order to select a suitable membrane technology, it must be taken into account that its performance is affected by the solution composition and its chemical speciation, as well as on the membrane properties. In the scenario of ALWs, and taking into account a circular economy perspective, membrane technologies can be used for: (a) the retention of an added-value solute (either metallic or non-metallic) for its concentration and further separation, and (b) the recovery of a valuable compound (e.g. acid) in the permeate. From the described, properties, the possibility to concentrate streams and to separate given components of interest with a concentration factor are both significant as could reduce in a meaningful way the volumes to be treated and a reduction of the recovery units.

This review is focused on the application of membrane technologies for the valorisation of ALWs within the last 20 years. **Figure 1** shows the growth research activity regarding the application of membrane technologies to valorise acidic effluents. Among the different membrane technologies, nanofiltration (NF), diffusion dialysis (DD), reverse osmosis (RO), electrodialysis (ED), forward osmosis (FO) and membrane distillation (MD) are the most promising ones to tackle these challenges. Other technologies, such as pervaporation, which has proven to be useful for seawater desalination, have not been applied to acidic liquid effluents [47].

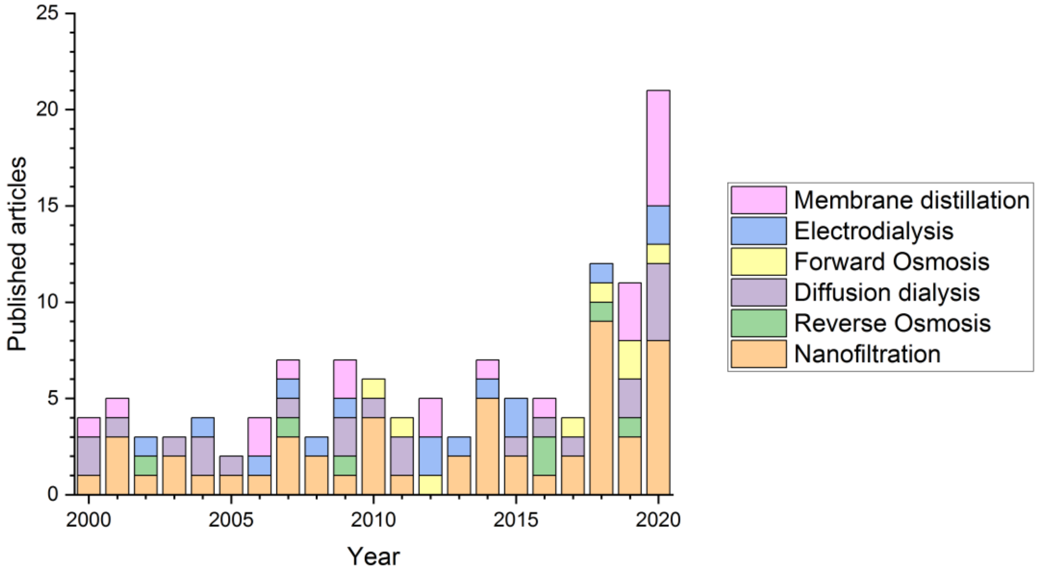

Figure 1. *Articles published involving the treatment of acidic liquid effluents with membrane technologies from 2000 to present. Source: Scopus*

2. Pressure-driven membrane processes

Regarding pressure-driven membranes, they can be classified according to their effective pore size. For instance, Microfiltration (MF) is used to filter colloids and bacteria from 0.1 to 10 µm. Ultrafiltration (UF) allows to remove particles even smaller, such as dissolved macromolecules (e.g. proteins, 2-100 nm). The transport mechanism of these two membrane technologies is the sieving through pores. RO even presents a lower effective pore size (<0.5 nm), allowing only the transport of water. It is assumed that these “pores” are not fixed ones; instead, they are originated due to the movement of polymer chains. NF presents characteristic of both UF and RO. It has an effective pore size between 0.5 and 2.0 nm, allowing the removal of dissolved organic matter and multivalent ions. It remains unclear if the transport mechanism is the one of UF or the one of RO membranes [48,49].

2.1. Nanofiltration

NF is a pressure-driven membrane process that presents characteristics of both UF and RO membranes. NF membranes provide high rejection for multi-charged ionic species (>90%), whereas the single-charged ones can permeate across the membrane (**Figure 2**). There is a current discussion regarding NF membrane structure, as it is suggested that presents a dense structure like RO membranes (not fixed pores, a free-volume instead), or instead that it has fixed pores, similarly to UF membranes. In the first case, the transport of species across the membrane is due to differences in diffusivities across the membrane active layer, whereas in the second case size or steric hindrance is the main exclusion mechanism [50,51].

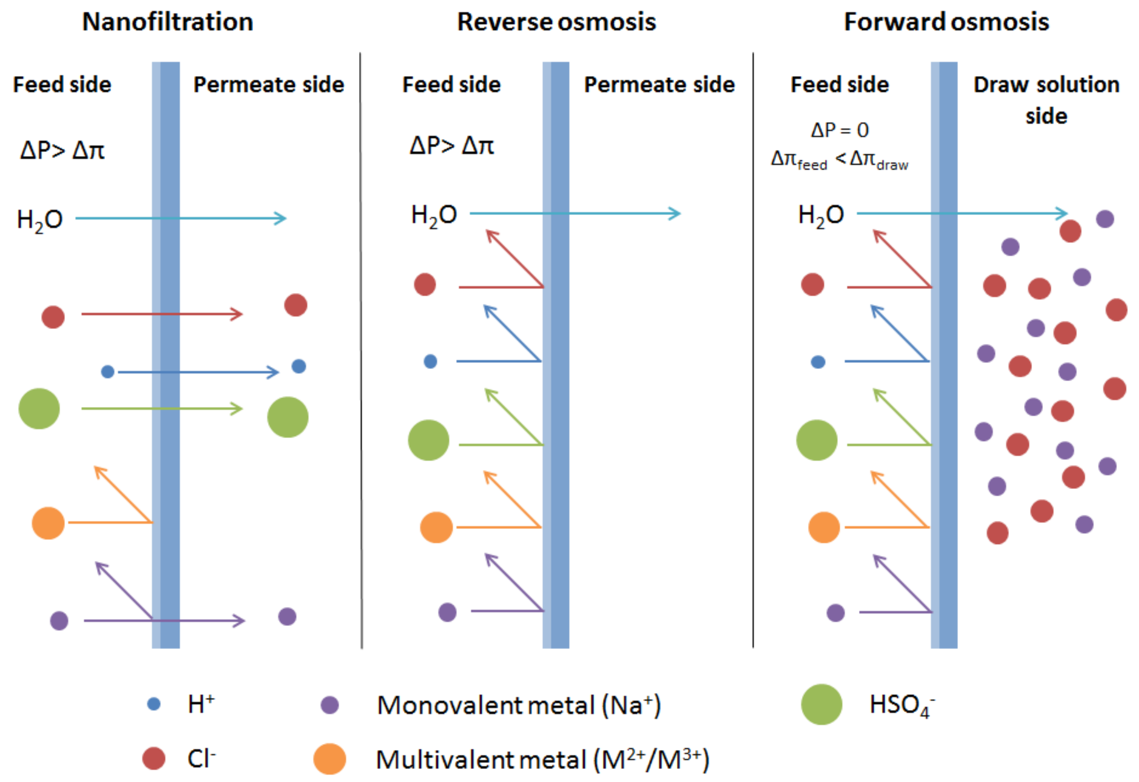

Figure 2. *Schematic representation of nanofiltration, reverse osmosis and forward osmosis membrane processes for the valorisation of acidic waters*

The structure of NF membranes is not fully cross-linked, so functional groups along the surface and inside the active layer are presented. When the membrane is in aqueous solution, these groups can be either protonated or deprotonated. Thus the membrane will present an electric charge. The pH value in which the membrane exhibits no charge is denominated Iso-Electric Point (IEP). If the solution pH is above the IEP, the membrane presents a negative charge and, at pH values below the IEP, the membrane is positively charged [52]. In the case of polyamide-based NF membranes with carboxylic (R-COOH) and amine (R-NH_2) functional groups, at acidic pHs both functional groups will be protonated (R-COOH and R-NH_3^+), conferring the membrane a positively charged surface. Therefore, the anions will be transported across the membrane, whereas anions will be rejected. Instead, at basic pH values, the opposite trend is expected. Carboxylic groups will be deprotonated (R-COO^-) thus, the negatively charged membrane will favour the transport of cations [50,51,53]. Although the selectivity of the NF membranes towards anions or cations, a stoichiometry number of cations or anions should permeate in order to meet the electroneutrality conditions. Then at the acidic pHs of the ALWS, it could be possible to recover purified acids in the permeate.

One issue of importance when treating solutions in NF is the solution speciation, as not all the species are affected in the same way. The main NF membrane exclusion mechanisms are the Donnan and dielectric exclusion. Due to the membrane charge, Donnan exclusion postulates the exclusion of the co-ions (same charge as the membrane). In contrast, the membrane is selective for the ions with opposite charge (counter-ions) [49]. Dielectric exclusion arises due to a difference in the dielectric constant between the solution and the membrane. The higher dielectric constant of the solution than the one of the medium, causes an additional exclusion mechanism for each ion, independently of its sign (positive or negative) [54]. Then, it is expected that multi-charged ions to be better excluded than the monovalent ones. Another exclusion mechanism that should be taken into account is the steric hindrance, especially for those molecules that are not affected by the membrane electric fields, such as neutral species (fully protonated inorganic compounds, H_3PO_4, H_3AsO_4) or organic compounds.

Regarding the effect of speciation, Visser et al. [55] used both aromatic and semi-aromatic polyamide-based NF membranes to study the transport of H_2SO_4. They observed that at $pH>pK_a=1.92$ (predominance of SO_4^{2-} in solution), the acid rejection reached values of 99.9%. However, at lower pH values than the pK_a (predominance of HSO_4^-), rejection dropped to values of 20%. This change in rejection was related to the (1) an inversion of the membrane charge, from negative to positive values, and, (2) the higher amount of HSO_4^-, which according to dielectric exclusion, is less rejected than SO_4^{2-}. H_3PO_4 transport across the NF200 membrane was studied by Ballet et al. [56]. They observed an increase in H_3PO_4 rejection when pH was increased from 40 to 90%, which was related to the lower fraction of $H_2PO_4^-$. Niewersch et al. [57] studied the performance of different NF membranes (Desal DL, DK and NF270) to treat pre-treated sewage and sewage sludge ash at pH ranging from 1 to 4. They observed that acid rejection (H_3PO_4 or H_2SO_4) was minimum at pH 1, which was related to the low degree of acid dissociation and to the membrane positive charge. In recent work, López et al. [58] studied the performance of the NF270 membrane filtering diluted H_2SO_4 from pH 1 to 3 and provided a mathematical model to describe the transport of the acid by means of membrane permeances. The same effect was observed: at pH>pK$_a$ (1.92), the presence of SO_4^{2-} in solution made H_2SO_4 rejections higher (around 80%), whereas at lower pH values these values dropped to 20%.

The speciation of metals should also be considered in the performance of NF membranes. Shang et al. [59] studied the V speciation with the Desal DL and DK membranes at different pH values. They observed that V(V) rejection barely varied from pH 2.5 to 6.5 (98% for DK and 96% DL). In contrast, at higher pHs the shift in equilibrium favoured the presence of lower molecular weight (from $V_{10}O_{28}^{6-}$ to $V_4O_{12}^{4-}$ and $V_3O_9^{3-}$) species, and rejections decreased to 84% for DK and 85% for DL. Hoyer et al. [60] studied the treatment of U-contaminated mining waters with NF, and they observed higher rejections (around 100%) at pH>5 because of the presence of U as high molecular mass species (e.g. $Ca_2UO_2(CO_3)_3$, $UO_2(CO_3)_3^{4-}$).

Additionally, some inorganic solutes can be present in solution as a non-charged species, as is the case of phosphoric acid at pH<2, where H_3PO_4(aq) predominates over $H_2PO_4^-$ [61–66]. Guastalli et al. [62] recovered in the permeate side 56% and 77% of H_3PO_4 from industrial rinsing water containing dissolved Al by using MPF-34 and Desal-DL membranes, respectively. When comparing the rejections of $H_2PO_4^-$ and H_3PO_4 species, the lower rejections of the non-charged species was related to a smaller size than the pores radii. Diallo et al. [63] filtered H_3PO_4 solutions at different concentrations (11.8, 118 and 578 g/L) with the MPF-34 membrane. They observed that rejections varied from 40% at 11.8 g/L to almost zero rejections at 578 g/L due to the higher fraction of the H_3PO_4(aq) species at higher concentrations (i.e. lower pHs). By determining the pore size at these acidic conditions, it was found that the pore size was reduced by a factor of 2 at 578 g/L H_3PO_4. Moreover, the almost zero rejections suggested that there is no size exclusion. Instead, the global rejection of phosphoric acid was governed by the electric effects, such as the interactions between $H_2PO_4^-$ and the membrane. Additionally, Mo and Ge can be presented in solution as neutral species (H_2MoO_4 and $Ge(OH)_4$, respectively) [64,65]. For example, Mo(VI) is found as neutral species (H_2MoO_4) at pH 2, and it was not rejected by the membrane, while the full deprotonation of the molecule (MoO_4^{2-}) at pH 7, increased its rejection (87% for UTC-60 and 75% for NP010). Concerning Ge(IV), which is present in solution as neutral species ($Ge(OH)_4$) in the pH range studied (pH 2-7), rejections were independent of pH and lower than 20%. From the experimental results, the authors determined that the main Mo exclusion mechanism was steric hindrance, whereas the transport for non-charged species was a combination of diffusion and convection. Werner et al. [66] performed a comparative study for In(III) and Ge(IV). They observed similar rejections for Ge(IV) in acidic media (below 15%) because of the presence of $Ge(OH)_4$, whereas In(III) was fully rejected from pH 5 to 12 despite of being present as $In(OH)_3$. At pH of 2, In(III) was mainly found as In^{3+}, which was barely rejected by the membrane (10%) due to its negative charge. The authors related this behaviour to the structure of $Ge(OH)_4$ and $In(OH)_3$. Ge(IV) is coordinated with four OH^- groups in a tetrahedral structure, whereas In(III) is linked to the OH^- groups and surrounded by three water molecules forming a bigger structure. Recently, Boussouga et al. [67] evaluated the influence of both pH (2-12), ionic strength (0.6 – 20 g/L NaCl) and the presence organic matter onto As(V) rejection with NF270 and NF90. They observed that As(V) rejection was dependent of pH for NF270 (10% at pH 2 to 86% at pH 12 for 0.6 g/L NaCl, and from 36% at pH 2 to 78% at pH 12 for 0.6 g/L NaCl), whereas for NF90 it was independent of pH and salinity (93-98%). They related the charge exclusion mechanism for NF270 and size hindrance for NF90. NF has proven to be a suitable technology for the recovery of metals and acids from mining, metallurgical and hydrometallurgical effluents.

The treatment of AMD with NF membranes has already been addressed [52,55,68–71]. Mullet et al. [52] treated an AMD with the NF270 and TriSep TS80 NF membranes, and they observed that at pH values lower than the IEP, the metals were effectively rejected because of the positive membrane charge. Zhong et al. [68] also achieved high metal rejections (>93%) treating a Cu mine effluent (pH 3) with the DK4040F membrane. Al-Zoubi et al. [69] compared the performance of Alfalaval NF99 and Osmonics DK membranes for treating an AMD at pH 2.6. They achieved sulphate rejections higher than 80%, whereas metals were rejected by more than 98%. In a posterior work [70], NF99 and DK showed permeate fluxes of 75 and 60 LMH, respectively and rejections for metals and sulphate higher than 98%. Fornarelli et al. [71] obtained high metal rejections (>95% for Ca, Cu, Mg and Mn(III)) with the NF270 at pH lower than 3. These high rejections were related to the charge exclusion (positively charged membrane). Instead, at higher pH values (above IEP), rejections decreased to 89% due to a negatively charged membrane, which was related to the attraction between the cations and membrane. They observed that sulphate rejections decreased from 97% to 89% due to the lower effect of dielectric exclusion on HSO_4^- than on SO_4^{2-}. Data was not provided regarding the transport of H^+. Visser et al. [55] evaluated the performance of NF70 and NF90 for the treatment of an Au mine effluent (pH 4.1). Both membranes showed a good performance in terms of rejections (>90% for sulphate, Cl, Na and Ca). Rejections of H^+ were not given. López et al. [72,73] evaluated the performance of different NF membranes (NF270, Desal DL and HydraCoRe 70pHT) filtering synthetic AMD solutions. They observed that, at different feed water compositions, the polyamide-based membranes (e.g. NF270 and Desal DL) exhibited high metal rejections (>95%). At the same time, the transport of acid was favoured, achieving even negative H^+ rejections. Recently, Pino et al. [74] evaluated the recovery of Cu from AMD (pH 3.5, 0.5 g/L Cu, 0.4 g/L Al and 4.7 g/L SO_4, among others) by combining NF (NF270) and solvent extraction (LIX 84-IC). NF allowed to concentrate Cu up to 2.4 g/L at 80% of permeate recovery, but gypsum scaling might limit the capacity of recovering water.

The application of NF to industrial ALWs has also been studied. Nÿstrom et al. [75] applied the NF-45 for separating sulphate and nitrate salts from acids, achieving high metal rejections (>95%). Erikson et al. [76] achieved high metal rejections (>99% for Fe, Zn, Cd and Cu) and recovered 50% of the acid with NF for treating a stream containing 330 g/L H_2SO_4. Gonzálet et al. [77] studied the purification of H_2SO_4 solutions. A comparison of NF and RO performances concluded that both achieved similar metal rejections (>95% for Fe, Mg and Al, among others) but NF membranes attained higher fluxes (almost 4 times) and higher acid permeation (80%). Skidmore and Hutter [78] patented a method for purifying H_3PO_4 with NF. They achieved metals rejections higher than 90% (for Al, Fe and Mg). They also reported that working at temperatures below 35°C can increase the membrane lifetime from 300 to 2000 h. Galiana-Aleixandre et al. [79,80] applied NF to treat effluents from the tannery industry achieving high removals for sulphate (>97%) and Cr (not specified). Gherasim and Mikulášek [81] studied the performance of AFC80 membrane for Pb removal (>98%). Tanninen et al. [82–84] carried out studies on the filtration of electrolytes mixtures ($CuSO_4$ or $MgSO_4$) at acidic pH (H_2SO_4). With $CuSO_4$-containing solutions, they observed high Cu rejections (> 95 % for NF45, NF270 and Desal-5DK at 30 g/L) at different H_2SO_4 concentrations (5, 10, 20, 40 and 80 g/L), while acid passed easily across the membrane, also exhibiting negative rejections [82]. Moreover, the effect of the H_2SO_4 dissociation (SO_4^{2-}/HSO_4^-, $pK_a = 1.9$) was observed, especially at high acid concentrations [83]. By adding $MgSO_4$ to the solution instead of $CuSO_4$, the Desal-5DK achieved the also a good performance, with high metal rejections (> 98 % and ~90% for Mg and Cu, respectively) and low H_2SO_4 rejections, varying from 17 to 24% [84]. Manis et al. [85] filtered a solution mimicking an effluent from a copper electroplating plant with the MPF-34 and DK membranes. When H_2SO_4 concentration was increased from 0 to 196 g/L, Cu rejection decreased (from 90 to 80% and from 85 to 45%, for DK and MPF34, respectively at 2 g/L) whereas the acid was more transported across the membrane (rejections from 30 to 10 % and from 20 % to 15 % for DK and MPF34, respectively). Changes in acid rejection were related to higher diffusive transport, while variations in Cu rejection were related to changes in the membrane charge. Ortega et al. [86] treated acid leachate (pH 2, HCl or H_2SO_4-NaCl) of soil with the purpose of extracting metals with the Desal-5 DK membrane. With the HCl leachate, metals were effectively rejected (e.g. >85% for Co, Cr, Fe), while H^+ exhibited negative rejections. However, with the H_2SO_4-NaCl leachate, metals were also effectively rejected, but no H^+ negative rejections were observed. Gomes et al. [87] evaluated the separation of Cr(III) (100 mg/L) from HCl or HNO_3 solutions (2<pH<2.5) with Desal 5 DK membrane. Results showed Cr(III) rejections ranging from 77 to 86%, with lower anion (e.g. Cl^- and NO_3^-) rejections (from 25 to 40%) and even negative rejections. Schütte et al. [88] evaluated the recovery of phosphorous from sewage sludge with NF membranes (DL, NF270, AS and Duracid). They observed high metal rejections (around 90% for Cu, Ni, Zn, among others), while phosphorous rejections varied from 20 to 70%. Working by diafiltration model (i.e. by semi-continuously rediluting the feed solution), 84% of phosphate was recovered at 90% of permeate recovery with AS membrane at pH 0.5. López et al. [89] evaluated the performance of NF270 for acid recovery from an effluent of a gas scrubber from a copper smelter. High metals rejections (>80%) were observed, while acid was transported across the membrane. However, As also permeated (<40%) because of its presence as a non-charged species (H_3AsO_4). Recently, López et al. [8] evaluated the Duracid membrane for the treatment of acidic effluents from Cu smelters (0.6<pH<1.6, 8-15 g/L Fe and 0.7-1.5 g/L, among others). They obtained a permeate mainly composed of H_2SO_4 with a low content of multivalent metals, whereas the main impurity in the acid was Na and As. They also observed a decrease in rejections with pH due to the equilibrium reactions.

One of the main drawbacks of NF membranes with an active-layer made of polyamide is their low stability working in concentrated acidic media since they are susceptible of suffering hydrolysis at long-term exposition [84,85,90–93]. Plat et al. [90] studied the stability of NF45 and Desal DK membranes in HNO_3 and H_2SO_4 solutions under different conditions (temperature, time exposure and acid concentration). Both membranes exhibited worse stability in 50 g/L HNO_3 than in 200 g/L H_2SO_4 after three months of exposure. The effects of the acid attack were remarkably severe at high temperatures. For example, both membranes exhibited near-zero sucrose and glucose rejections after being immersed at 80°C for one month. Manis et al. [85] aged the Desal DK in 196 g/L H_2SO_4 for two months, and after that, they observed an increase in both permeate flux and Cu transport. Navarro et al. [91] studied how Desal 5DL membrane properties (absolute and volume density charge) and performance (rejection and permeate fluxes) were affected after immersion in H_3PO_4 solutions. They concluded that immersion changed the membrane charge as well as its selectivity. For instance, the treatment with H_3PO_4 solutions implied a decrease in the absolute value of zeta potential but also lowers rejections for cation species. Tanninen et al. [84] evaluated the stability of polyamide-based membranes (NF270, Desal KH and Desal-5DK) in H_2SO_4 (20 g/L) at 60°C. From the membranes mentioned above, the Desal-5DK was the first one on suffering hydrolysis, which resulted in higher permeate fluxes (around the double) and lower Cu rejections (from 96% to 77%) after 3 days of immersion. López et al. [92] evaluated the stability of N270 by immersing the membrane in 98 g/L H_2SO_4 for 30 days. Chemical changes quantified by XPS and FTIR-ATR revealed hydrolysis of amide groups that increased the permanent ionised groups and the size of the free volume, reducing the sieving mechanism controlled by the dielectric exclusion. By filtering AMDs with this membrane, a decrease in metal rejections from 99% to 70% was observed, which was related to the weaker effect of dielectric exclusion caused by the higher free volume. Ricci et al. [93] studied the stability of MPF-34 in acidic media by immersing the membrane in an effluent from a gold mine (pH 1.5) and in 15 g/L H_2SO_4 for 2 months. After exposure, an increase in membrane permeability and a decrease in metal rejection were observed, which were related to the acid attack that led to an increase of pore size (from 0.42 nm to 0.61 and 0.74 for both solutions). Jun et al. [94] studied the effect of acid sulphuric (150 g/L, typical concentration of smelting processes) on polyamide membrane's (NE40, NE70, NE90) physical and chemical properties. Characterisation revealed the membrane degradation by acid-catalyzed hydrolysis, converting amide groups into carboxyl and amine groups. Besides, piperazine polyamide semi-aromatic membranes (NE40, NE70) were more unstable than the aromatic polyamide membrane (NE90).

In order to overcome the stability of membranes in acidic media, researchers are developing a new generation of NF membranes. For example, Zeng et al. [95] developed a poly (amide-s-triazine-amine) NF membrane that showed a similar performance before and after being immersed in 5 g/L H_2SO_4 for 720 h ($MgSO_4$ rejection of 94%). No morphological or chemical changes were observed after immersion. Park et al. [96] prepared acid-resistant membranes using piperazine (1 %wt), sulfonated melamine formaldehyde (0.3 %wt) and sulphanilamide (0.5 %wt) through interfacial polymerization. Results showed $MgSO_4$ rejections higher than 96% that decreased by 6% after soaking the membrane in 150 g/L H_2SO_4 for 30 days. Yun et al. [97] developed an acid-resistant membrane via a water-based coating process by introducing a branched-polyethyleneimine layer onto a loose polyethersulfone in a high-humidity atmosphere. The synthesized membrane achieved 95% of Mg rejection, while acid was transported by 70%. Additionally, the membrane maintained its filtration performance 1 month later after immersion in HCl (pH 1.8). Elshof et al. [98] evaluated different combinations of polyelectrolyte multilayer NF membranes for working in high-acidic media (69 g/L HNO_3). The best results were obtained with the combination of strong polycations (poly(diallyldimethylammonium chloride)) and polyanions (poly(styrenesulfonate)), showing little variations on the polyelectrolyte multilayer NF membrane performance after 2 months (permeate flux of 10.7 L/m^2h and rejections of 95.5% $MgSO_4$). Shin et al. [99] developed acid-stable polyamide NF membranes with strong polar aprotic solvents (dimethyl sulfoxide (DMSO), dimethylformamide and N-methyl-2-pyrrolidone). The DMSO activated membrane exhibited the same performance for filtering NaCl (rejection of 85%) after being immersed in 150 g/L H_2SO_4 for 4 weeks because of its higher chemical stability due to their fully-aromatic chemistry. Yu et al. [100] synthesized Janus acid-resistant membranes with an opposite charge with polyethyleneimine and cyanuric chloride. With 0.15 g/L cyanuric chloride in the organic solution, the membrane rejected $MgCl_2$ by 95%, whereas the one for Na_2SO_4 was 45%. After soaking the membrane in 30 g/L HCl for 1800 h, the membrane performance did not show any variation.

Nowadays, acid-stable NF membranes are commercialised offering as good rejections as polyamide membranes, such as Hydracore 70pHT (Hydranautics), MPF-34 (Koch Membrane Systems) and Duracid (GE Osmonics) [62,88,101]. Regarding their stability, for example, MPF-34 kept its performance (permeate flux and rejections) after eight weeks immersion in 196 g/L H_2SO_4 [85]. Despite the composition of the active layer of these membranes to be proprietary, it is expected that is any kind of sulphamide or a sulphonated polyether-sulphone.

As an alternative to polymeric NF membranes, ceramic ones can be employed. The active layer is usually made of zirconia (ZrO_2) or titania (TiO_2) and is supported on alumina (Al_2O_3). These membranes offer a higher chemical, mechanical and thermal stability than polymeric ones. Nevertheless, the fabrication costs and low selectivity of ceramic membranes have limited their application at large scale [102,103]. The literature is scarce regarding the application of ceramic NF membranes [104–108]. Benfer et al. [104] utilized the sol-gel method for synthesizing ZrO_2 and TiO_2 based NF membranes. They observed that the ZrO_2 membrane had smaller pore size and narrower distribution (0.75-1.75 nm) than the TiO_2 one (0.5-2.5 nm). When they evaluated the performance of both membranes, the ZrO_2 showed higher rejections than the TiO_2 membrane (27% NaCl and 66% Na_2SO_4 for the former and 6% NaCl and 11% Na_2SO_4 for the latter). Instead, the TiO_2 membrane exhibited higher permeate flux (3 times higher). Voigt et al. [105] fabricated a ceramic membrane made of TiO_2 with a Molecular

Weight Cut-Off (MWCO) of 450 Da (pore size of 0.9 nm) for decolouring textile wastewater, attaining a colour removal of 70-100%. In a posterior work, a TiO_2 NF membrane was developed by a two-step coating process, characterised by a MWCO of 250 Da and water permeability of 10 $L/(m^2 \cdot h \cdot bar)$. Wadekar and Vidic [107] treated a coal mine drainage (pH 7.8) with polymeric (NF270) and ceramic (TiO_2, 500 Da MWCO) membranes. They observed that the polymeric membrane achieved higher multi-charged species rejections (>96%) than the ceramic one (50-70%). Recently, López et al. [108] treated an AMD with both polymeric (MPF-34) and ceramic (TiO_2, 1 nm) membranes. As in the previous case, the polymeric one exhibited higher rejections (80%) than the TiO_2 membrane (<30%).

During the treatment of ALWs with NF, membrane fouling can be present. Fouling directly impacts membrane performance (higher pressure drop, lower permeate fluxes and higher salt passages) and cleanings (chemicals such as acids or bases). Besides, the membrane is usually replaced in cases of severe fouling [109]. Due to the high acidic conditions, organic fouling (algae and biofilms, among others) is not likely to happen. Instead, because of the high metal concentrations in AWLs, the precipitation of inorganic mineral phases (i.e. scaling) can take place. For instance, and despite the low pH of ALWs, the precipitation of Fe(III) as hydroxide ($Fe(OH)_3(s)$) or oxyhydroxide ($FeOOH(s)$), and gypsum ($CaSO_4 \cdot 2H_2O(s)$) can occur at the membrane surface. Rieger et al. [110] observed the precipitation of gypsum and metal hydroxides when filtering AMW (pH 2.7). Al-Zoubi et al. [70] also reported gypsum formation during the treatment of AMWs (pH 2.5). Recently, López et al. [8] when treating acidic copper effluents (pH 0.83) observed scaling related to calcium sulphate ($CaSO_4(s)$), iron oxyhydroxide ($FeOOH(s)$) and iron sulphate ($FeSO_4(s)$). Besides, scorodite ($FeAsO_4 \cdot 2H_2O(s)$) was also found.

2.2. Reverse osmosis

RO is a pressure-driven process which provides rejections higher than 99.9% for dissolved species (both inorganic and organic). Due to its performance in terms of rejections is widely used for water desalination. However, the high osmotic pressure of the acidic waters and the low stability of RO membranes (mostly made of polyamide) make this technology to be not preferred for the valorisation of acidic effluents. **Figure 2** shows a scheme of a RO operating with ALWs.

RO membranes have been tested to treat AMD either directly or following a NF unit. Rieger et al. [110] treated mine water (pH 2.7, 1.1 g/L Al, 2.3 g/L Cu, 0.6 g/L Fe) with a RO membrane (AlfaLaval RO 98Ht). The membrane exhibited rejections higher than 97% for multivalent species, while Na showed the lowest rejection (95%). After the continuous operation at 30 bar, a decline in permeate flux with time was observed, which was related to membrane scaling caused by the relatively high concentrations of Mg (630 mg/L), Ca (325 mg/L) and SO_4 (14 g/L). Al-Zoubi et al. [69] evaluated the HR98PP membrane for the treatment of AMD at different concentration levels. The membrane exhibited rejections around 94%. However, by comparing its performance with NF membranes (NF99 and DK), these two exhibited rejections even higher (98%). In terms of permeate flux (at 20 bar), the RO membrane had the lowest flux (39 L/m^2h), whereas the NF membranes showed permeate fluxes of 67 and 50 L/m^2h for the NF99 and DK membranes, respectively. Zhong et al. [68] also studied the performance of an ultra-low pressure RO (ULPRO, RE-4040-BL) with wastewater from a Cu mine (pH 3, 2010 mg/L TDS). The membrane showed rejections higher than 97% for metals (e.g. Ni, Cu, Zn, Pb). Nasir et al. [111] evaluated the performance of a pilot plant for the treatment of AMD (pH 3.9, 1.34 g/L SO_4, 1.65 g/L TDS, 10 mg/L Mn and 0.8 mg/L Fe) consisting on a sand filter, adsorption (rice husk-ash and coal fly-ash), UF and RO. The RO allowed to remove efficiently the SO_4 by more than 98%, whereas the main metals in solution were removed by 94% (Fe) and 95% (Mn). Aguiar et al. [112] studied the effect of different operational variables in the treatment of AMD with TFC-HR and BW30 RO membranes. They observed that RO membranes presented lower permeability (between 4 to 10 times lower) than NF membranes (MPF-34, NF90 and NF270). Additionally, they observed that RO membranes are prone to be fouled in comparison to NF membranes. However, the RO membranes achieved a better quality than NF membranes, especially the TFC-HR as provided an overall rejection of 98% of TS. Ricci et al. [101] integrated NF and RO for the treatment of an Au mining effluent at pH 1.4. The concentrate of the NF membrane (pH 1.3, 535 mg/L metals) was treated with a RO membrane (TFC-HR), which rejected metals by 92% and H_2SO_4 by 98%. In a posterior study, the treatment of this Au mining effluent was evaluated at pilot-scale by Amaral et al. [113]. The RO unit rejected metals by more than 90%, while acid was rejected by 93%.

The performance of RO membranes has been evaluated with other kinds of acidic waters. For example, González et al. [77] employed the SXO1 membrane to purify H_3PO_4 (196 g/L) from Fe (4.9 g/L), Mn (3.4 g/L) and Al (3 g/L), achieving metal rejections higher than 98% with an acid permeation of 46%.

These membranes, usually made of polyamide as NF membranes, present low chemical stability, which makes them susceptible to suffer from acid attack. This has promoted new membranes resistant to acids are being developed. For example, Ricci et al. [93] studied the stability of the TFC-HR membrane in acidic media by immersing the membrane in 7.8 and in 14.7 g/L H_2SO_4 for two months. Over the exposure time, membranes exhibited little increase in their permeability (from 0.92 to 1.22 L/m^{2}hbar) and a slight decrease in their NaCl rejection (from 97% to 94%). Membranes were characterized with ATR-FTIR, SEM, AFM and contact angle. Ishii et al. [114] developed their acid-stable silica-based RO membranes using counter diffusion chemical vapour deposition (CVD) method and diphenyldimethoxysilane as a silica precursor. The membrane rejected H_2SO_4 by 81%, but the γ-alumina substrate dissolved because of acid permeation. Improving the synthesis of the membrane by applying the sol-gel method, the authors developed a modified membrane able to resist at 700 g/L H_2SO_4.

The use of RO membranes is quite limited in this field, mainly because of the characteristics of the solutions to be treated. First of all, the high concentration of metals (implying a high osmotic pressure), makes necessary a large hydraulic pressure to drive needed water transport. Instead, in NF, the difference of osmotic pressure at both membrane sides is noticeably lower due to acid permeation. Besides, RO is also limited by the acidity of the solutions. RO membranes are usually made of polyamide, which makes them susceptible to suffering from acid attack in the long term exposition. Finally, the low salt passage across the membrane (rejections higher than 95%) can cause severe scaling due to the high concentrations at the membrane surface. Therefore, RO is generally implemented to concentrate moderate acidic solutions ($2<pH<5$) or to produce high-quality water that can be reused on-site.

3. Concentration-driven membrane processes

3.1. Diffusion dialysis

DD is a concentration-driven process used for acid recovery. It employs Anion Exchange Membranes (AEMS), which favour the transport of acid (HX) across the membrane due to its positive charge (given by quaternary ammonium groups). Instead, metals are effectively rejected because of electrostatic repulsions (**Figure 3**) [115]. The transport of the acid anions (X^-) must be accompanied by the one of a cation. Due to the H^+ properties, such as the low ionic radii and high diffusivity in comparison to any other positively charged cation in solution (single or multi-charged) its co-transport is promoted. It was also observed that the acid transport through the AEM was favoured if salts containing the same anion as the one of the acid were added to the solution. This is known as electrolyte-effect [116]. Additionally, water can also be transported across the AEM because of (1) differences in osmotic pressure, and then an osmotic flux takes place from the water to the acid side, and (2) the solvation of acid molecules, which results in water transport from the acid to the water side [117].

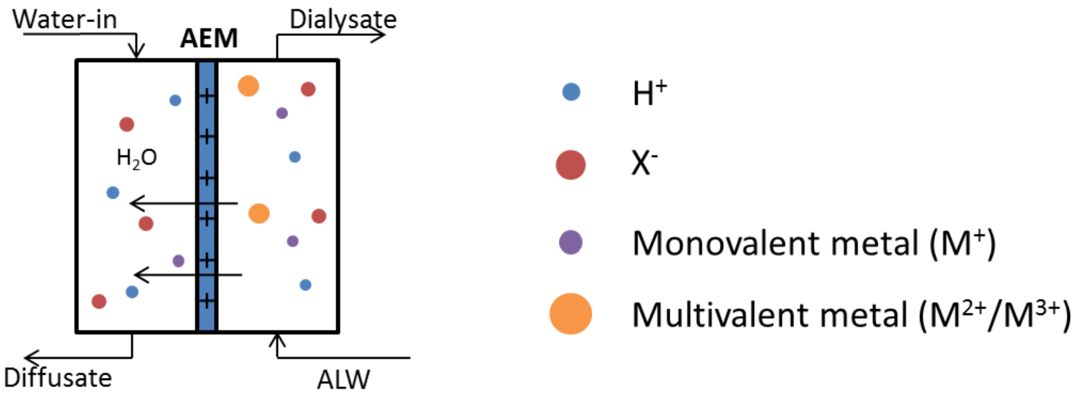

Figure 3. *Schematic representation of a diffusion dialysis unit incorporating an anion exchange membrane(AEM) for the recovery of a strong mineral acid (HX)*

DD has been successfully applied for the purification and recovery of H_2SO_4, HCl or H_3PO_4. Wei et al. [116] used the DF120-I and DF120-III for treating an acidic leaching solution (H_2SO_4). They observed that the addition of $FeSO_4$ and $VOSO_4$ promoted the transport of H^+ across the membrane due to the electrolyte-effect. When they studied the effect of flow rates, they achieved a recovery of 83% of H_2SO_4 with high metal rejections (>93%) at a flow rate ratio of 1. When they increased that ratio to 1.6, rejection of metals decreased to 90%, but higher acid recovery (87%) was attained. Gueccia et al. [117] evaluated HCl recovery from pickling solutions (<105 g/L HCl, <150 g/L Fe(II)) with Fumasep membranes. They observed that the water flux due to ion solvation prevailed at high acid concentrations, whereas osmotic flux predominated at lower concentrations. Additionally, they characterised species transport to determine membrane permeabilities to acid, salt ($FeCl_2$) and water. Li et al. [118] evaluated the performance of the DF120 membrane for acid recovery from leaching solutions (2.4 mol/L H^+, 4.2 g/L V(V), 13.8 g/L Al), achieving values of 84% at feed to water flow rates ratios of 1-1.3. Under the same conditions, metals were rejected by more than 90%. Jeong et al. [119] studied the performance of Selemion DSV for treating a solution containing 440 g/L H_2SO_4, 52 g/L Fe and 18 g/L Ni. They observed that acid recovery depended on operational parameters, such as the flow rates and temperature, but also on initial acid concentration. They achieved acid recoveries of almost 80% with low impurities of metals (<2 g/L). In a recent work, Gueccia et al. [120] evaluated the HCl recovery from pickling solutions (5-20 g/L Zn, 50-150 g/L Fe and 70-100 g/L HCl) in continuous configuration with Fumasep membranes, achieving acid recoveries around 80% with a 30% of Fe and 60% of Zn leakages. The high metal leakages were related to the formation of negatively charged metal-chloride complexes. Xu et al. [121] treated a contaminated acidic solution (1.8 mol/L H^+, 11 g/L Al and 6 g/L Cu) generated in an anoxic oxidation process with the DF120 membrane. By increasing the feed flow rate from $3 \cdot 10^{-4}$ to $7 \cdot 10^{-4}$ m^3/h, acid recovery decreased from 76 to 61 %. By increasing the flow rate ratio (feed flow rate was $4.5 \cdot 10^{-4}$ m^3/h) from 0.3 to 1.2, higher acid recovery was achieved (90%). However, the increase in the ratio led to a higher metal passage (Cu: 4 to 15 %, Al: 3 to 8 %). Pilot-scale tests showed an acid recovery of 85 % and an Al leakage of 5 %. Wang et al. [122] evaluated the DF120-III membrane for the treatment of a stone coal acid leaching solutions (mixture of HF, H_3PO_4 and H_2SO_4). They observed that the F rejection was the highest one (98%), followed by the one for P (90%) and S (68%). Despite of the presence of fluorides, they were effectively rejected because of the presence of AlF^{2+} and AlF_2^+ species. Luo et al. [123] studied the performance of DF120 membrane in a spiral wound module for H_2SO_4 recovery. Best results in terms of acid recovery and concentration were achieved with a series connection in both acid and water side with a counter-current flow pattern. This configuration was compared with a single, double and triple spiral wound membrane module. Triple spiral-wound membrane module allowed to obtain the same acid recovery working at higher flow rates (65% recovery at 6.5 mL/min in the single and 50.5 mL/min with the triple). Lan et al. [124] evaluated the recovery of a spent solution (HNO_3-based) with ED with DF120. Acid recovery increased from 83 to 94% by increasing water to feed ratio from 1.0 to 1.2. The membrane more effectively rejected bivalent cations since they have charges that are strongly rejected by the membrane. The selectivity of the membrane followed the trend: $Mg^{2+} > Ca^{2+} > Li^+ > Na^+ > K^+$. By working at low water to acid ratio, the transport of metals is more impeded.

Working at flow rate ratio water to acid of 1.07, and by changing the acid concentration from 6.3 to 189 g/L, a maximum acid recovery at 189 g/L was observed (96.2%). However, at higher concentrations, the mass transfer was controlled by the membrane itself, so the acid recovery started to decrease. Xu et al. [125] studied the potential for acid recovery from a galvanizing waste (110 g/L HCl, 150 g/L Fe(II) and 4.5 g/L Zn) with the DF120 membrane. At flow rate ratio between 2.0 and 3.1 (0.4 L/h of acid), acid recovery was over 88% (>72 g/L). However, both Fe and Zn leakages increased with the flow rate ratio. Fe leakage varied from 11 to 23%, while the one for Zn was higher than 56% because of its presence as an anion ($ZnCl_3^-$, around 85 % of total zinc in solution). It was possible to obtain higher HCl concentrations in the diffusate (i.e. recovered acid stream) at high Fe concentrations because of the salt effect.

Palatý and Žáková have studied and characterised the transport of species across the Neosepta-AFN membrane [126–132]. Their works cover a wide range of acids and salts, and the effect of solution speciation was also investigated. These works are explained in the paragraphs below.

Palatý and Žáková have studied the transport of inorganic acids [131,132]. They employed Fick's first and second laws to determine the apparent diffusivity of H_2SO_4, HCl, HNO_3, H_3PO_4 and HF through the membrane [131]. The highest values were obtained for HCl (<28 g/L) and HNO_3 (<12 g/L), whereas the lowest values were observed for H_3PO_4. Additionally, they detected that H_2SO_4 and HF diffusivities increased with concentration, whereas the ones for HNO_3 and H_3PO_4 showed the opposite trend. The transport of acids (HNO_3 and H_2SO_4) was described taking into account their dissociated forms (i.e. HNO_3 flux was the sum of NO_3^- and HNO_3(aq) fluxes, H_2SO_4 flux was the sum of HSO_4^- and SO_4^{2-} fluxes) using the Nernst-Planck equation [132]. They observed that H_3O^+ had higher mobility than the other species, which could be beneficial for separating acids from salts due to the high proton leakage. Regarding the NO_3^- and SO_4^{2-} ions, both showed similar mobilities at concentrations below 0.5 mol/L, but they increased with acid concentration.

Palatý and Žáková have found that the membrane permeability to H_2SO_4 was dependent on its concentration, and the major resistance to its transport was found in the liquid films at both membrane sides [126]. Working with electrolyte mixtures (H_2SO_4 and $CuSO_4$ or H_2SO_4 and $ZnSO_4$), they observed that metal transport across the membrane was proportionally related to its concentration but inversely to acid concentration. This effect was related to the changes of metal speciation, which shifted the equilibrium towards the presence of the free metal ion form.

Similar studies have been carried out with HCl [129,130]. By studying HCl-$FeCl_3$ mixtures [129], the addition of $FeCl_3$ salts enhanced acid transport, achieving concentrations in the diffusate even higher than in the feed side. Additionally, they observed that the membrane was prone to better transport HCl than H_2SO_4. For HCl-$NiCl_2$ experiments [130], $NiCl_2$ was fully rejected by the membrane. However, higher acid concentrations promoted the transport of $NiCl_2$ across the membrane.

Ersoz et al. [133] characterised the transport of H_2SO_4 and HCl through an aminated polyether-sulphone AEM (SB-6407) and Neosepta AMH membranes. Both membranes showed higher affinity for H_2SO_4 than for HCl, which was reflected in the diffusion dialysis coefficients. They observed that strong basic anion-exchange groups have permeability for mineral acids two orders higher than the corresponding values of electrolytes.

A new generation of AEMs is being developed to enhance acid transport and the separation factor. Khan et al. [134] developed AEMs using brominated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO) as a polymer backbone and 4-methylpyridine (MP) as an ion exchange element. They studied the effect of the content of 4-methylpyridine onto the membrane's properties. The increase of MP content (from 14% to 35%) resulted in higher ion-exchange capacity (from

1.94 mmol/g to 2.24 mmol/g) and the water uptake (from 17% to 31%). The performance of the AEM was compared with the one of DF-120B using 36.5 g/L HCl and 31.7 g/L $FeCl_2$. The developed AEM with 35% MP showed an acid dialysis coefficient of 0.066 m/h (0.004 m/h for DF-120B) and a separation factor of 78 (23 for DF-120B). Ji et al. [135] functionalized BPPO with tris(2-(2-methoxyethoxy) ethyl) amine (TDA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) to achieve hydrophilic transport channels and high selectivity. Syntehtised membrane was tested with 36.5 g/L HCl and 33.7 g/L $FeCl_2$, and its performance was compared with a commercial DF-120. The membrane containing a 45% of DMAEMA achieved the best results, with an acid dialysis coefficient of 0.0325 m/h and a selectivity factor of 49. Instead, the DF-120 membrane had lower values for acid dialysis coefficient (0.009 m/h) and separation factor (19). Besides, the membrane kept their properties for 10 cycles. Ji et al. [136] prepared an AEM by introducing quaternary ammonium groups with long hydrophilic side chains into BPPO (namely QPPO). After that, membranes were also put in an oven at 90 °C for 2 h (namely TQPPO) to enhance crosslinking. Consequently, QPPO membranes had a higher ion-exchange capacity than TQPPO membranes, but a lower water uptake. When authors evaluated the membrane performance with 36.5 g/L HCl and 33.7 g/L $FeCl_2$, they observed that the BPPO-1.75 membrane had higher acid dialysis coefficient (0.059 m/h) than TQPPO-1.75 membrane (0.047 m/h). However, the BPPO-1.75 membrane had lower separation factor (19) than the TQPPO-1.75 one (33). Yadav et al. [137] synthesised graphene quantum dot quaternized polysulfone membranes to enhance both acid recovery and separation factor. Synthesised membranes had a water uptake ranging from 22% to 32%, without and with 1% of graphene quantum dots, respectively. Besides, graphene quantum dots' presence increased the ion exchange capacity, from 1.52 meq/g to 1.81 meq/g for the above conditions. When evaluating the membrane performance with 73 g/L HCl and 30 g/L $FeCl_2$, the AEM containing 1% of graphene quantum dots showed the best performance, in terms of acid dialysis coefficient (0.006 m/h) and separation factor (39).

3.2. Forward osmosis

The application of FO in desalination and wastewater treatment has attracted the attention of researchers. In comparison to RO, no external pressure is needed to drive the separation process in FO, and only a high osmotic pressure difference is needed to drive the transport of water. In order to achieve that, the feed solution is separated from the draw solution (high osmotic pressure) by a semi-permeable membrane. Therefore, water flows from the feed to the draw solution to equalize salinity [138,139]. **Figure 2** shows a scheme of a FO operating with ALWs. The FO membrane can be operated either with the active layer facing the draw solution (AL-DS) or the feed solution (AL-FS). Jin et al. [140] observed higher permeate fluxes facing the active layer the draw solution, whereas Tang et al. [141] reported higher organic fouling in the AL-DS mode. Nevertheless, in the case of ALWs, low content of dissolved organic matter is typically reported, but the main concern with ALWs is associated with the formation of Al and Fe hydroxides at even low pH values. Phuntsho et al. [142] reported that temperature and pH are also key factors in mass transfer in FO, as the increase of temperature promotes both solvent and solute transport.

Nevertheless, only a few studies regarding the application of FO in the treatment of ALWs can be found in the literature. You et al. [143] tested an inorganic membrane to remove metals (Cu, Zn, Cd and Pb with a total concentration of 200 mg/L) from AMD at pH 4.5. By using 117 g/L NaCl as draw solution, they were able to remove metals by 94% and a permeate flux of 69 LMH. Vital et al. [144] evaluated the application of FO for the treatment of AMD using a thin-film composite membrane (*FOMEM-0415* – Hayward), using 58.5 g/L NaCl or NH_4HCO_3 as draw solution. Metals from AMD were rejected by more than 97% using both draw solutions. However, the salts of the draw solution were also transported and, and metal precipitation occurred working with NH_4HCO_3. Pramanik et al. [145] evaluated flat-sheet polyamide membranes supported on polysulphone (Porífera) and studied how orientation (AL-DS or AL-FS), temperature and pH (from 3 to 7) affects the permeate flux and the rejection of three

REEs (Ce, La and Dy) mimicking an AMD. They obtained higher fluxes at high pH and temperatures with the AL-DS mode. REEs rejection in the AL-FS (89-96%) was slightly higher than in the AL-DS mode (83-88%). In addition, the REEs rejection was influenced by the solution pH and temperature. For example, rejections increased with the temperature of feed and draw solution as well as with the pH. Choi et al. [146] evaluated the metal recovery from AMD by the integration of FO and NF. Two different draw solutions were evaluated, EDTA-4Na and PSS-Na for the FO unit. Some metals (e.g. Mn, As, Cd and Pb) were completely rejected by the membrane, while Fe, Cu and Zn exhibited lower rejections (80-85%). Baena-Moreno et al. [147] evaluated the effect of draw solution (NaCl, KCl, $CaCl_2$, and $MgCl_2$ from 1 to 5 mol/L) in the water recovery and metal rejection from AMD (pH 2.7, 11.7 g/L SO_4, 1.1 g/L Mg, 1 g/L Zn and 0.7 g/L Fe). They observed that the water flux increased with concentration in the order $KCl<NaCl<CaCl_2<MgCl_2$, whereas metal rejections were higher than 99.5%. In all cases, working with 475 g/L $MgCl_2$ as draw solution, 90% of water was recovered (around 5 L/m^2h), but scaling was observed, mainly a mixture of metallic sulphates and carbonates.

4. Electrically-driven membrane processes

ED is an electrically-driven membrane process which uses ion-exchange membranes to drive the transport of ions under the application of an external electric field. Functional groups from ion-exchange membranes provide the membrane a charge, which allows them to exclude fully or partially ionic species with the same charge of the membrane (co-ions). Therefore, the stack is formed by intercalating Anion and Cation Exchange membranes (AEMs and CEMs, respectively), and each set of AEM and CEM form a cell pair. By applying an external electric field, cations will migrate towards the cathode, and in their path, cations pass through CEM (negatively charged) but are retained by AEM (positively charged). Anions in solutions will migrate towards the anode and experience the opposite trend. Finally, two streams are produced, one with a higher ion concentrations than feed solution, and another depleted of them [148–150].

4.1. Conventional electrodialysis

Conventional ED has been applied to purify and concentrate industrial ALWs. Most of the works published in the literature are for H_2SO_4-based streams, ranging from 50 to 200 g/L. For example, Cifuentes et al. [151] studied the separation of species from Cu electrorefining electrolytes (50 g/L H_2SO_4, 3-9 g/L Cu, 3 g/L As (As(III) or As(V)), 0.025 g/L Sb) with the Ionac AEM MA-3745 and CEM MC-3470. The separation of sulphate from Cu and As was achieved and the transport rates were determined (0.2-0.6 mol Cu/m^2 h, 0.65-2.8 mol SO_4/m^2 h, 0.016-0.03 mol As/m^2 h). Both As and Sb form cations, anions and uncharged species in H_2SO_4 media (e.g. H_3AsO_3 and $H_4AsO_3^+$ for As(III); $H_2AsO_4^-$ and H_3AsO_4 for As(V), $H_2Sb_2O_2^+$ and H_3SbO_3 for Sb(II)), which can be transported towards the anode and cathode according to their charge. At lab-scale operations with recirculation, the further separation of Cu from As can be achieved because of the high transport rate ratio (12.5 for Cu(II)/As(III) and 20 for Cu(II)/As(V)), whereas the transport of sulphate was the highest one (2.8 mol/m^{2}h). Therefore, it could be possible to obtain a stream containing Cu with traces of As in the cation concentrate compartment. By working at higher temperatures (44 °C) in the semi pilot cell, the transport rate of Cu increased a 38% (0.52 mol Cu/m^{2}h) in comparison to the operation at 22°C (0.38 mol Cu/m^{2}·h). At the same acidity level, Cifuentes et al. [152] studied the system $CuSO_4$-H_2SO_4-Fe from a copper electrowinning bath (9 g/L Cu, 50 g/L H_2SO_4 and 0.5 g/L Fe(II)). The removal rates for metals increased linearly with cell current, and its transport rates at 250 A/m^2 were between 0.5-1.1 mol Cu/m^2·h and 0.035-0.071 mol Fe/m^2·h. By moving from a laminar to a turbulent flow regime (Re=8200), the transport rate of Cu increased by 15%. Moreover, Cu and Fe were removed by 96.6 and 99.5 %, respectively after 24h of operation. Besides, the fact that anions (SO_4^{2-} and HSO_4^-) were transported towards the anode made feasible the recovery of water with a specific energy consumption of 1 kWh/kg. Chekioua and Delimi [153] evaluated the treatment of acid pickling bath (150 g/L H_2SO_4 and 26 g/L Fe(II)) with ED using different membranes (AEM: AMX; CEM: CMX, Nafion 117 and CMV). Working with the CMX, the best results were obtained in terms of Fe(II) rejection (66%) and energy consumption (1.85 kWh/kg). The rejection of Fe(II) improved from 7.4% to 66.4% when the current density increased from 1 to 20 mA/cm^2. However, further increases in the current density (30 mA/cm^2) resulted in lower rejections (60.5%) due to Fe(II) scaling. Moreover, they observed that, by increasing Fe(II) concentration up to 52 g/L, the membrane performance improved (Fe(II) rejection of 70%), which was related to the higher pH, and then, the lower amount of the competitive H^+ in solution. The addition of Fe(II) also promoted a higher recovery of H_2SO_4 in the anodic compartment (from 14 g/L to 25 g/L H_2SO_4 when Fe(II) increased from 1 to 52 g/L). Boucher et al. [148] evaluated the recovery of H_2SO_4 from solutions coming from Zn industry (200 g/L) polluted with metals (10 g/L Zn, 10 g/L Mg and 1 g/L Mn). Finally, they recovered 69% of H_2SO_4 with a low passage of metals (<8%). Sistat et al. [154] evaluated the recovery of H_2SO_4 from a contaminated effluent (200 g/L H_2SO_4, 10 g/L Zn and Mg, 5 g/L Mn) with a Nafion CEM modified by electrodeposition of polyethyleneimine on one side of the membrane. Acid recoveries between 58 to 67% were achieved with energy consumptions ranging between 1.0 and 1.2 kWh/kg H_2SO_4. The total metal leakage was below 0.5% for each metal, without implying any additional cost. Recently, Melnikov et al. [155] evaluated ED for concentrating H_2SO_4 and HNO_3. The ED allowed to concentrate H_2SO_4 from 49 to 137 g/L and HNO_3 from 19 to 132 g/L at a current density of 4.3 A/dm^2. Current efficiency was quite low (27% for H_2SO_4 and 22% for HNO_3), which was related to the proton leakage across the AEMs.

The treatment of other streams containing another kind of acids has also been studied. For instance, Sun and Xu [156] evaluated the treatment of waste H_3PO_4 solutions (196 g/L H_3PO_4, 0.5 g/L Al, 0.5 g/L Mo) with ED. Experiments were carried at a voltage of 15V in order to achieve higher removals of Al and Mo. They observed that at higher H_3PO_4 concentrations, the transport of Al and PO_4 decreased (7% and 15%, respectively), whereas it accelerates the ones of Mo due to its presence as an anion, $Mo_2O_4^{2-}$. They also evaluated different membranes: CMX/AMX, CM1/AM1 and CMX-SB/ACS and at least 30% and 7% of Al and Mo were removed from the acidic solution. Zhang et al. [157] studied the recovery of HCl from Al foils wastewaters (49 g/L HCl and 20 g/L $AlCl_3$) by the integration of DD and ED. By working with a feed flow rate of 0.60 L/m^2h in the DD unit and 2 A in the ED stack, the average acid recovery and Al leakage ratios were 75% and 12% respectively, while the energy consumption was only 0.41kWh.

Conventional ED has also been applied for the treatment of AMD. For example, Buzzi et al. [149] treated an AMD at pH 2.4 polluted with Na, Mg, Ca and Fe(III). Finally, water at pH 3 was recovered with a low content of metal (removal of 97%), with their concentrations below detection limits. Martí-Calatayud et al. [150] studied the H_2SO_4 recovery from synthetic AMD (pH 1.68, 8 g/L $Fe_2(SO_4)_3$, 1.5 g/L Na_2SO_4). After 10h of operation, they were able to concentrate H_2SO_4 in a factor of 2.6, 3.4 and 4.0 for 5, 10 and 15 mA/cm^2, respectively. During the experiments, it was observed that AEMs with high ion-exchange capacities originated a stronger Donnan exclusion of co-ions, which led to the dissociation of HSO_4^- ions in the membrane and then reduced the efficiency for H_2SO_4 recovery. With regard to Fe(III), at the beginning of the experiments its concentration in the cathodic compartment increased, but at a certain time reached a value lower than the initial one. Moreover, Fe(III) concentration in the central compartment was the same at 10 and 15 mA/cm^2 (1.2 g/L), which was related to the formation of $Fe(OH)_3$ precipitates in the anodic side of the CEM as a result of surpassing the limiting current density (16 mA/cm^2). In addition, more of the half of the imposed current density was used to drive the transport of SO_4^{2-} ions across the membrane. In terms of specific energy consumption, it increased drastically with the increase of the current density from 6 kWh/kg) at 5 mA/cm^2 to 20 kWh/kg 15 mA/cm^2 because of the precipitation at the membrane surface.

4.2. Advanced electrodialysis

A continuous effort on improving the performance of conventional ED has promoted the development of enhanced configurations such as: i) Selectrodialysis (SED) with the integration of mono-selective and standard ion-exchange membranes to promote the separation of monovalent ions from multivalent ions; ii) Bipolar ED (BMED) by the integration of bipolar membranes with AEM and CEM, and; iii) reactive ED (RED) where metallic ions with redox properties could be reduced. Details of such configurations are described schematically in **Figure 4**. From the described configuration, the possibility to concentrate streams and to separate a compound of interest provides the option to reduce the volume to be treated and, therefore, the number or recovery units.

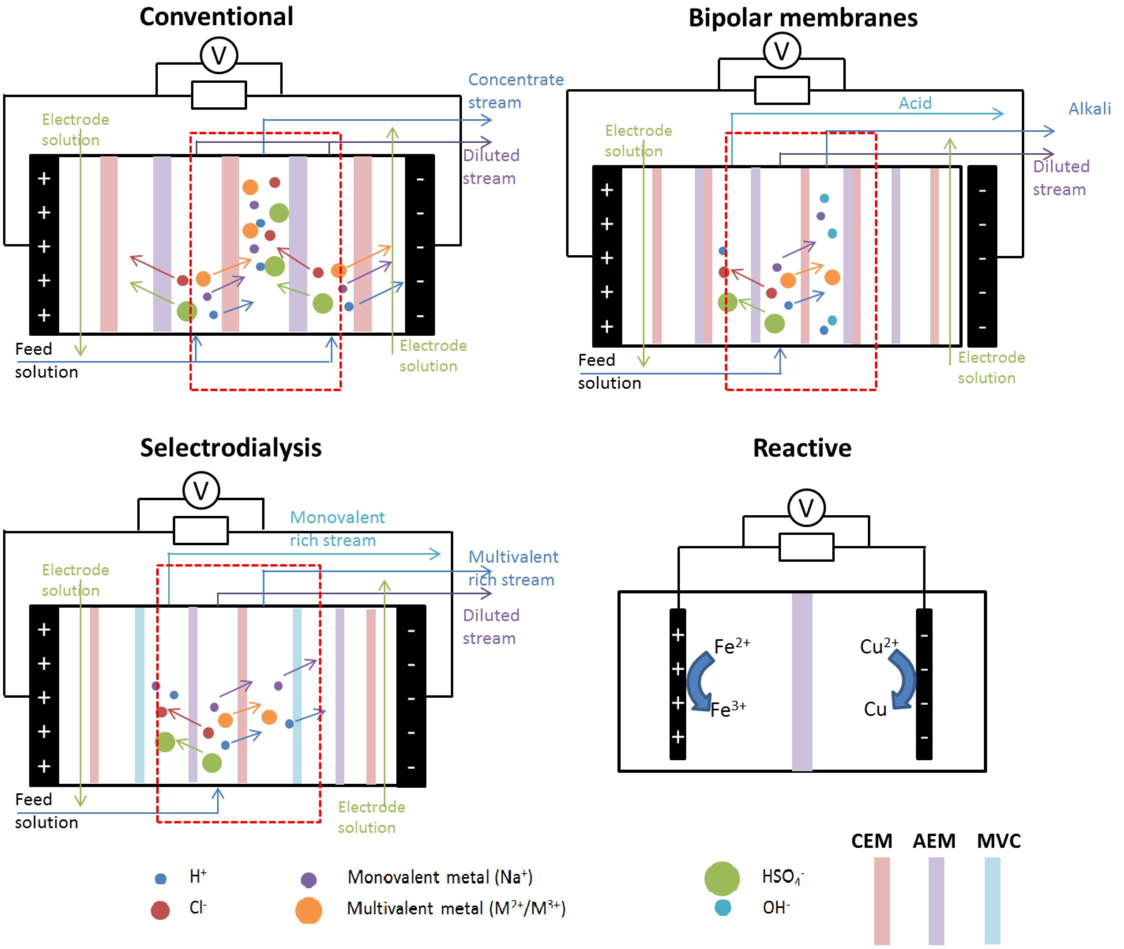

Figure 4. *Schematic representation of electrical-driven membrane processes for the valorisation of acidic waters: conventional ED, bipolar membrane ED, selectrodialysis and reactive ED*

Bipolar membranes are formed by an anion exchange layer overlapped with a cation exchange layer, where water split occurs, and then acid and alkaline solutions are produced [158]. Melnikov [155] evaluated BMED for concentrating different salts and acids (e.g. 14.7 and 29.4 g/L H_2SO_4, and 18.9 g/L HNO_3). The current efficiency for both acids was lower than 25%, which was related to the transfer of protons across the AEM. The concentration of the acid can be limited by the osmotic and electroosmotic transport of water across the membrane. Liu et al. [159] treated the raffinate from a Cu ore hydrometallurgical processing (pH 1.4, 45 g/L SO_4^{2-}, 11.8 g/L Fe, 336 mg/L Zn and 135 mg/L Cu, among others) with BMED. The optimum current density and the volume raffinate to transition metal chamber ratio were 3 mA/cm^2 and 1:15, respectively. Moreover, by increasing the number of chambers from one to three, the energy consumption decreased from 0.160 to 0.089 kWh/L of raffinate. After 40 h of operation of the BMED, it was possible to recover the 86% of the total sulphate, mainly as H_2SO_4 (39 g/L), whereas the metal impurities were rejected (99.3% Fe, 99.1% Zn, 99% Cu, 84.9% Ni, 70.6% Cr, 96% Cd and 95% As) and its amount in the recovered acid was below 100 mg/L. Then, this acid can be reused as leaching influent.

SED incorporates a monovalent selective ion-exchange membrane in the stack, usually a monovalent selective cation membrane (MVC) to remove metals. Reig et al. [160] studied the performance of SED with a MVC in order to separate As(V) from Cu and Zn from an acidic metallurgical process stream (pH 2.3, 2 g/L Cu, 9.6 g/L Zn and 2.4 g/L As). The SED configuration showed it was possible to obtain a Cu/Zn-rich (80% of Cu, 87% of Zn and 0.02% of As) and As-rich stream (95% of As) with a specific energy consumption of 2.6 kWh/kg $CuSO_4$ and $ZnSO_4$.

The main purpose of ED is to separate or concentrate species, but when the main objective is the production of chemicals at the electrodes, it is named as RED. Cifuentes et al. [161] evaluated the recovery of Cu with RED. The system consisted of anolyte (180 g/L H_2SO_4, 56 g/L Fe(II)) and catholyte (180 g/L H_2SO_4, 40 g/L Cu) solutions separated by an AEM (Ionac MA-3475 Tokuyama, Tokuyama ACS) at a current density of 300 A/m^2 to achieve the electrodeposition of Cu in the cathode. The transport of Cu and Fe decreased around 80% with two membranes instead of one, at the expenses of increasing the cell voltage by 20%. However, if another membrane was placed, the transport of metals across the membranes barely varied. Two ACS membranes exhibited better performance, with the lower transport rates for Cu ($4·10^{-4}$ mol/m^{2}h) and Fe ($17·10^{-4}$ mol/m^{2}h) at 0.77 V. The higher transport rate for Fe was related to its presence as an anion in H_2SO_4 media ($Fe(SO_4)_2^-$) and its higher concentration. In a posterior work, with the Ionac MA-3475 membrane under the same conditions, Cifuentes et al. [162] studied the effect of temperature (30-60 °C) and applied cell current (0.4-0.8 A) on the RED performance. At a constant cell current, by increasing the temperature, the voltage of the two-compartment cell decreased because of the higher diffusivities and lower electrical resistance. In the three-compartment cell, the cathodic current efficiency was quite high (98-99%) with an energy consumption between 0.94 to 1.39 kWh/kg Cu at current densities ranging from 200 to 600 A/m^2. In comparison to conventional electrowinning, these values were quite lower (2 kWh/kg Cu at 350 A/m^2). In a latter work, they were able to model the data with deviations between experimental data and model prediction lower than 3% [163,164].

The integration of liquid membranes inside the ED stack has also been studied to separate metals selectively. Sadyrbaeva [165] integrated a liquid membrane in an ED stack for the treatment of a solution containing 110-146 g/L HCl, 0.6 g/L Co(II) and 0.6 g/L Ni(II). At such acidity, Ni(II) is present as Ni^{2+} and $NiCl^+$, whereas Co(II) can be found either as Co^{2+} or $CoCl_4^{2-}$. The removal of Co(II) increased with the current density and HCl and Co(II) concentration, whereas it barely varied with Ni(II) concentration and the carrier concentration in the liquid membrane. They were able to separate selectively Co(II) and Ni(II) with a separation factor $\beta_{Co/Ni}$ of 145, which could be improved at higher Ni(II) ($\beta_{Co/Ni}$ of 330) and Co(II) ($\beta_{Co/Ni}$ of 400) concentrations. They also evaluated whether the type of acid (e.g. H_2SO_4, HNO_3 or $HClO_4$) affects the separation, but no effect was observed.

5. Thermally-driven membrane processes

5.1. Membrane distillation

MD is a thermally-driven process which uses a micro-porous non-wetted hydrophobic membrane to drive the transport of vapours and volatile compounds (e.g. water, HCl) due to a difference of vapour pressure, and then they condensate at the surface of the membrane [166,167]. MD presents some advantages, such as: i) high rejection of non-volatile and dissolved species (>99%); ii) lower operation conditions (temperature and pressure) than conventional processes, and; iii) low fouling due to solution/membrane surface interactions. Nevertheless, they present some drawbacks such as lower permeate flux than RO, mass transfer resistance due to air trapped and heat lost due to conduction [168,169]. During operation, the applied hydrostatic transmembrane pressure must be lower than the membrane liquid entry pressure. If not, the liquid will enter the pores due to surface tension force [166]. A review on the application of MD for the recovery of valuable-added components from acidic waters has recently been published [168].

Different models have been proposed for describing mass transfer across MD membranes. Generally, it takes place by a combination of convection and diffusion through membrane structure. In the absence of air, the membrane resistance can be described either by the Knudsen diffusion model or Poiseuille (viscous) flow model, while molecular diffusion model is used in the presence of air [166].

Figure 5 shows a scheme of the different operation configuration of MD for HCl effluents. The direct contact membrane distillation (DCMD) is the most employed configuration, which puts the feed solution at high temperatures in contact through the membrane with a cold solution. Therefore, the vapour pressure gradient promotes the transport of vapours and volatile compounds. Other configurations, such as the air gap MD (AGMD) and water gap MD (WGMD) are based on putting a space filled with air (or water) between the membrane and the cold solution, so the molecules in the gap condense and can be recovered. Another configuration of interest is the vacuum MD (VMD), which consists of applying vacuum in the permeate side to enhance the vapour pressure gradient [168].

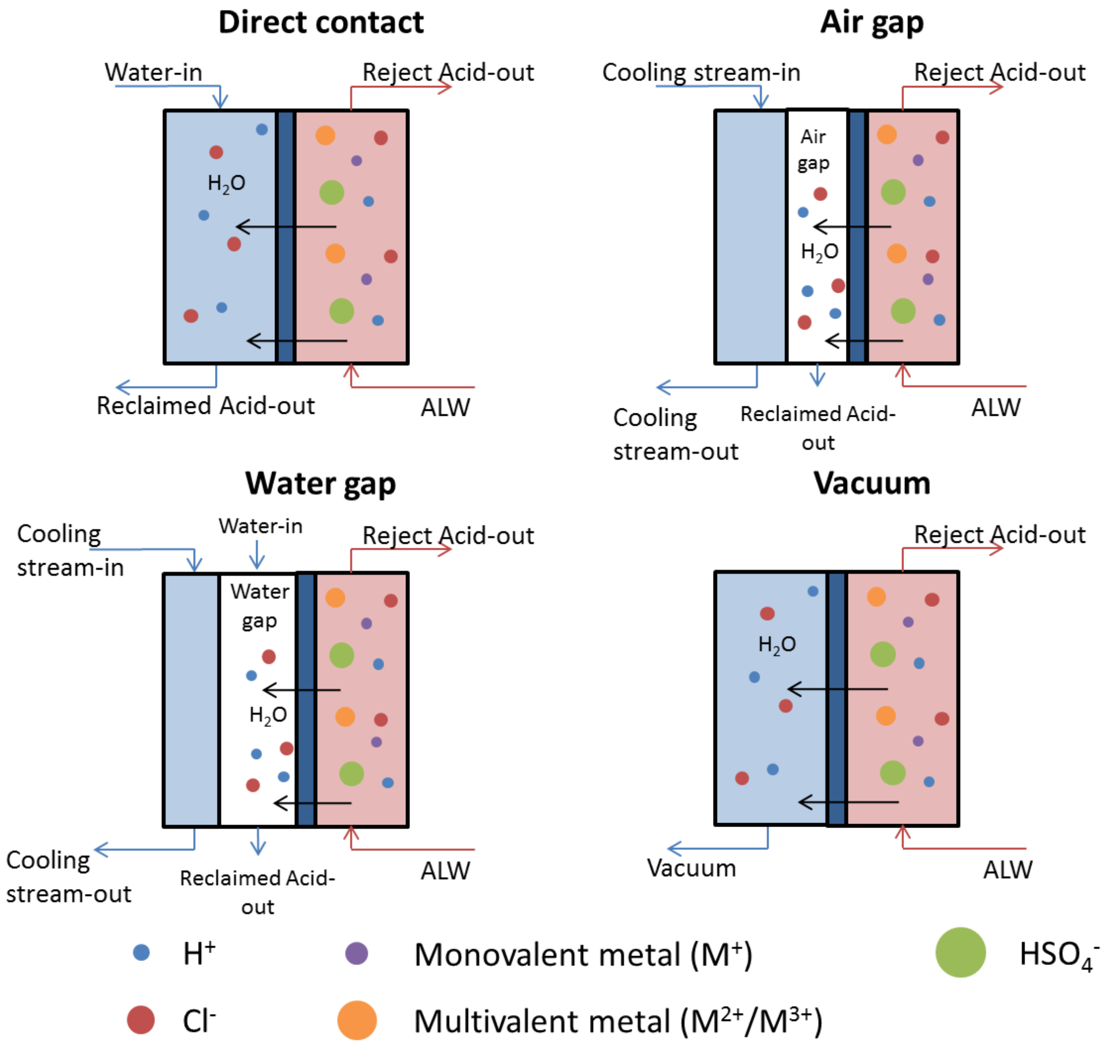

Figure 5. *Schematic representation of thermal-driven membrane processes for the valorisation of acidic waters: direct contact, air gap, water gap and vacuum MD*

The application of MD has been studied for the recovery of different kind of acids [170–174]. Zhang et al. [170] evaluated the permeation of H_2SO_4 in MD, observing an acid transport below 2% through the membrane. Additionally, the authors noticed that the acid flux decreased at higher acid concentrations, but increased with temperature. Caputo et al. [171] evaluated the concentration of HI or H_2SO_4 for H_2(g) production from the sulphur–iodine (S–I) process using DCMD at 58°C feed temperature with a polypropylene (PP) capillary membrane and AGMD at 80°C with a PTFE flat-sheet membrane. Better results were obtained with the AGMD configuration, achieving higher permeate fluxes (16.97-7.8 L/m^{2}h for HI and 5.0-0.7 L/m^{2}h for H_2SO_4) than with the DCMD configuration (2.0 L/m^{2}h for HI and 1.3 L/m^{2}h for H_2SO_4). Moreover, the former also achieved higher concentration factors, from 88 to 980 g/L H_2SO_4 with a negligible concentration in the reclaimed acid-out, and from 38 to 1024 g/L HI, which was higher than the azeotrope concentration (973 g/L). However, part of the HI permeated across the membrane (666 g/L). Recently, Si et al. [174] evaluated the combination of VMD (PTFE membrane) and mechanical vapour recompression for the treatment of H_2SO_4 solution (100 g/L). The solution was concentrated up to values of 500 g/L, assuming an energy saving of 65.5%. Thiruvenkatachari et al. [173] studied the performance of AGMD for HNO_3-water mixtures with a PTFE membrane. They observed that by increasing the concentration of the acid from 126 to 378 g/L, the permeate flux decreases. However, an increase in the permeate flux was observed at concentrations higher than the azeotrope (680 g/L) due to the permeation of HNO_3. They were able also to concentrate 126 g/L HNO_3 at 80 °C, achieving a final concentration of 346 g/L (below the azeotrope). Nevertheless, part of the acid was lost in the permeate (31.5 g/L). The performance of MD has also been evaluated for acid mixtures. For instance, Tomaszewska and Mientka [172] evaluated the separation of HCl from HCl-H_2SO_4 solutions with capillary PP membranes. Working at the same acid concentration (51 g/L HCl and H_2SO_4) at 60 °C, the permeation of HCl across the membrane was very small, while the H_2SO_4 was rejected. At higher HCl concentrations (111 g/L HCl and 61 g/L H_2SO_4), the acid permeated in a greater extent. In the opposite case, with higher concentrations of H_2SO_4, the transport of HCl was enhanced. Moreover, it was also favoured working at higher temperatures (70 °C). Kim et al. [175] evaluated the potential concentration and purification of H_3PO_4 from a stream containing 702 g/L H_3PO_4, 82 g/L HNO_3, 69 g/L acetic acid and 2.36 mg/L Al with VMD. Working at a vacuum of 730 mmHg at 125 °C, the desired concentration was achieved and also the acetic acid and HNO_3 were separated from H_3PO_4. However, impurities of 3.68 mg/kg were found in the purified acid.

As in the case of DD, the addition of salts to the solution promoted the transport of acid across the membrane (“salt-effect”) [176–178]. For example, Tomaszewska et al. [177] evaluated the concentration and recovery of HCl with PP membranes at different concentrations (50-300 g/L) and temperatures (60 and 70 °C). At low acid concentration (<150 g/L, 60 °C) the permeate was practically pure water. However, at higher acid concentrations and temperature, the flux of acid across the membrane increased because of its higher vapour pressure. The addition of $FeCl_3$ to the solution improved the HCl flux because of the salt effect, allowing the recovery of pure HCl as permeate ($FeCl_3$ rejected more than 99.9%). Experiments performed with a pickle liquor (8.9 g/L Fe(III) and 101 g/L HCl) showed that at concentrations below 150 g/L HCl and 28 g/L Fe(III) it was possible to obtain pure water as permeate. Beyond this point, pure acid was obtained instead, with Fe(III) being rejected by 100%. Tomaszewska et al. [178] evaluated the transport of HCl across PTFE and Polyvinylidene fluoride (PVDF) flat-sheet and PP capillary membranes. They observed that the PP membrane exhibited the lowest water and permeate fluxes within a wide range of HCl concentrations (50-260 g/L) and temperatures (40-70 °C). Within the range 140-200 g/L HCl was transported across the membrane. At high concentrations (>200 g/L), they observed that it was possible to obtain even higher concentrations in the permeate than in the feed side. The presence of $FeCl_3$ favoured the transport of the HCl, yielding an acid-rich permeate with a low amount of metals (Fe rejection >99.5%). Feng et al. [176] evaluated the concentration of titanium white waste acid by DCMD with self-prepared PVDF hollow fibres. By working only with 200 g/L H_2SO_4, they were able to concentrate the acid to values between 360-390 g/L with acid rejections higher than 99.9%. Experiments containing also 30 g/L $FeSO_4$ exhibited rejections higher than 99%, but a considerable flux decline was observed. Supersaturation of the solution in the membrane occurred, leading to pore blocking. After HCl cleaning for $FeSO_4$ crystals removal, the flux was partially restored without seeing any chemical or physical deterioration of the membrane.

The applicability of MD has been studied for treating different acidic effluents. For example, the MD performance has been evaluated for the treatment of AMD [179–181]. Amaya-Vías et al. [179] evaluated WGMD and AGMD using polytetrafluoroethylene (PTFE) membranes at different temperatures (50-80 °C) with AMD from the Tinto River (pH 2.1 and composed mainly by 10.5 g/L SO_4^{2-}, 0.81 g/L Mg^{2+} and 0.73 g/L Fe). Both MD configurations allowed to obtain high permeate fluxes (up to 16.8 L/m^2h for WGMD and 10.2 L/m^2h for AGMD) achieving rejections higher than 99% for the metals in solution, whereas the permeate pH was close to one of the natural waters. Ryu et al. [180] integrated adsorption on zeolite with DCMD for the recovery of water from AMD (pH 2, 340 mg/L Fe, 220 mg/L Mg, 170 mg/L Ca, 150 mg/L Al and 120 mg/L Cu). Zeolite achieved transition metal removals between 26 to 31%. The DCMD was fed with effluent from the zeolite unit, which contained 6.4 g/L TDS and, after recovering 50% of the water, its total concentration was 12.9 g/L TDS. The TDS concentration in the permeate remained below 0.01 g/L. Membrane fouling by Fe and Al was avoided by a pH adjustment to 4, and a high-quality freshwater was obtained, while H_2SO_4 and metals were concentrated in solution. In a latter work, Ryu et al. [181] integrated DCMD (PTFE membrane) with adsorption (amine grafted SBA-15) for Cu recovery from AMD (pH 2.0, 4.3 g/L SO_4 and 92 mg/L Cu). They were able to achieve a permeate flux of 14.5 L/m^2h and a final Cu concentration of 233 mg/L at a water recovery of 80%.

The treatment of H_2SO_4-based solutions (e.g. leaching or mining effluents) has been also addressed [182,183]. Kesieme et al. [182] employed MD for treating H_2SO_4 leaching solutions (1.08 mol/L H^+, 15.7 g/L Fe, 4.4 g/L Al). They were able to recover water by more than 80%, with a low presence of acid (<0.1 g/L). Finally, acid and metals were concentrated with a factor of 4, except for Ca, which caused scaling. Jimenez and Ulbricht [183] evaluated the water recovery and concentration of the acid (H_2SO_4) and metals from a Cu mining effluent (pH 2, 300 mg/L Fe, 50 mg/L Cu) with DCMD. With a feed temperature of 60 °C, D845 and 3M membranes exhibited average water fluxes of 5.9 and 6.2 L/m^{2}h, respectively. Moreover, salt rejections higher than 99.9% were achieved. Concerning the acid, it was barely transported across the membrane and was concentrated by 40%.

Besides, the MD has also been applied to HCl-based solutions contaminated with metals [184–187]. For example, Cai and Guo [184] evaluated the application of MD (PTFE membrane) for the treatment of wastewaters from the hot-dip galvanising industry, which was characterised by the presence of HCl ($0.5<pH<1.5$), $FeCl_2$ (50-300 g/L) and $FeCl_3$ (4-35 g/L). The increase in the acidity in the feed solution (0-200 g/L) resulted in a lower permeate flux across the membrane (from 8 to 6 kg/m^{2}h at 75°C). However, a more acidic permeate was obtained at higher acid feed concentrations. By the addition of $FeCl_2$, the acidity in the permeate was increased, with high metal rejections (>99.99%). Nevertheless, the permeate flux decreased because of the lower H_2O activity. Chen et al. [185] evaluated the recovery of PGMs from refining_wastewater (pH 0.03, 48 g/L Cl^-, 11.4 g/L Na, 10 g/L K, among others) at 60 °C using DCMD. The increase in feed pH from 0.03 to 7 resulted in a lower permeate flux because of the lower partial vapour pressure or membrane scaling. Membrane analysis revealed silica scaling when pH was adjusted to 5 and 7, and Cr(III) scaling at pH 3. During operation, the permeate was mainly composed of HCl with low amounts of metals (<5 mg/L). Tang and Zhou [186] evaluated the recovery of HCl from a solution containing REEs using VMD. At batch experiments (60 °C), from a feed solution composed of 190 g/L HCl and 0.3 mol/L REEs, it was possible to recover 84% of the acid, with very low concentrations of REEs (3 mmol/L). Working at continuous VMD experiments, the potential of VMD for concentrating REEs was observed, achieving concentrations 3 to 4 times higher than the feed solution. Tomaszewska et al. [187] applied MD for treating pickling solutions with capillary PP membranes at 70 °C. After operation with synthetic solutions (106 g/L HCl and 94 g/L Fe(III)), it was possible to recover all of the HCl in the permeate while Fe was completely rejected. Water rinse in the feed side was needed to prevent the formation of salt crystals in the membrane pores. By treating the pickling effluent (86-135 g/L HCl, 361 g/L metals (Cu, Fe, Zn and Mg)), the permeate was richer in HCl than the feed side (165 g/L), whereas metals were rejected and their concentration in the feed stream rose to 600 g/L. Moreover, crystals $CuCl_2 \cdot 2H_2O$ crystals were found in that stream. Recently, Chen et al. [188] evaluated DCMD (PTFE-PVDF/PET membrane, 20°C and 60°C for permeate and feed solutions, respectively) from refining wastewater produced for the recovery of precious metals in spent catalysts (pH 0.03, 490 g/L Cl^-, 11 g/L Na, 10 g/L K, 537 mg/L Zn, 6 mg/L and 1 mg/L Ag). Flux decreased from 15 to 5 kg/m^2 h when recovery reached 60%. Permeate was composed of HCl (545 mg/L) with low presence of metals (<6 mg/L). Working at higher pH values led to membrane scaling, mainly by silica and Cr (III) species.

6. Comparison of membrane technologies for the valorisation of acidic liquid wastes

As can be seen in the previous sections, membrane technology covers a wide range of applications, from the treatment of AMD to different metallurgical and hydrometallurgical effluents. **Tables 2-4** collect some examples of the performance of the above-explained membrane technologies for the treatment of AMD, industrial with a moderate (<0.5 mol/L) and high (>0.5 mol/L) acidity.

Regarding the treatment of AMD (**Table 2**), NF membranes offer an alternative to the valorisation of acidic effluents, since the acid can be recovered as permeate, while metals are rejected effectively (>90%). Their use for AMD treatment is recommended; because they would allow lower alkali consumption to recover the metals selectively [68,92]. The other membrane technologies (ED, FO, MD and RO) are more focused on the purification and recovery of water. All of them can reject metals effectively (>95%). ED seems not to be the preferred one if Fe(III) is present, because at higher water recoveries, the precipitation of Fe on the membranes as $Fe(OH)_3$ can increase the specific energy consumption [150]. Among the others, FO is a promising technology (instead of RO) because it does not require an external hydraulic force to achieve water recovery. However, the selection of an appropriate draw solution can be difficult because of scaling issues [144]. Another kind of draw solutions may be useful, such as NaCl [145] or even chelating agents (PSS-Na or EDTA-4Na) [146]. Due to the low acidity of these waters, DD is not a suitable option for the treatment of AMD.

Concerning the applicability of membrane technologies to the treatment of industrial effluents, they were grouped depending on the acidity of the stream: those for moderate (<0.5 mol/L, **Table 3**) and high (>0.5 mol/L, **Table 4**) acidities.

For moderate acidity streams, ED (with different configurations as shown in **Figure 2**), MD and NF are currently researched. BMED has proved to be effective at producing a stream rich in H_2SO_4 with a low content of metal impurities [159]. Instead, the application of SED has been more focused on the separation of different components by the use of selective ion-exchange membranes (MVC) (e.g. separation of As from Cu/Zn) [160]. MD distillation, when applied for the treatment of AMD, can be useful for concentrating the different compounds in solution, and if HCl is present, its recovery and purification can be achieved [184]. Regarding NF membranes, acid can be purified. However, weak electrolytes as non-charged species (e.g.

H_3AsO_4 or H_3AsO_3) are not rejected by the membrane, and then contaminate the obtained acid [89]

If a higher acidity is present in the solution (>0.5 mol/L), then DD may be the preferred option, because of the presence of an AEM that favours the transport of anions while most metals are successfully rejected. With this technology, more than 70% of the acid can be recovered with a low amount of metal impurities. ED can also be applied for acid recovery, but the high concentration of acid makes necessary to provide a higher voltage to increase the acid transport rate. As in the previous case, MD can be used for the recovery of volatile compounds (HCl or HNO_3) [172,173]. Moreover, it can be used for purifying acids (e.g. H_3PO_4) from volatile compounds (acetic acid, HNO_3) [175]. The driven-pressure membrane technologies (i.e. NF and RO) are not suitable for the valorisation of acidic effluents. RO membranes are not suitable because of the need for high pressure and low acid permeation and subsequent recovery [77]. Instead, NF membranes can provide the recovery of acid in the permeate and concentrated metal stream in the concentrate [77,85]. However, the fact that both kinds of membranes are usually made of polyamide makes them susceptible to acid attack [85,91,93].

In relation to an economic point of view, no data comparing operational expenditures (OPEX) and capital expenditures (CAPEX) among the different membrane technologies to treat acidic liquid effluents have been reported. However, it is estimated that membrane treatment can imply a CAPEX of 500-1000 US $/m^3 and an OPEX of 0.5-1.0 US $/m^3. Instead, the current management options, such as chemical precipitation, has a CAPEX of 300-1250 US $/m^3 and an OPEX of 0.2-1.5 US $/m^3, whereas biological sulphate removal has a CAPEX of 800-1500 US $/m^3 and an OPEX of 0.7-1.5 US $/m^3 [189].

Figure 6 sums up the potential uses of the streams obtained from the above-mentioned membrane separation processes. All of them produce a concentrate stream, which is very rich in metals, and can be used for: i) selective precipitation for metal recovery, whereas the supernatant (i.e. water) can be discharged to the natural receiving bodies or be reused internally; ii) solvent extraction; iii) ion-exchange for the selective recovery of a target metal (e.g. REEs, Cu, Zn), and; iv) electrowinning for the electrodeposition of one specific metal (e.g. Cu). With some technologies, such as NF, DD and MD (the latter depending on the acid, mainly HCl), the recovery of a purified acid stream is quite feasible. This one can be used for: i) leaching processes to dissolve the raw minerals; ii) pickling processes to remove impurities from the metal surface; iii) regeneration of the solvent extractant; iv) regeneration of the ion-exchange resin, and; v) electrolyte in the electrowinning baths. Nevertheless, other technologies obtain a stream containing water instead of acid, as it is the case of ED, FO, RO and MD. In this case, water can be either reused internally or discharged to the natural water receiving bodies.

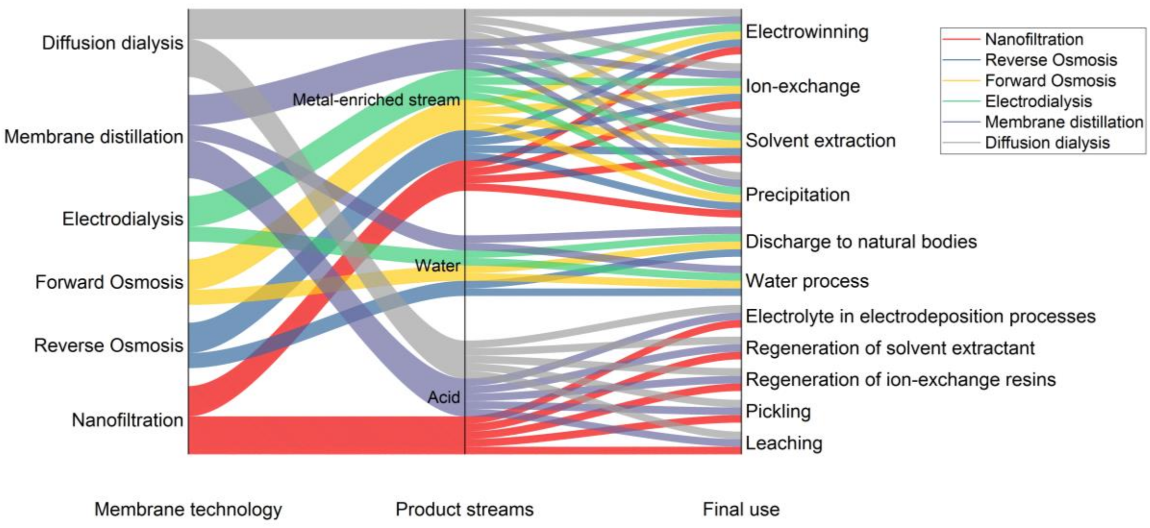

Figure 6. *Schematic representation of the membrane processes for the valorisation of acidic waters, the product streams obtained and their potential use.*

As already stated, most of the described ALWs are characterised by elevated concentrations of acids and dissolved metallic species, which can be recovered as valuable by-products and used to balance the cost of the treatment. When the value of the by-products and the treated water exceeds the cost of the treatment train, it is feasible to design valorisation routes that provide economic benefits as well as to solutions to the associated environmental problem. Generally, the above-described membrane processes will not provide a single treatment stage for the recovery of by-products, but their integration could be beneficial for:

i) Reduction of the generated waste sludge and concentrated streams, which require a long-term handling and disposal with associated long-term environmental liabilities.

ii) Creation of a revenue from the rich acid or metallic streams to partly or fully offset the treatment costs.

iii) Selective separation of target components taking benefit of the species and membrane properties.

iv) Contribution to the long-term sustainability of industrial and mining ALWs, as the on-site recovery of acids and metals is promoted.

Table 2. *Performance of membrane technologies treating AMD. Details on feed composition and operation conditions are provided.*

Membrane technology	**Water composition (mg/L)**		**Membrane used**	**Operation conditions**	**Results**	**Ref.**
ED	pH 2.8 Na: 296 Mg: 71 Ca: 230	Fe(III): 80 Cl: 194 SO_4: 1570	CEM: HDX100 AEM: HDX200	5 compartments with recirculation Current density: 2.6 mA/m^2 55 h operation	pH 2.92 Extraction efficiency: >97%	Buzzi et al. [149]
	pH 1.7 Na: 460	Fe(III): 2230 SO_4: 6720	CEM: HDX100 AEM: HDX200	3 compartments with recirculation Current density: 5-15 mA/m^2 10h of operation	Concentration factor for H_2SO_4: 2.64 (5), 3.36 (10) and 4.00 (15) Specific energy consumption: 6(5)-20(15) kWh/kg $Fe(OH)_3$ precipitation at 15 mA/m^2	Martí-Calatayud et al. [150]
FO	pH: n.a. Cu: 615 Al: 293 Ca: 313	Mg: 436 Mn: 203 SO_4: 8250	FOMEM-0415 – Hayward	Draw solution: 58.5g/L NaCl or 78 g/L NH_4CO_3	NaCl as draw solution Average permeate flux: 12 L/m^2 h Rejection: >97% NH_4CO_3 as draw solution Experiments not completed because of scaling (carbonates)	Vital et al. [144]
	pH 3.0 La: 1.2 Ce: 3.3 Dy: 0.4 Na: 120	Ca: 250 Mg: 100 K: 20 Mn: 4.2 Al: 8.8	Polyamide-based	80% of water recovery Draw solution: 279 g/L NaCl	Permeate flux: 12 – 9 L/m^{2}h REEs rejections: from 84 to 90%	Pramanik et al. [145]
	pH 3.1 Mn: 4.2 Fe: 19.2 Cu: 5.6	Zn: 3.6 As: 0.24 Pb: 0.45	Polyamide-based	Draw solution (π=8.9 bar): PSS-Na: 100 g/L EDTA-4Na: 42 g/L	Permeate flux: 7.5 L/m^{2}h (PSS-Na) 9.8 L/m^{2}h (EDTA-4Na) Rejections: Mn, As, Cd and Pb: >99% Fe, Cu and Zn: 80%	Choi et al. [146]

MD	pH 2.1 Fe: 735 Zn: 202 Cu: 185 Mn: 49 K: 30	NO_3^-: 50 Na: 54 Cl: 54 Ca: 170 Mg: 809 SO_4: 10418	PTFE membrane	AGMD WGMD Feed solution: 50, 60, 70, 80 °C Cooling water: 15 °C	Permeate flux WGMD: 4.0 (50 °C) to 16.8 (80 °C) L/m^2h Permeate flux AGMD: 2.8 (50 °C) to 10.1 (80 °C) L/m^2h Rejections: Cu, Fe, Zn, Mn, Mg, NO_3 ,SO_4: >99.9% Na, K, Ca, Cl: >95%	Amaya-Vías et al. [179]
	pH 2.0 Ca: 170 Mg: 220 Na: 50 Fe: 340	Zn: 120 Cu: 90 Al: 150 SO_4: 4300	PVDF membrane	DCMD Feed solution: 55 °C Permeate solution: 22 °C 50% water recovery	Permeate flux: 2.5 L/m^2h Permeate solution: <10 mg/L TDS SO_4 concentration in the permeate: 50 mg/L Feed solution concentration factor: 2	Ryu et al. [180]
NF	pH 3 Na: 653 K: 173 Cu: 79 Zn: 18	Ni: 17 Pb: 10 SO_4: 375 Cl: 530 NO_3: 107	DK-4040F	2-12 bar	Permeate flux: 12 to 60 L/m^2 h Rejections: Ni: >91% Cu: >91.5% Zn: >92.5% Pb: >93.5% H^+, Na, K: n.a.	Zhong et al. [68]
	pH: 4.5 Ca: 480 Cu: 410 K: 310 Mg: 770	Mn(III): 440 Na: 2000 Cl: 2300 SO_4: 6900	NF270	5-8 bar Permeate flux: 25-35 L/m^2 h	Rejections: Mn(III),Mg: 95% Ca: 92% Cu: 88% SO_4: 96% H^+, K, Na, Cl: n.a.	Fornarelli et al. [71]
	pH 1.0 Al: 560 Zn: 44 Cu: 40	Ca: 24 REEs: 140 SO_4: 9410	NF270	4-20 bar	Permeate flux: 18-90 L/m^2 h Rejections: Metals: >98% SO_4: 40% H^+: -5 to 5%	López et al. [92]

RO	pH 2.7 Al: 1139 Ca: 326 Mg: 630	Mn_{tot}: 225 Cu_{tot}: 2300 Fe_{tot}: 628 SO_4: 14337	AlfaLaval RO 98Ht	15 bar	Permeate flux: 50 L/m^2 h Rejections: Multicharged metals and SO_4: >98% Na: 96% Membrane scaling (Mg-Ca-SO_4) at twofold concentrated AMD	Rieger et al. [110]
	pH 2.5 Al: 1290 Ca: 395 Cu: 2735 Fe(III): 446	Mn(III): 295 Mg: 776 SO_4: 20400 CO_3: 1320	HR98PP	5-20 bar	Permeate flux: 3-32 L/m^2h Rejections: Cu, Fe(III), Mn(III), Ca, Mg, Al: >97% SO_4: 80% H^+, CO_3: n.a.	Al-Zoubi et al. [69]
	* pH 1.3 Cu: 32 Ni: 24 Co: 5 Al: 25	As: 28 Ca: 90 Mg: 277 Fe: 44 Mn: 10	TFC-HR	10 bar 50% water recovery	RO initial permeate flux: 11.4 L/m^2h pH 2.5 Rejection: Cu: 99.3% Ni: 94.8% Co: 98.2% Al: 97.4% As: 92.7% Ca: 98.2% Mg: 95.7% Fe: 98.7% Mn: 98.8%	Ricci et al. [101]

n.a. not available

*The solution composition refers to the NF permeate of an AMD

Table 3. *Performance of membrane technologies treating effluents with a moderate acidity (<0.5 M). Details on feed composition and operation conditions are provided.*

Membrane technology		Water composition (mg/L)		Membrane used	Operation conditions	Results	Ref.
ED	Conventional	H_2SO_4: 50000 Cu: 9000	As (V): 3000 Sb: 25	CEM: MC-3470 AEM: MA-3475	Lab-scale with recirculation Current density: 225 A/m^2	Cu transport rate: 0.61 mol/m^2h SO_4 transport rate: 2.8 mol/m^2h As(III) transport rate: 0.03 mol/m^2h	Cifuentes et al. [151]
	BMED	pH 1.4 SO_4: 45200 Fe: 11800 Zn: 336	Cu: 135 As: 64 Cd: 5	CEM: NRE212 AEM: IONSEP EDI BPM: BP-1E	Three membrane pairs 40 h operation Current density: 3.0 mA/cm^2	H_2SO_4 recovery: 85.9% (39 g/L) Removal rate: Cu, Zn, Fe: >95% Ni: 78% Cr: 68% Specific energy consumption: 0.09 kWh/L Cell voltage: 8.5 V	Liu et al. [159]
	SED	pH 2.3 Cu: 2920	Zn: 9417 As: 2250	Fujifilm MVC, CEM and AEM Type 2	Three membrane pairs 300 min of operation	Specific energy consumption: 2.34 kWh/(kg $CuSO_4$+$ZnSO_4$) Cu/Zn-rich stream: pH 1.3 Cu: 2133 mg/L Zn: 8109 mg/L As: 9 mg/L As-rich stream: pH 0.7 Cu: 911 mg/L Zn: 2753 mg/L As: 2832 mg/L	Reig et al. [160]
MD		pH 2 Fe: 300 Cl: 50	SO_4: 590 Cu: 50	D845 (PTFE) or 3M PVDF	5 h operation Feed temperature: 60°C Cold water: 20°C	Permeate flux D845: 5.9 L/m^2h Permeate flux 3M: 6.2 L/m^2h Salt rejection: 99.9%	Jimenez and Ulbricht [183]

	50 g/L HCl 95 g/L FeCl$_2$		PTFE	Feed temperature: 75°C Cold water: 20°C	Permeate flux: 6.5 kg/m^2 h HCl concentration in the permeate: 7 g/L Fe(II) rejection: 99.99%	Cai and Guo [184]
NF	pH 2.2 Al: 12.4 Ca: 1574 Cu: 9.8 K: 298 Mg: 238	Mn: 85 Na: 77744 Pb: 475 SO$_4$: 5739 Si: 34	Desal DK	17 bar	Rejections: H: 36% Al: 92% Ca: 42% Cu: 12% K: 0% Mg: 79% Mn: 66% Na: -3% Pb: 36% SO$_4$: 89% Si: 3%	Ortega et al. [86]
	pH 2 – 2.5 Cr(III): 500		Desal DK	4 – 18 bar	Cr(III): 70 – 85% Cl: 40 – 58% H$^+$: -40 – -30 % (theoretical)	Gomes et al. [87]
	pH 0.28 As(V): 610 Na: 170 Fe(III): 29 Zn: 100	K: 40 Ca: 20 Cu: 13 SO$_4$: 40510 Cl: 9040	NF270	4.5 – 20 bar	H$^+$, As(V): 5–25% Na, K: 45–80% Fe(III), Ca, Cu: >85% Zn: >85% SO$_4$: 10–40% Cl: -5 – -20%	López et al. [89]

Table 4. *Performance of membrane technologies treating effluents with a high acidity (>0.5 M). Details on feed composition and operation conditions are provided.*

Membrane technology	Water composition (g/L)		Membrane used	Operation conditions	Results	Ref.
DD	H_2SO_4: 450 Fe: 52 Ni: 18	Na: 0.61 Mg: 0.10	Asahi Type T-0b Dialyzer	Flow rate ratio: 1 Flow rate: $0.26\cdot10^{-3}$ m^3/m^2h	Acid recovery: 80% Rejection: Ni (96%), Fe (99%) Concentration in the diffusate: 421 g/L H_2SO_4 and metals impurities (<2 g/L)	Jeong et al. [119]
	HCl: 76 g/L Fe: 150 g/L		Fumasep type FAD	Batch configuration 7h operation	Acid recovery: 75% (due to salt-effect) Fe leakage: 7% Prevalence of drag flux (t<0.5 h) Prevalence of osmotic flux (t>0.5 h)	Gueccia et al. [117]
	H^+: 1.75 V: 2.1 Al: 17.6 Fe: 5.8 Mg: 4.5	K: 6.8 F: 11.2 P: 1.4 S: 185	DF120-III	Flow rate ratio: 1 – 1.1 Flow rate: 12 mL/min	H_2SO_4 acid recovery: 71% (1.5 g/L H^+) Rejections: V: 95% Al: 99% Fe: 97% Mg: 98% K: 85% F: 98% P: 91%	Wang et al. [122]
ED	H_2SO_4: 150 $FeSO_4$: 26		CEM: CMX AEM: AMX	7h operation Current density: 20 mA/cm^2	Acid concentration factor: 13% Fe removal: 66% Specific energy consumption: 1.8 kWh/kg	Chekioua and Delimi [153]
	H_3PO_4: 196 Al: 13.5 Mo: 48		CEM: CMX-SB AEM: ACS	15 V	P removal: 15% Al removal: 45% Mo removal: 7%	Sun and Xu [156]
MD	HCl: 52	H_2SO_4: 183	PP capillary membrane (Accurel PP S6/2)	5 h operation Feed temperature: 70°C Cold water: 20°C	Feed side: 280 g/L H_2SO_4 60 g/L HCl	Tomaszewska and Mientka [172]

	HNO_3: 252		PTFE	AGMD Feed temperature: 80°C Cooling water: 15°C	Permeate side: 8 g/L HCl Permeate flux: 2 L/m^2 h Membrane selectivity: 0.17	Thiruvenkatachari et al. [173]
	* H_3PO_4: 702 HNO_3: 82	Al: 0.023 Acid acetic: 69		VMD: 730 mm Hg Feed temperature: 125°C	H_3PO_4: 850 g/L Al concentration: 1mg/kg Separation efficiency: 100% HNO_3, HAc	Kim et al. [175]
NF	H_2SO_4: 200 Cu: 2		DK MPF-34	Permeate recovery: 10% Membrane immersion in 196 g/L H_2SO_4 for 8 weeks	Permeate flux: 50 (DK) and 10 (MPF-34) L/m^2 h Rejections DK: H_2SO_4 (10%), Cu (85%) Rejections MPF-34: H_2SO_4 (10%), Cu (45%) After 8 weeks immersion Permeate flux: 360 (DK) and 50 (MPF-34) L/m^2 h Cu Rejections: DK (5%), MPF-34 (35%)	Manis et al. [85]
	H_3PO_4: 200 Fe: 0.71 Mg: 0.50	Al: 0.44 V: 0.06 Zn: 0.10	DL DK MPF-34	35 bar	Permeate flux: 17.1 (DL), 11.3 (DK) and 4.5 (MPF-34) L/m^2 h Acid permeation: 83.3 (DL), 80.2 (DK) and 90.8 (MPF-34) % Acid purification: 92.3 (DL), 83.3 (DK) and 19.6 (MPF-34) %	González et al. [77]
RO	H_3PO_4: 200 Fe: 0.71 Mg: 0.50	Al: 0.44 V: 0.06 Zn: 0.10	SX01 ESPA SW30HR	125 bar	Permeate flux: 13.7 (SX01), 20.0 (ESPA) and 5.6 (SW30HR) L/m^2 h Acid permeation: 46.3 (SX01),2.5 (ESPA) and 4.2 (SW30HR) % Acid purification: 98.4 (SX01), 34.4 (ESPA) and 76.8 (SW30HR) %	González et al. [77]

* After being pre-treated with DD

7. Application of membrane technologies at industrial scale for the valorisation of acidic liquid effluents

Mining and hydrometallurgical industries play an essential role in the sustainable management of water resources, especially in its balance (e.g. water discharge and consumption). Despite the high water volumes of mining and hydrometallurgical industries needed to be treated, literature is scarce in relation to the industrial application of membrane technologies to valorise acidic effluents. Several examples can be found related to acidic mine water treatment, but no data were found regarding the hydrometallurgical industry (**Table 5**).

Chesters et al. [190] reported more than 363 mines (69% of them are copper and gold sites) that generate waters that can be potentially treated with membrane technology. They also reported to be 67 operational membrane plants by 2016. One of the first large scale applications is at Mexicana de Cananea Mine (Mexico) to remove and treat water from the pit. A RO plant designed to treat 900 m^3/h (50% recovery) allows to concentrate copper to 1.6 g/L (which is fed to a SX/EW process) and to generate a clean permeate. Another example is located in Minera Yanacocha (Perú). The RO plant treats the pregnant liquor solution during the rainy season to concentrate them and to make the gold extraction process viable [190]. In another example, AMD from a coal mine is treated to produce potable water in South Africa. The influent is characterised by a pH of 2.7 with a TDS content of 4930 mg/L. The AMD also presents 660 mg/L Ca, 230 mg/L Mg, 3090 mg/L SO_4 and 210 mg/L Fe, among others. The treatment consists of a neutralization and precipitation step using limestone/lime followed by a three-stage membrane process combining UF and RO in series. The treatment process allows to recover more than 97% of water, obtaining 25 ML/d of potable water. The capacity of the plant was increased to 50 ML/d in 2014. The purified water is characterised by a pH 6.0-9.0 with an electrical conductivity below 70 mS/cm and a TDS content lower than 450 mg/L. The treatment cost is 1.50 US $\$/m^3$, whereas the municipality pays 1.00 $\$/m^3$ for the water. The plant consums an average value of 2500 kWh/m^3. Initially, problems related to membrane blockage due to suspended solids and presence of foams were observed [191,192]. Another study case can be found at the Bingham Canyon Mine of the Kennecott Utah Copper company, where mining activities have resulted in two groundwater plumes. The big one (247 million m^3) has a sulphate concentration ranging from 500 to 5000 mg/L, whereas waters from the other plume (62 million m^3) are characterised by elevated concentrations of heavy metals (including lead, arsenic and cadmium, among others), low pH ($2.9<pH<3.4$) and a high concentration of sulphate (>20 g/L). A RO treatment plant (using Hydronautics ESPA2) was built for the treatment of waters from both plumes, which presented a mean concentration of 1200 mg/L and a TDS of 2000 mg/L. Along the six years of operation of the RO plant, the water recovery was around 70-75%. Permeate was send to the district distribution system, whereas the concentrate was sent back to the plumes [193]. NF was also tested to treat the water from the Bingham Canyon Mine after the suspended solid removal stage. In this case, the raw water contained a 92 g/L TDS (mainly 73.8 g/L SO_4, 9.9 g/L Mg and 5.9 g/L Al) and the NF membrane allowed to remove metals and sulphate by more than 97%. Antiscalants were dosed to avoid gypsum precipitation inside the pressure vessels and concentrate lines [194,195]. Another example is the on-site water treatment of the complex of Ulan Coal Mines (Australia) (with both underground and open-pit mining sites). An on-site water treatment scheme allows to produce a clean permeate blended with on-site waters, generating a flow of 30000 m^3/d that is discharged into surface water bodies. The plant incorporates a pre-treatment based on the oxidation of Fe(II) and Mn(II) and its subsequent removal. This is achieved by combining chlorine oxidation and a sand filter with $MnO_2(s)$ that catalyses their oxidation. Therefore, scaling is avoided in the UF and RO units. The RO has a capacity of 12 ML/d [196]. Mine water from a coal mine in Queensland is being treated with a system containing MF followed by RO with a water capacity of 500 m^3/h. Prior to the treatment with MF, several dissolved contaminants are removed by oxidation, coagulation or precipitation [197]. Another plant was built in Tweefontein (South Africa) to treat mine water. The plant can treat 15000 m^3/d producing 10000 m^3/d of potable water. The treatment contains 2-stage of RO membrane processes with an inter-stage softening, and the RO permeate is sent to mineralizing and chlorinating units [198,199]. One example of Zero Liquid Discharge can be found in Collahuasi Copper Mine in Chile. Most of the Chilean Copper mine industry is located up to 150 km from the sea, which implies pumping seawater at a cost of 3.00 US $\$/m^3$, whereas the desalination cost of the mining waste waters is sensitively lower. The treatment plant can treat 5000 m^3/d (80% recovery) and incorporates UF/RO membranes with an extensive pretreatment [200,201].

Table 5. *Examples of full-scale membrane plants for the treatment of acidic waters*

Location	Feedwater	Membrane process	Treatment capacity (%recovery)	Ref.
Mexicana de Cananea (Mexico)	Water from pit	RO	900 m^3/h (50%)	[190]
Minera Yanacocha (Perú)	Pregnant liquour	RO	2750 m^3/h	[190]
eMalahleni (South Africa)	AMD	UF+RO	26000 m^3/d (97%)	[191,192]
Bingham Canyon Mine (USA)	Acidic groundwater	RO	n.d. (75%)	[193]
Bingham Canyon Mine (USA)	Acidic groundwater	NF	n.d.	[194,195]
Ulan Coal Mines	On-site water	UF + RO	30000 m^3/d	[196]

(Australia)				
Queensland's coal mine (Australia)	Mine water	MF+RO	500 m^3/h	[197]
Tweefontein (South Africa)	Mine water	RO	15000 m^3/d (66%)	[198,199]
Collahuasi Copper Mine (Chile)	n.d.	UF + RO	5000 m^3/d (80%)	[200,201]

n.d.: no data

8. Market perspectives for membranes in acidic mine waters processing technologies

Membrane market analysis projected a growth from 4.4 billion € in 2019 to 6.7 billion € by 2024, at a compound annual growth rate (CAGR) of 9.0%. The highest growth is expected to be in the Asian Pacific, including some large and rapidly growing economies (China, India, Indonesia), because of the increasing demand for physical water treatment. This is related to modifications in regulations concerning water treatment and wastewater discharge. The major drivers are found in the rising awareness about wastewater reuse, rapid industrialization and increasing populations. Besides, the strict regulations regarding water treatment and discharge, the shift from chemical to physical water treatments as well as the variation in the climate, which is related to rains are also driving the membrane market. Accordingly, membranes can be classified concerning their application: food and beverages, water and wastewater (including mining and hydrometallurgical effluents) [202]. Limited reports are found in relation to acidic effluents, and most of the data are related to the global market on membranes.

One of the main characteristics of mining and hydrometallurgical operations are the high volumes of water needed for processing stages and the wastewater generated (e.g. typically higher than 500 m^3/h). Consequently, the membrane suppliers can found a market opportunity in these industries. Besides, a second group of drivers can be found on the changing regulations regarding discharge limits, the increasing investment for water treatment, and the industrialization and automatization of mining sites.

Regarding the membrane type, the polymeric ones are currently leading the market. They can be classified according to the presence of natural (e.g. wool, rubber, and cellulose) or synthetic (e.g. polyamide, PTFE, polysulfone and polyethersulfone, among others) polymers. The last ones are the most promising to be used in the mining and hydrometallurgical field, as they provide a cost-effective solution, achieving a good selectivity, efficiency and they are easy to operate [203]. In relation to the technology, NF is widely applied to both chemical and mining processing stages, and it is projected to register the highest CAGR between 2019 and 2024 [202]. Its application is expected to grow because of its ability to transport mono-charged species (e.g. main strong acids or bases used in the mineral processing stages), while rejecting multi-charged metallic species (e.g. transition metal as precious metals and rare earth elements). This specific separation provides advantages in mining applications, especially during pre-treatment or enrichment. Besides, the use of NF provides lower discharge volumes than RO membranes, also reducing the salinity content. The key market players are DuPont (USA), Toray (Japan), Hydranautics (US), Koch Separation Solutions (USA) and Pentair (UK) with a substantial market share [202]. In the case of mining and hydrometallurgical applications, the development of acid-stable membranes has called for major efforts by most of the key providers. In order to meet the growing demand, the market players have launched new membranes and stabilised new collaborations with research centres to improve the performance of their membranes [203]. The requirements of membranes with high stability in acidic media in industrial and mining applications have made the ceramic membranes market to increase significantly in the next seven years. Among the key market players, TAMI

Industries, Pall Corporation, Ceram Hyd Ltd., Atech Innovations GmbH, Hyflux Ltd., Siva and Jiangsu Jiuwu Hi-Tech Co. Ltd. can be found [204].

9. Conclusions

The exhaustion of mining sites has made necessary to promote circular schemes in order to valorise residual effluents. Along the whole production chain, the mining and hydrometallurgical industries produce acidic waters with a relatively high amount of dissolved metals and non-metals that require an appropriate treatment before their discharge. Conventional treatments of such streams rely on neutralisation-precipitation, solvent extraction or ion-exchange, which require a high amount of chemicals and generate a waste difficult to handle. Nowadays, membrane technologies are emerging as an alternative to conventional treatments, because they offer the possibility of recovering valuable components and can be easily integrated with other treatment units. Among them, the following ones are the most promising to promote circularity:

- Diffusion dialysis. It is suitable for treating streams with high acid concentrations (>1 mol/L) because its AEM allows the recovery of acid (>70%) with a low transport of metals (<5%). However, due to the low flow rates to achieve the separation, high membrane area may be needed.
- Electrodialysis. It is useful for desalination since it allows to obtain a purified water stream. However, the presence of Fe(III) may produce scaling on the membrane surface, which will increase the need for electric current to achieve the separation. Despite this disadvantage, other kinds of configurations such as BMED or SED are promising. The BMED can be useful for the production of a purified acid stream, whereas the SED may remove any undesirable compound from the feed solution.

- Forward osmosis. It is under development for the valorisation of acidic effluents. Promising results are being achieved for water recovery from AMD. The main drawback is associated with the selection of an appropriate draw solution to avoid membrane scaling.
- Membrane distillation. Different kinds of acids can be concentrated with MD. Moreover, volatile acids (e.g. HCl, HNO_3) can be transported across the membrane and purely obtained in the permeate.
- Nanofiltration. It is widely used for acidities lower than 1 mol/L as it allows the transport of the acid, while metals are rejected. However, its performance is affected by the solution composition, especially by pH.
- Reverse osmosis. The use of RO is discarded at high acidity levels because of the high need for hydraulic pressure and the lower acid recovery.

As can be seen, membrane technologies are able to treat acidic effluents. Nevertheless, the stability of the membranes at acidic media must be studied. Commercial ion-exchange membranes for DD and ED operation are stable under acidic media, as well as MD membranes (PP, PTFE or PVDF). Nonetheless, most of the NF and RO membranes (usually those made of polyamide) are not stable at acidic media and suffer from hydrolysis in the long term exposure. Nowadays, acid-resistant membranes (both polymeric and ceramic) are emerging as an alternative for the treatment of acidic waters. However, some of them still show poor performance, and research must be towards improving their performance in terms of selectivity. One issue that must be studied is the ways to improve the separation factor for NF and ion-exchange membranes. The transport of non-charged species (e.g. $H_3AsO_4(aq)$) across them may be a limitation regarding the re-use of the purified acid internally. In addition, despite low pH values, scaling can occur. In fact, the low pH of the ALWs and the presence of dissolved metals can cause the precipitation of iron, aluminium and calcium mineral phases, which can limit the applicability of membranes-based systems.

The review on full-scale treatment of AWLs at several mining sites over the last years indicates that recycling such waters by mechanical purification systems (e.g. UF, NF and RO) is preferable than adding chemicals to wastewater (i.e. neutralisation/precipitation).

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References

[1] 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.

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

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

[4] S.A. Welch, A.G. Christy, L. Isaacson, D. Kirste, Mineralogical control of rare earth elements in acid sulfate soils, Geochim. Cosmochim. Acta. 73 (2009) 44–64. doi:10.1016/j.gca.2008.10.017.

[5] D. Merten, J. Geletneky, H. Bergmann, G. Haferburg, E. Kothe, G. Büchel, Rare earth element patterns: A tool for understanding processes in remediation of acid mine drainage, Chemie Der Erde - Geochemistry. 65 (2005) 97–114. doi:10.1016/j.chemer.2005.06.002.

[6] Ma. Nicolle, M. Lampi, K. Valkama, J. Karonen, Leaching of Copper Sulphides, in: Copp. Cobalt Africa, Inc. 8th South. African Base Met. Conf., Southern African Institute of Mining and Metallurgy, Livingstone, Zambia, 2015: pp. 183–194. doi:10.1533/9781845694616.341.

[7] European IPPC Bureau, Reference Document on Best Available Techniques for the Non-Ferrous Metals Industries, 2017. doi:10.2760/8224.

[8] J. López, O. Gibert, J.L. Cortina, Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents, Chem. Eng. J. (2020) 127015. doi:10.1016/j.cej.2020.127015.

[9] M. Regel, A.M. Sastre, J. Szymanowski, Recovery of zinc(II) from HCl spent pickling solutions by solvent extraction, Environ. Sci. Technol. 35 (2001) 630–635. doi:10.1021/es001470w.

[10] M.E. Schlesinger, M.J. King, K.C. Sole, Electrowinning, in: Extr. Metall. Copp., Elsevier Ltd, 2011: pp. 349–372. doi:10.1016/b978-0-08-096789-9.10017-4.

[11] A. Culcasi, R. Gueccia, S. Randazzo, A. Cipollina, G. Micale, Design of a novel membrane-integrated waste acid recovery process from pickling solution, J. Clean. Prod. 236 (2019) 117623. doi:10.1016/j.jclepro.2019.117623.

[12] A. Agrawal, K.K. Sahu, An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, J. Hazard. Mater. 171 (2009) 61–75.

doi:10.1016/j.jhazmat.2009.06.099.

[13] A.S. Sheoran, V. Sheoran, Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review, Miner. Eng. 19 (2006) 105–116. doi:10.1016/j.mineng.2005.08.006.

[14] D.B. Johnson, K.B. Hallberg, Acid mine drainage remediation options: A review, Sci. Total Environ. 338 (2005) 3–14. doi:10.1016/j.scitotenv.2004.09.002.

[15] D.W. Blowes, C.J. Ptacek, J.L. Jambor, C.G. Weisener, D. Paktunc, W.D. Gould, D.B. Johnson, The Geochemistry of Acid Mine Drainage, in: Treatise on Geochemistry, Elsevier, 2014: pp. 131–190. doi:10.1016/B978-0-08-095975-7.00905-0.

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

[17] E. Macingova, A. Luptakova, Recovery of metals from acid mine drainage, Chem. Eng. Trans. 28 (2012) 109–114. doi:10.3303/CET1228019.

[18] European Commission, Report on Critical Raw Materials and the Circular Economy PART 3/3, 2018. doi:10.1097/PPO.0b013e3181b9c5d5.

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

[20] R.D. Abreu, C.A. Morais, Study on Separation of Heavy Rare Earth Elements by Solvent Extraction with Organophosphorus Acids and Amine Reagents, Miner. Eng. 61 (2014) 82–87. doi:10.1016/j.mineng.2014.03.015.

[21] J. Kulczycka, Z. Kowalski, M. Smol, H. Wirth, Evaluation of the recovery of Rare Earth Elements (REE) from phosphogypsum waste - Case study of the WIZÓW Chemical Plant

(Poland), J. Clean. Prod. 113 (2016) 345–354. doi:10.1016/j.jclepro.2015.11.039.

[22] L. Wang, Y. Yu, X. Huang, Z. Long, D. Cui, Toward greener comprehensive utilization of bastnaesite: Simultaneous recovery of cerium, fluorine, and thorium from bastnaesite leach liquor using HEH(EHP), Chem. Eng. J. 215–216 (2013) 162–167. doi:10.1016/j.cej.2012.09.126.

[23] J. Sánchez España, E. López Pamo, E. Santofimia, O. Aduvire, J. Reyes, D. Barettino, Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications, Appl. Geochemistry. 20 (2005) 1320–1356. doi:10.1016/j.apgeochem.2005.01.011.

[24] M. Olías, C.R. Cánovas, J.M. Nieto, A.M. Sarmiento, Evaluation of the dissolved contaminant load transported by the Tinto and Odiel rivers (South West Spain), Appl. Geochemistry. 21 (2006) 1733–1749. doi:10.1016/j.apgeochem.2006.05.009.

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

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

[27] G. Lee, J.M. Bigham, G. Faure, Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee, Appl. Geochemistry. 17 (2002) 569–581. doi:10.1016/S0883-2927(01)00125-1.

[28] X. Wei, R.C. Viadero, K.M. Buzby, Recovery of iron and aluminum from acid mine drainage by selective precipitation, Environ. Eng. Sci. 22 (2005) 745–755. doi:10.1089/ees.2005.22.745.

[29] M. Bissen, F.H. Frimmel, Arsenic - A review. Part II: Oxidation of arsenic and its removal in water treatment, Acta Hydrochim. Hydrobiol. 31 (2003) 97–107. doi:10.1002/aheh.200300485.

[30] T.S.Y. Choong, T.G. Chuah, Y. Robiah, F.L. Gregory Koay, I. Azni, Arsenic toxicity, health hazards and removal techniques from water: an overview, Desalination. 217 (2007) 139–166. doi:10.1016/j.desal.2007.01.015.

[31] V.K. Sharma, M. Sohn, Aquatic arsenic: Toxicity, speciation, transformations, and remediation, Environ. Int. 35 (2009) 743–759. doi:10.1016/j.envint.2009.01.005.

[32] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418. doi:10.1016/j.jenvman.2010.11.011.

[33] O. Gibert, J. de Pablo, J.L.L. Cortina, C. Ayora, Treatment of acid mine drainage by sulphate-reducing bacteria using permeable reactive barriers: A review from laboratory to full-scale experiments, Rev. Environ. Sci. Biotechnol. 1 (2002) 327–333. doi:10.1023/A:1023227616422.

[34] C.-M. Neculita, G.J. Zagury, B. Bussière, Passive Treatment of Acid Mine Drainage in Bioreactors using Sulfate-Reducing Bacteria: Critical review and research needs, J. Environ. Qual. 36 (2007) 1–16. doi:10.2134/jeq2006.0066.

[35] European Commission, Communication from the Commission - Towards a circular economy: A zero waste programme for Europe, 2014.

[36] Spire, SPIRE 2050 Vision. Towards the Next Generation of European Process Industries, (2019). https://www.spire2030.eu/what/walking-the-spire-roadmap/spire-2050-vision.

[37] U. Wingenfelder, C. Hansen, G. Furrer, R. Schulin, Removal of heavy metals from mine waters by natural zeolites, Environ. Sci. Technol. 39 (2005) 4606–4613.

doi:10.1021/es048482s.

[38] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, Water Res. 18 (1984) 1501–1507. doi:10.1016/0043-1354(84)90124-6.

[39] M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren, D.E. Shanks, Removal of Heavy Metals and Other Cations from Wastewater Using Zeolites, Sep. Sci. Technol. 25 (1990) 13–15. doi:10.1080/01496399008050409.

[40] IBC Advanced Technologies, Superlig Products, (n.d.). http://www.ibcmrt.com/products/superlig/ (accessed November 16, 2020).

[41] Koch Separation Technologies, BARS, AsRU and SSU Ion Exchange, (n.d.). https://www.kochseparation.com/technologies/ion-exchange/bars-asru-and-ssu-ion-exchange/ (accessed November 16, 2020).

[42] M.J. Hatch, J.A. Dillon, ACID RETARDATION A Simple Physical Method for Separation of Strong Acids from Their Salts, I&EC Process Des. Dev. 2 (1963) 253–263.

[43] E. Petkova, H. Vassilev, V. Shkodrova, Separation of waste plating solution sulphuric acid from metal cations by anion exchange, Hydrometallurgy. 6 (1981) 291–297.

[44] F.J. Alguacil, F.A. López, The extraction of mineral acids by the phosphine oxide Cyanex 923, Hydrometallurgy. 42 (1996) 245–255. doi:10.1016/0304-386X(95)00101-L.

[45] U. Kerney, Treatment of spent pickling acids from hot dip galvanizing, Resour. Conserv. Recycl. 10 (1994) 145–151. doi:10.1016/0921-3449(94)90047-7.

[46] M. Wisniewski, Extraction of arsenic from sulphuric acid solutions by Cyanex 923, Hydrometallurgy. 46 (2003) 235–241. doi:10.1016/s0304-386x(97)90003-7.

[47] R. Castro-Muñoz, Breakthroughs on tailoring pervaporation membranes for water desalination: A review, Water Res. 187 (2020) 116428. doi:10.1016/j.watres.2020.116428.

[48] M. Mulder, Basic Principles of Membrane Technology, Springer Netherlands, 1996. doi:10.1007/978-94-009-1766-8.

[49] R.W. Baker, Membrane Technology and Applications, 2nd ed., John Wiley & Sons, 2004.

[50] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review : Recent advances and future prospects, Desalination. 356 (2015) 226–254. doi:10.1016/j.desal.2014.10.043.

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

[52] M. Mullett, R. Fornarelli, D. Ralph, Nanofiltration of mine water: impact of feed pH and membrane charge on resource recovery and water discharge, Membranes (Basel). 4 (2014) 163–180. doi:10.3390/membranes4020163.

[53] D.L. Oatley-Radcliffe, M. Walters, T.J. Ainscough, P.M. Williams, A.W. Mohammad, N. Hilal, Nanofiltration membranes and processes: A review of research trends over the past decade, J. Water Process Eng. 19 (2017) 164–171. doi:10.1016/j.jwpe.2017.07.026.

[54] S. Bandini, D. Vezzani, Nanofiltration modeling: The role of dielectric exclusion in membrane characterization, Chem. Eng. Sci. 58 (2003) 3303–3326. doi:10.1016/S0009-2509(03)00212-4.

[55] T.J.K. Visser, S.J. Modise, H.M. Krieg, K. Keizer, The removal of acid sulphate pollution by nanofiltration, Desalination. 140 (2001) 79–86.

[56] G.T. Ballet, A. Hafiane, M. Dhahbi, Influence of operating conditions on the retention of

phosphate in water by nanofiltration, J. Memb. Sci. 290 (2007) 164–172. doi:10.1016/j.memsci.2006.12.046.

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

[58] J. López, M. Reig, A. Yaroshchuk, E. Licon, O. Gibert, J.L. Cortina, Experimental and theoretical study of nanofiltration of weak electrolytes: SO 4 2– /HSO 4 – /H + system, J. Memb. Sci. 550 (2018) 389–398. doi:10.1016/j.memsci.2018.01.002.

[59] G. Shang, G. Zhang, C. Gao, W. Fu, L. Zeng, A novel nanofiltration process for the recovery of vanadium from acid leach solution, Hydrometallurgy. 142 (2014) 94–97. doi:10.1016/j.hydromet.2013.11.007.

[60] M. Hoyer, D. Zabelt, R. Steudtner, V. Brendler, R. Haseneder, J.U. Repke, Influence of speciation during membrane treatment of uranium contaminated water, Sep. Purif. Technol. 132 (2014) 413–421. doi:10.1016/j.seppur.2014.05.044.

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

[62] A.R. Guastalli, J. Labanda, J. Llorens, Separation of phosphoric acid from an industrial rinsing water by means of nanofiltration, Desalination. 243 (2009) 218–228. doi:10.1016/j.desal.2008.04.024.

[63] H. Diallo, M. Rabiller-Baudry, K. Khaless, B. Chaufer, On the electrostatic interactions in the transfer mechanisms of iron during nanofiltration in high concentrated phosphoric acid, J. Memb. Sci. 427 (2013) 37–47. doi:10.1016/j.memsci.2012.08.047.

[64] K. Meschke, B. Daus, R. Haseneder, J.U. Repke, Strategic elements from leaching solutions by nanofiltration – Influence of pH on separation performance, Sep. Purif. Technol. 184 (2017) 264–274. doi:10.1016/j.seppur.2017.04.048.

[65] K. Meschke, N. Hansen, R. Hofmann, R. Haseneder, J.U. Repke, Characterization and performance evaluation of polymeric nanofiltration membranes for the separation of strategic elements from aqueous solutions, J. Memb. Sci. 546 (2018) 246–257. doi:10.1016/j.memsci.2017.09.067.

[66] A. Werner, A. Rieger, M. Mosch, R. Haseneder, J.U. Repke, Nanofiltration of indium and germanium ions in aqueous solutions: Influence of pH and charge on retention and membrane flux, Sep. Purif. Technol. 194 (2018) 319–328. doi:10.1016/j.seppur.2017.11.006.

[67] Y.A. Boussouga, H. Frey, A.I. Schäfer, Removal of arsenic(V) by nanofiltration: Impact of water salinity, pH and organic matter, J. Memb. Sci. 618 (2021) 118631. doi:10.1016/j.memsci.2020.118631.

[68] C.-M. Zhong, Z.-L. Xu, X.-H. Fang, L. Cheng, Treatment of Acid Mine Drainage (AMD) by Ultra-Low-Pressure Reverse Osmosis and Nanofiltration, Environ. Eng. Sci. 24 (2007) 1297–1306. doi:10.1089/ees.2006.0245.

[69] H. Al-Zoubi, A. Rieger, P. Steinberger, W. Pelz, R. Haseneder, G. Härtel, Optimization Study for Treatment of Acid Mine Drainage Using Membrane Technology, Sep. Sci. Technol. 45 (2010) 2004–2016. doi:10.1080/01496395.2010.480963.

[70] H. Al-Zoubi, A. Rieger, P. Steinberger, W. Pelz, R. Haseneder, G. Härtel, Nanofiltration of Acid Mine Drainage, Desalin. Water Treat. 21 (2010) 148–161. doi:10.5004/dwt.2010.1316.

[71] R. Fornarelli, M. Mullett, D. Ralph, Factors influencing nanofiltration of acid mine drainage, Reliab. Mine Water Technol. (2013) 563–568.

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

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

[74] L. Pino, E. Beltran, A. Schwarz, M.C. Ruiz, R. Borquez, Optimization of nanofiltration for treatment of acid mine drainage and copper recovery by solvent extraction, Hydrometallurgy. 195 (2020) 105361. doi:10.1016/j.hydromet.2020.105361.

[75] M. Nyström, J. Tanninen, M. Mänttäri, Separation of metal sulfates and nitrates from their acids using nanofiltration, Membr. Technol. 2000 (2000) 5–9. doi:10.1016/S0958-2118(00)86633-1.

[76] P.K. Eriksson, L.A. Lien, D.H. Green, Membrane technology for treatment of wastes containing dissolved metals, in: V. Ramachandram, C.C. Nesbitt (Eds.), Second Int. Symp. Extr. Process. Treat. Minimization Wastes, 1996: pp. 649–658.

[77] M.P. González, R. Navarro, I. Saucedo, M. Avila, J. Revilla, C. Bouchard, Purification of phosphoric acid solutions by reverse osmosis and nanofiltration, Desalination. 147 (2002) 315–320. doi:10.1016/S0011-9164(02)00558-1.

[78] H.J. Skidmore, K.J. Hutter, Methods of purifying phosphoric acid, US 5945000 A, 1999. https://www.google.es/patents/US5945000?dq=purification+of+aqueous+phosphoric+

acid+by+hot+filtration+using+a+polyamide+nanofilter&hl=es&sa=X&ved=0ahUKEwiA8Z2CxKfLAhWDVRQKHYXxCm4Q6AEIHDAA (accessed March 4, 2016).

[79] M. V. Galiana-Aleixandre, A. Iborra-Clar, A. Bes-Piá, J.A. Mendoza-Roca, B. Cuartas-Uribe, M.I. Iborra-Clar, Nanofiltration for sulfate removal and water reuse of the pickling and tanning processes in a tannery, Desalination. 179 (2005) 307–313. doi:10.1016/j.desal.2004.11.076.

[80] M. V. Galiana-Aleixandre, J.A. Mendoza-Roca, A. Bes-Piá, Reducing sulfates concentration in the tannery effluent by applying pollution prevention techniques and nanofiltration, J. Clean. Prod. 19 (2011) 91–98. doi:10.1016/j.jclepro.2010.09.006.

[81] C.-V. Gherasim, P. Mikulášek, Influence of operating variables on the removal of heavy metal ions from aqueous solutions by nanofiltration, Desalination. 343 (2014) 67–74. doi:10.1016/j.desal.2013.11.012.

[82] J. Tanninen, M. Mänttäri, M. Nyström, Nanofiltration of concentrated acidic copper sulphate solutions, Desalination. 189 (2006) 92–96. doi:10.1016/j.desal.2005.06.017.

[83] J. Tanninen, M. Mänttäri, M. Nyström, Effect of electrolyte strength on acid separation with NF membranes, J. Memb. Sci. 294 (2007) 207–212. doi:10.1016/j.memsci.2007.02.042.

[84] J. Tanninen, S. Platt, M. Nyström, Nanofiltration of sulphuric acid from metal sulphate solutions, Proc. Imstec 2003, Sydney. (2003) 1–6.

[85] A. Manis, K. Soldenhoff, E. Jusuf, F. Lucien, Separation of copper from sulfuric acid by nanofiltration, in: Fifth Int. Membr. Sci. Technol. Conf., 2003.

[86] L.M. Ortega, R. Lebrun, J.F. Blais, R. Hausler, P. Drogui, Effectiveness of soil washing, nanofiltration and electrochemical treatment for the recovery of metal ions coming

from a contaminated soil, Water Res. 42 (2008) 1943–1952. doi:10.1016/j.watres.2007.11.025.

[87] S. Gomes, S.A. Cavaco, M.J. Quina, L.M. Gando-Ferreira, Nanofiltration process for separating Cr(III) from acid solutions: Experimental and modelling analysis, Desalination. 254 (2010) 80–89. doi:10.1016/j.desal.2009.12.010.

[88] T. Schütte, C. Niewersch, T. Wintgens, S. Yüce, Phosphorus recovery from sewage sludge by nanofiltration in diafiltration mode, J. Memb. Sci. 480 (2015) 74–82. doi:10.1016/j.memsci.2015.01.013.

[89] J. López, M. Reig, O. Gibert, J.L. Cortina, Increasing sustainability on the metallurgical industry by integration of membrane nanofiltration processes: Acid recovery, Sep. Purif. Technol. 226 (2019) 267–277. doi:10.1016/j.seppur.2019.05.100.

[90] S. Platt, M. Nyström, A. Bottino, G. Capannelli, Stability of NF membranes under extreme acidic conditions, J. Memb. Sci. 239 (2004) 91–103. doi:10.1016/j.memsci.2003.09.030.

[91] R. Navarro, M.P. González, I. Saucedo, M. Avila, P. Prádanos, F. Martínez, A. Martín, A. Hernández, Effect of an acidic treatment on the chemical and charge properties of a nanofiltration membrane, J. Memb. Sci. 307 (2008) 136–148. doi:10.1016/j.memsci.2007.09.015.

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

[93] B.C. Ricci, C.D. Ferreira, L.S. Marques, S.S. Martins, B.G. Reis, M.C.S. Amaral,

Assessment of the chemical stability of nanofiltration and reverse osmosis membranes employed in treatment of acid gold mining effluent, Sep. Purif. Technol. 174 (2017) 301–311. doi:10.1016/j.seppur.2016.11.007.

[94] B.M. Jun, S.H. Kim, S.K. Kwak, Y.N. Kwon, Effect of acidic aqueous solution on chemical and physical properties of polyamide NF membranes, Appl. Surf. Sci. 444 (2018) 387–398. doi:10.1016/j.apsusc.2018.03.078.

[95] Y. Zeng, L. Wang, L. Zhang, J.Q. Yu, An acid resistant nanofiltration membrane prepared from a precursor of poly(s-triazine-amine) by interfacial polymerization, J. Memb. Sci. 546 (2018) 225–233. doi:10.1016/j.memsci.2017.10.022.

[96] H.M. Park, H. Takaba, Y.T. Lee, Preparation and characterization of TFC NF membrane with improved acid resistance behavior, J. Memb. Sci. 616 (2020) 118620. doi:10.1016/j.memsci.2020.118620.

[97] T. Yun, S.Y. Kwak, Recovery of hydrochloric acid using positively-charged nanofiltration membrane with selective acid permeability and acid resistance, J. Environ. Manage. 260 (2020) 110001. doi:10.1016/j.jenvman.2019.110001.

[98] M.G. Elshof, W.M. de Vos, J. de Grooth, N.E. Benes, On the long-term pH stability of polyelectrolyte multilayer nanofiltration membranes, J. Memb. Sci. 615 (2020) 118532. doi:10.1016/j.memsci.2020.118532.

[99] M.G. Shin, S.J. Kwon, H. Park, Y.I. Park, J.H. Lee, High-performance and acid-resistant nanofiltration membranes prepared by solvent activation on polyamide reverse osmosis membranes, J. Memb. Sci. 595 (2020) 117590. doi:10.1016/j.memsci.2019.117590.

[100] L. Yu, Y. Zhang, L. Xu, Q. Liu, B. Borjigin, D. Hou, J. Xiang, J. Wang, One step prepared

Janus acid-resistant nanofiltration membranes with opposite surface charges for acidic wastewater treatment, Sep. Purif. Technol. 250 (2020) 117245. doi:10.1016/j.seppur.2020.117245.

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

[102] S.M. Samaei, S. Gato-Trinidad, A. Altaee, The application of pressure-driven ceramic membrane technology for the treatment of industrial wastewaters – A review, Sep. Purif. Technol. 200 (2018) 198–220. doi:10.1016/j.seppur.2018.02.041.

[103] V. Gitis, G. Rothenberg, Ceramic Membranes. New opportunities and Practical Applications, 1st ed., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2016. doi:10.1002/9783527696550.

[104] S. Benfer, U. Popp, H. Richter, C. Siewert, G. Tomandl, Development and characterization of ceramic nanofiltration membranes, Sep. Purif. Technol. 22–23 (2001) 231–237. doi:10.1016/S1383-5866(00)00133-7.

[105] I. Voigt, G. Fischer, P. Puhlfürß, M. Schleifenheimer, M. Stahn, TiO2-NF-membranes on capillary supports, Sep. Purif. Technol. 32 (2003) 87–91. doi:10.1016/S1383-5866(03)00064-9.

[106] I. Voigt, M. Stahn, S. Wöhner, A. Junghans, J. Rost, W. Voigt, Integrated cleaning of coloured waste water by ceramic NF membranes, Sep. Purif. Technol. 25 (2001) 509–512. doi:10.1007/978-3-642-54734-2.

[107] S.S. Wadekar, R.D. Vidic, Comparison of ceramic and polymeric nanofiltration membranes for treatment of abandoned coal mine drainage, Desalination. 440 (2018)

135–145. doi:10.1016/j.desal.2018.01.008.

[108] J. López, M. Reig, X. Vecino, O. Gibert, J.L. Cortina, Comparison of acid-resistant ceramic and polymeric nanofiltration membranes for acid mine waters treatment, Chem. Eng. J. 382 (2020) 122786. doi:10.1016/j.cej.2019.122786.

[109] M. Jafari, M. Vanoppen, J.M.C. van Agtmaal, E.R. Cornelissen, J.S. Vrouwenvelder, A. Verliefde, M.C.M. van Loosdrecht, C. Picioreanu, Cost of fouling in full-scale reverse osmosis and nanofiltration installations in the Netherlands, Desalination. 500 (2021) 114865. doi:10.1016/j.desal.2020.114865.

[110] A. Rieger, P. Steinberger, W. Pelz, R. Haseneder, G. Härtel, Mine water treatment by membrane filtration processes - Experimental investigations on applicability, Desalin. Water Treat. 6 (2009) 54–60. doi:10.5004/dwt.2009.644.

[111] S. Nasir, E. Ibrahim, A.T. Arief, Design and experimental testing of small-scale acid mine drainage treatment plant, J. Mater. Environ. Sci. 7 (2016) 3004–3010.

[112] A.O. Aguiar, L.H. Andrade, B.C. Ricci, W.L. Pires, G.A. Miranda, M.C.S. Amaral, Gold acid mine drainage treatment by membrane separation processes: An evaluation of the main operational conditions, Sep. Purif. Technol. 170 (2016) 360–369. doi:10.1016/j.seppur.2016.07.003.

[113] M.C.S. Amaral, L.B. Grossi, R.L. Ramos, B.C. Ricci, L.H. Andrade, Integrated UF–NF–RO route for gold mining effluent treatment: From bench-scale to pilot-scale, Desalination. 440 (2018) 111–121. doi:10.1016/j.desal.2018.02.030.

[114] K. Ishii, A. Ikeda, T. Takeuchi, J. Yoshiura, M. Nomura, Silica-based ro membranes for separation of acidic solution, Membranes (Basel). 9 (2019). doi:10.3390/membranes9080094.

[115] J. Luo, C. Wu, T. Xu, Y. Wu, Diffusion dialysis-concept, principle and applications, J. Memb. Sci. 366 (2011) 1–16. doi:10.1016/j.memsci.2010.10.028.

[116] C. Wei, X. Li, Z. Deng, G. Fan, M. Li, C. Li, Recovery of H2SO4 from an acid leach solution by diffusion dialysis, J. Hazard. Mater. 176 (2010) 226–230. doi:10.1016/j.jhazmat.2009.11.017.

[117] R. Gueccia, S. Randazzo, D. Chillura Martino, A. Cipollina, G. Micale, Experimental investigation and modeling of diffusion dialysis for HCl recovery from waste pickling solution, J. Environ. Manage. 235 (2019) 202–212. doi:10.1016/j.jenvman.2019.01.028.

[118] W. Li, Y. Zhang, H. Jing, X. Zhu, Y. Wang, Separation and recovery of sulfuric acid from acidic vanadium leaching solution by diffusion dialysis, J. Environ. Chem. Eng. 4 (2016) 1399–1405. doi:10.1016/j.jece.2015.11.038.

[119] J. Jeong, M.S. Kim, B.S. Kim, S.K. Kim, W.B. Kim, J.C. Lee, Recovery of H2SO4 from waste acid solution by a diffusion dialysis method, J. Hazard. Mater. 124 (2005) 230–235. doi:10.1016/j.jhazmat.2005.05.005.

[120] R. Gueccia, A.R. Aguirre, S. Randazzo, A. Cipollina, G. Micale, Diffusion dialysis for separation of hydrochloric acid, iron and zinc ions from highly concentrated pickling solutions, Membranes (Basel). 10 (2020) 1–17. doi:10.3390/membranes10060129.

[121] J. Xu, D. Fu, S. Lu, The recovery of sulphuric acid from the waste anodic aluminum oxidation solution by diffusion dialysis, Sep. Purif. Technol. 69 (2009) 168–173. doi:10.1016/j.seppur.2009.07.015.

[122] K. Wang, Y. Zhang, J. Huang, T. Liu, J. Wang, Recovery of sulfuric acid from a stone coal acid leaching solution by diffusion dialysis, Hydrometallurgy. 173 (2017) 9–14. doi:10.1016/j.hydromet.2017.07.005.

[123] F. Luo, X. Zhang, J. Pan, A.N. Mondal, H. Feng, T. Xu, Diffusion dialysis of sulfuric acid in spiral wound membrane modules: Effect of module number and connection mode, Sep. Purif. Technol. 148 (2015) 25–31. doi:10.1016/j.seppur.2015.04.033.

[124] S. Lan, X. Wen, Z. Zhu, F. Shao, C. Zhu, Recycling of spent nitric acid solution from electrodialysis by diffusion dialysis, Desalination. 278 (2011) 227–230. doi:10.1016/j.desal.2011.05.031.

[125] J. Xu, S. Lu, D. Fu, Recovery of hydrochloric acid from the waste acid solution by diffusion dialysis, J. Hazard. Mater. 165 (2009) 832–837. doi:10.1016/j.jhazmat.2008.10.064.

[126] Z. Palatý, A. Žáková, Transport of sulfuric acid through anion-exchange membrane NEOSEPTA-AFN, J. Memb. Sci. 119 (1996) 183–190.

[127] Z. Palatý, A. Žáková, Separation of H2SO4 + CuSO4 mixture by diffusion dialysis, J. Hazard. Mater. 114 (2004) 69–74. doi:10.1016/j.jhazmat.2004.06.023.

[128] Z. Palatý, A. Žáková, Separation of H2SO4 + ZnSO4 mixture by diffusion dialysis, Desalination. 169 (2004) 277–285. doi:10.1016/j.desal.2004.01.001.

[129] Z. Palatý, A. Žáková, P. Doleček, Modelling the transport of Cl- ions through the anion-exchange membrane NEOSEPTA-AFN systems HCl/membrane/H2O and HCl-FeCl3/membrane/H2O, J. Memb. Sci. 165 (2000) 237–249. doi:10.1016/S0376-7388(99)00239-2.

[130] Z. Palatý, A. Žková, Separation of HCl+NiCl2 mixture by diffusion dialysis, Sep. Sci. Technol. 42 (2007) 1965–1983. doi:10.1080/15363830701313362.

[131] Z. Palatý, A. Žáková, Apparent diffusivity of some inorganic acids in anion-exchange membrane, J. Memb. Sci. 173 (2000) 211–223. doi:10.1016/S0376-7388(00)00363-X.

[132] Z. Palatý, A. Žáková, Transport of some strong incompletely dissociated acids through anion-exchange membrane, J. Colloid Interface Sci. 268 (2003) 188–199. doi:10.1016/j.jcis.2003.07.034.

[133] M. Ersoz, I.H. Gugul, a. Sahin, Transport of Acids through Polyether-Sulfone Anion-Exchange Membrane., J. Colloid Interface Sci. 237 (2001) 130–135. doi:10.1006/jcis.2001.7487.

[134] M.I. Khan, M. Khraisheh, F. Almomani, Fabrication and characterization of pyridinium functionalized anion exchange membranes for acid recovery, Sci. Total Environ. 686 (2019) 90–96. doi:10.1016/j.scitotenv.2019.05.481.

[135] W. Ji, X. Ge, N.U. Afsar, Z. Zhao, B. Wu, W. Song, Y. He, L. Ge, T. Xu, In-situ crosslinked AEMs with self-assembled nanostructure for acid recovery, Sep. Purif. Technol. 247 (2020) 116927. doi:10.1016/j.seppur.2020.116927.

[136] W. Ji, B. Wu, Y. Zhu, M. Irfan, N. Ul Afsar, L. Ge, T. Xu, Self-organized nanostructured anion exchange membranes for acid recovery, Chem. Eng. J. 382 (2020) 122838. doi:10.1016/j.cej.2019.122838.

[137] V. Yadav, S.K. Raj, N.H. Rathod, V. Kulshrestha, Polysulfone/graphene quantum dots composite anion exchange membrane for acid recovery by diffusion dialysis, J. Memb. Sci. 611 (2020) 118331. doi:10.1016/j.memsci.2020.118331.

[138] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, J. Memb. Sci. 281 (2006) 70–87. doi:10.1016/j.memsci.2006.05.048.

[139] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, J. Memb. Sci. 396 (2012) 1–21.

doi:10.1016/j.memsci.2011.12.023.

[140] X. Jin, C.Y. Tang, Y. Gu, Q. She, S. Qi, Boric acid permeation in forward osmosis membrane processes: Modeling, experiments, and implications, Environ. Sci. Technol. 45 (2011) 2323–2330. doi:10.1021/es103771a.

[141] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, J. Memb. Sci. 354 (2010) 123–133. doi:10.1016/j.memsci.2010.02.059.

[142] S. Phuntsho, S. Vigneswaran, J. Kandasamy, S. Hong, S. Lee, H.K. Shon, Influence of temperature and temperature difference in the performance of forward osmosis desalination process, J. Memb. Sci. 415–416 (2012) 734–744. doi:10.1016/j.memsci.2012.05.065.

[143] S. You, J. Lu, C.Y. Tang, X. Wang, Rejection of heavy metals in acidic wastewater by a novel thin-film inorganic forward osmosis membrane, Chem. Eng. J. 320 (2017) 532–538. doi:10.1016/j.cej.2017.03.064.

[144] B. Vital, J. Bartacek, J.C. Ortega-Bravo, D. Jeison, Treatment of acid mine drainage by forward osmosis: Heavy metal rejection and reverse flux of draw solution constituents, Chem. Eng. J. 332 (2018) 85–91. doi:10.1016/j.cej.2017.09.034.

[145] B.K. Pramanik, L. Shu, J. Jegatheesan, K. Shah, N. Haque, M.A. Bhuiyan, Rejection of rare earth elements from a simulated acid mine drainage using forward osmosis: The role of membrane orientation, solution pH, and temperature variation, Process Saf. Environ. Prot. 126 (2019) 53–59. doi:10.1016/j.psep.2019.04.004.

[146] J. Choi, S.J. Im, A. Jang, Application of volume retarded osmosis – Low pressure

membrane hybrid process for recovery of heavy metals in acid mine drainage, Chemosphere. 232 (2019) 264–272. doi:10.1016/j.chemosphere.2019.05.209.

[147] F.M. Baena-Moreno, M. Rodríguez-Galán, F. Arroyo-Torralvo, L.F. Vilches, Low-Energy Method for Water-Mineral Recovery from Acid Mine Drainage Based on Membrane Technology: Evaluation of Inorganic Salts as Draw Solutions, Environ. Sci. Technol. (2020). doi:10.1021/acs.est.0c03392.

[148] M. Boucher, N. Turcotte, V. Guillemette, G. Lantagne, A. Chapotot, G. Pourcelly, R. Sandeaux, C. Gavach, Recovery of spent acid by electrodialysis in the zinc hydrometallurgy industry : performance study of different cation-exchange membranes, Hydrometallurgy. 45 (1997) 137–160.

[149] D.C. Buzzi, L.S. Viegas, M.A.S. Rodrigues, A.M. Bernardes, J.A.S. Tenório, Water recovery from acid mine drainage by electrodialysis, Miner. Eng. 40 (2013) 82–89. doi:10.1016/j.mineng.2012.08.005.

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

[151] L. Cifuentes, G. Crisóstomo, J.P. Ibez, J.M. Casas, F. Alvarez, G. Cifuentes, On the electrodialysis of aqueous H2SO4-CuSO4 electrolytes with metallic impurities, J. Memb. Sci. 207 (2002) 1–16. doi:10.1016/S0376-7388(01)00733-5.

[152] L. Cifuentes, I. García, P. Arriagada, J.M. Casas, The use of electrodialysis for metal separation and water recovery from CuSO4-H2SO4-Fe solutions, Sep. Purif. Technol. 68 (2009) 105–108. doi:10.1016/j.seppur.2009.04.017.

[153] A. Chekioua, R. Delimi, Purification of H2SO4 of Pickling Bath Contaminated by Fe(II)

Ions Using Electrodialysis Process, Energy Procedia. 74 (2015) 1418–1433. doi:10.1016/j.egypro.2015.07.789.

[154] P. Sistat, G. Pourcelly, C. Gavach, N. Turcotte, M. Boucher, Electrodialysis of acid effluents containing metallic divalent salts: Recovery of acid with a cation-exchange membrane modified in situ, J. Appl. Electrochem. 27 (1997) 65–70. doi:10.1023/A:1026419000089.

[155] S.S. Melnikov, O.A. Mugtamov, V.I. Zabolotsky, Study of electrodialysis concentration process of inorganic acids and salts for the two-stage conversion of salts into acids utilizing bipolar electrodialysis, Sep. Purif. Technol. 235 (2020) 116198. doi:10.1016/j.seppur.2019.116198.

[156] G. Sun, J. Xu, Treatment of waste phosphoric acid containing metal ions by electrodialysis, Adv. Mater. Res. 455–456 (2012) 1228–1231. doi:10.4028/www.scientific.net/AMR.455-456.1228.

[157] X. Zhang, C. Li, X. Wang, Y. Wang, T. Xu, Recovery of hydrochloric acid from simulated chemosynthesis aluminum foils wastewater: An integration of diffusion dialysis and conventional electrodialysis, J. Memb. Sci. 409–410 (2012) 257–263. doi:10.1016/j.memsci.2012.03.062.

[158] A. Campione, L. Gurreri, M. Ciofalo, G. Micale, A. Tamburini, A. Cipollina, Electrodialysis for water desalination: A critical assessment of recent developments on process fundamentals, models and applications, Desalination. 434 (2018) 121–160. doi:10.1016/j.desal.2017.12.044.

[159] Y. Liu, X. Ke, H. Zhu, R. Chen, X. Chen, X. Zheng, Y. Jin, B. Van der Bruggen, Treatment of raffinate generated via copper ore hydrometallurgical processing using a bipolar membrane electrodialysis system, Chem. Eng. J. 382 (2020) 122956.

doi:10.1016/j.cej.2019.122956.

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

[161] L. Cifuentes, C. Mondaca, J.M. Casas, The effectiveness of membrane systems for the separation of anolyte and catholyte in a lab-scale copper electrowinning cell based on reactive electrodialysis, Miner. Eng. 17 (2004) 803–809. doi:10.1016/j.mineng.2004.01.010.

[162] L. Cifuentes, M. Grágeda, G. Crisóstomo, Electrowinning of copper in two- and three-compartment reactive electrodialysis cells, Chem. Eng. Sci. 61 (2006) 3623–3631. doi:10.1016/j.ces.2006.01.008.

[163] L. Cifuentes, J.M. Casas, J. Simpson, Modelling the effect of temperature and time on the performance of a copper electrowinning cell based on reactive electrodialysis, Chem. Eng. Sci. 63 (2008) 1117–1130. doi:10.1016/j.ces.2007.11.004.

[164] L. Cifuentes, J.M. Castro, G. Crisóstomo, J.M. Casas, J. Simpson, Modelling a copper electrowinning cell based on reactive electrodialysis, Appl. Math. Model. 31 (2007) 1308–1320. doi:10.1016/j.apm.2006.02.016.

[165] T.Z. Sadyrbaeva, Separation of cobalt(II) from nickel(II) by a hybrid liquid membrane-electrodialysis process using anion exchange carriers, Desalination. 365 (2015) 167–175. doi:10.1016/j.desal.2015.02.036.

[166] M. Khayet, Membranes and theoretical modeling of membrane distillation: A review, Adv. Colloid Interface Sci. 164 (2011) 56–88. doi:10.1016/j.cis.2010.09.005.

[167] E. Drioli, A. Ali, F. Macedonio, Membrane distillation: Recent developments and

perspectives, Desalination. 356 (2015) 56–84. doi:10.1016/j.desal.2014.10.028.

[168] A.F.S. Foureaux, V.R. Moreira, Y.A.R. Lebron, L.V.S. Santos, M.C.S. Amaral, Direct contact membrane distillation as an alternative to the conventional methods for value-added compounds recovery from acidic effluents: A review, Sep. Purif. Technol. 236 (2020) 116251. doi:10.1016/j.seppur.2019.116251.

[169] A. Alkhudhiri, N. Darwish, N. Hilal, Membrane distillation: A comprehensive review, Desalination. 287 (2012) 2–18. doi:10.1016/j.desal.2011.08.027.

[170] G. Zhang, Q. Zhang, K. Zhou, Study on concentrating sulfuric acid solution by vacuum membrane distillation, J. Cent. South Univ. Technol. 6 (1999) 99–102. doi:10.1007/s11771-999-0007-5.

[171] G. Caputo, C. Felici, P. Tarquini, A. Giaconia, S. Sau, Membrane distillation of HI / H2 O and H2 SO4 / H2 O mixtures for the sulfur-iodine thermochemical process, Int. J. Hydrogen Energy. 32 (2007) 4736–4743. doi:10.1016/j.ijhydene.2007.07.011.

[172] M. Tomaszewska, A. Mientka, Separation of HCl from HCl-H2SO4 solutions by membrane distillation, Desalination. 240 (2009) 244–250. doi:10.1016/j.desal.2007.10.093.

[173] R. Thiruvenkatachari, M. Manickam, T. Ouk Kwon, I. Shik Moon, J. Woo Kim, Separation of water and nitric acid with porous hydrophobic membrane by air gap membrane distillation (AGMD), Sep. Sci. Technol. 41 (2006) 3187–3199. doi:10.1080/01496390600854651.

[174] Z. Si, D. Han, J. Gu, Y. Song, Y. Liu, Exergy analysis of a vacuum membrane distillation system integrated with mechanical vapor recompression for sulfuric acid waste treatment, Appl. Therm. Eng. 178 (2020) 115516.

doi:10.1016/j.applthermaleng.2020.115516.

[175] J.Y. Kim, C.H. Shin, H. Choi, W. Bae, Recovery of phosphoric acid from mixed waste acids of semiconductor industry by diffusion dialysis and vacuum distillation, Sep. Purif. Technol. 90 (2012) 64–68. doi:10.1016/j.seppur.2012.02.013.

[176] X. Feng, L.Y. Jiang, Y. Song, Titanium white sulfuric acid concentration by direct contact membrane distillation, Chem. Eng. J. 285 (2016) 101–111. doi:10.1016/j.cej.2015.09.064.

[177] M. Tomaszewska, M. Gryta, A.W. Morawski, The influence of salt in solutions on hydrochloric acid recovery by membrane distillation, Sep. Purif. Technol. 14 (1998) 183–188. doi:10.1016/S1383-5866(98)00073-2.

[178] M. Tomaszewska, M. Gryta, A.W. Morawski, Mass transfer of HCl and H2O across the hydrophobic membrane during membrane distillation, J. Memb. Sci. 166 (2000) 149–157. doi:10.1016/S0376-7388(99)00263-X.

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

[180] S. Ryu, G. Naidu, M.A. Hasan Johir, Y. Choi, S. Jeong, S. Vigneswaran, Acid mine drainage treatment by integrated submerged membrane distillation–sorption system, Chemosphere. 218 (2019) 955–965. doi:10.1016/j.chemosphere.2018.11.153.

[181] S.C. Ryu, G. Naidu, H. Moon, S. Vigneswaran, Selective copper recovery by membrane distillation and adsorption system from synthetic acid mine drainage, Chemosphere. 260 (2020) 127528. doi:10.1016/j.chemosphere.2020.127528.

[182] U.K. Kesieme, N. Milne, C.Y. Cheng, H. Aral, M. Duke, Recovery of water and acid from leach solutions using direct contact membrane distillation, Water Sci. Technol. 69 (2014) 868–875. doi:10.2166/wst.2013.788.

[183] Y.P. Jimenez, M. Ulbricht, Recovery of Water from Concentration of Copper Mining Effluents Using Direct Contact Membrane Distillation, Ind. Eng. Chem. Res. 58 (2019) 19599–19610. doi:10.1021/acs.iecr.9b02499.

[184] J. Cai, F. Guo, Mass transfer during membrane distillation treatment of wastewater from hot-dip galvanization, Sep. Purif. Technol. 235 (2020) 116164. doi:10.1016/j.seppur.2019.116164.

[185] G. Chen, L. Tan, M. Xie, Y. Liu, Y. Lin, W. Tan, M. Huang, Direct contact membrane distillation of refining waste stream from precious metal recovery: Chemistry of silica and chromium (III) in membrane scaling, J. Memb. Sci. 598 (2020) 117803. doi:10.1016/j.memsci.2019.117803.

[186] J. Tang, K. Zhou, Hydrochloric acid recovery from rare earth chloride solutions by vacuum membrane distillation, Rare Met. 25 (2006) 287–292. doi:10.1016/S1001-0521(06)60055-7.

[187] M. Tomaszewska, M. Gryta, A.W. Morawski, Recovery of hydrochloric acid from metal pickling solutions by membrane distillation, Sep. Purif. Technol. 22–23 (2001) 591–600. doi:10.1016/S1383-5866(00)00164-7.

[188] G. Chen, L. Tan, M. Xie, Y. Liu, Y. Lin, W. Tan, M. Huang, Direct contact membrane distillation of refining waste stream from precious metal recovery: Chemistry of silica and chromium (III) in membrane scaling, J. Memb. Sci. 598 (2020) 117803. doi:10.1016/j.memsci.2019.117803.

[189] URS Infrastructure & Environment UK Limited, The Coal Authority-Metal Mine Water Treatment Review, (n.d.). https://www.gov.uk/government/collections/metal-mine-water-treatment.

[190] S.P. Chesters, P. Morton, M. Fazel, Membranes and minewater – waste or revenue stream, in: Proc. IMWA 2016, 2016: pp. 1310–1322.

[191] Pentair, Pentair - Case study BHP Billiton & Anglo American, (n.d.). https://xflow.pentair.com/en/case-studies/witbank (accessed February 4, 2021).

[192] E. Merta, eMalahleni water treatment plant, (n.d.). https://mineclosure.gtk.fi/emalahleni-water-treatment-plant/ (accessed February 5, 2021).

[193] Interstate Technology and Regulatory Council, Mining Waste Treatment Technology Selection. Pressure-driven membrane separation technologies, (2010) 1–33. https://www.itrcweb.org/miningwaste-guidance/to_membrane_sep.htm#case_study.

[194] H. Bayer, Sludge Management and Treatment of Weak Acid or Neutral pH Drainage, in: Proc. 2004 Ontario MEND Work., Sudbury, Ontario, 2004.

[195] S. Mortazavi, Application of Membrane Separation Technology to Mitigation of Mine Effluent and Acidic Drainage, 2008. http://mend-nedem.org/wp-content/uploads/2013/01/3.15.1.pdf.

[196] E. Cséfalvay, V. Pauer, P. Mizsey, Recovery of copper from process waters by nanofiltration and reverse osmosis, Desalination. 240 (2009) 2–6. doi:10.1016/j.desal.2007.11.070.

[197] Pall Corporation, Mine Water Treatment. Filtration and Separation Technologies for Mine Water Treatment, (n.d.).

https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwjcjbWm-tLuAhXTtXEKHV_9DjEQFjABegQIAhAC&url=https%3A%2F%2Fru.pall.com%2Fpdfs%2FIndustrial-Manufacturing%2FMEMWTEN_Pall_Mine_Water_Treatment.pdf&usg=AOvVaw2CehYFcONWeaaE8ZM5Yyqi.

[198] DRA Global, Tweefontein water reclamation plant, (n.d.). https://draglobal.com/projects/tweefontein-water-reclamation-plant/ (accessed February 5, 2021).

[199] Mining News, From waste to resource, (n.d.). https://miningnews.co.za/2019/10/21/from-waste-to-resource/ (accessed February 5, 2021).

[200] Mining Technology, Collahuasi Copper Mine, Northern Chile - Mining Technology | Mining News and Views Updated Daily, (n.d.). https://www.mining-technology.com/projects/collahuasi/ (accessed February 5, 2021).

[201] Water Online, Inseparable dependence, (n.d.). http://www.waterafrica.co.za/index.php/features/effluent-industrial-waste/35-inseparable-dependence (accessed February 5, 2021).

[202] Markets and Markets, Membranes Market by Material (Polymeric, Ceramic), Technology (RO, UF, MF, NF), Application (Water & Wastewater Treatment, Industrial Processing), Region (North America, APAC, Europe, MEA, South America) - Global Forecast to 2024 , (n.d.). https://www.marketsandmarkets.com/Market-Reports/membranes-market-1176.html (accessed February 8, 2021).

[203] Transparency Market Research, Membrane Filtration Market - Global Industry Analysis,

Size, Share, Growth, Trends and Forecast 2017 - 2026, (n.d.). https://www.transparencymarketresearch.com/membrane-filtration-market.html (accessed February 8, 2021).

[204] The Courier, Ceramic Membranes Market Analysis With Key Players, Applications, Trends And Forecasts 2027 || TAMI Industries, Pall Corporation, Atech Innovations GmbH, (n.d.). https://www.mccourier.com/ceramic-membranes-market-analysis-with-key-players-applications-trends-and-forecasts-2027-tami-industries-pall-corporation-atech-innovations-gmbh/ (accessed February 8, 2021).

Highlights

- Mining and hydrometallurgical industries as large generators of acidic liquid wastes
- Current management options do not contemplate their valorisation
- Membrane technologies provide resource recovery options
- New membranes with enhanced properties for long-term industrial operation

Integration of membrane technologies to enhance the sustainability in the treatment of metal-containing acidic liquid wastes. An overview

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Abstract

The mining and hydrometallurgical industries generate effluents characterised by a high acidity (pH < 3) and a high content of metals (e.g. Fe, Al, Cu and Zn, among others) and non-metals (e.g. As, Sb, Bi), which confers them toxicity that makes necessary their treatment. The conventional treatments of such streams mainly rely on neutralisation/precipitation, solvent extraction, ion-exchange and adsorption. However, these options are often not feasible because of their high consumption of chemicals and the generation of large volumes of sludge. On the other hand, due to the exhaustion of natural resources, circular economy schemes are increasingly promoted for the recovery of valuable elements (e.g. Cu, Zn, rare earth elements) from waste effluents as an alternative to mining the already over-exploited mine sites. Within this new paradigm, the integration of membrane technologies are gaining importance for the valorisation of such effluents since they provide the possibility of: i) reducing the volume of the streams to be treated, ii) favour the selective separation of metal ions from acids, and, iii) the concentration of metals in acidic streams. Membrane technologies are promoting the recovery of valuable dissolved components and the reuse of the acid, reducing the generation and disposal of sludge. Among the different membrane technologies, nanofiltration (NF), diffusion dialysis (DD), reverse osmosis (RO), electrodialysis (ED), forward osmosis (FO) and membrane distillation (MD) are the most promising ones to tackle these challenges and promote circularity.

Keywords: acidic effluents; membrane technology; valorisation; circular economy; resource recovery

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Symbols and abbreviations

AEM	Anion Exchange Membrane
AGMD	Air Gap Membrane Distillation
AL-DS	Active layer facing the draw solution
AL-FS	Active layer facing the feed solution
ALW	Acidic Liquid Waste
AMD	Acid Mine Drainage
BMED	Bipolar Membrane Electrodialysis
BPPO	Brominated poly (2,6-dimethyl-1,4-phenylene oxide)
CAGR	Compound Annual Growth Rate
CAPEX	Capital expenditure
CEM	Cation Exchange Membrane
CVD	Chemical Vapour Deposition
DCMD	Direct Contact Membrane Distillation
DD	Diffusion Dialysis
DMAEMA	2-(dimethylamino) ethyl methacrylate
DMSO	Dimethyl Sulfoxide
ED	Electrodialysis
EU	European Union
FO	Forward Osmosis
IEP	Iso-Electric Point
MD	Membrane Distillation
MF	Microfiltration

MP	4-methylpyridine
MVC	Monovalent Selective Cation Membrane
MWCO	Molecular Weight Cut-Off
NF	Nanofiltration
OPEX	Operational expenditure
PGM	Platinum Group Metals
PP	Polypropylene
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene Fluoride
RED	Reactive Electrodialysis
REEs	Rare Earth Elements
RO	Reverse Osmosis
SBR	Sulphate-reducing Bacteria
SED	Selectrodialysis
SPIRE	Sustainable Process Industry through Resource and Energy Efficiency
TDA	Tris(2-(2-methoxyethoxy) ethyl) amine
UF	Ultrafiltration
ULPRO	Ultra-low Pressure Reverse Osmosis
VMD	Vacuum Membrane Distillation
WGMD	Water Gap Membrane Distillation

1. Introduction: management of metal-polluted acidic liquid wastes

1.1. Linear and circular management options

Mining, metallurgical and hydrometallurgical industries generate acidic liquid wastes (ALWs) that are characterised by their low pH and high content in transition metals. The generation of these ALWs may suppose an environmental issued, especially if they are not treated properly and these contaminants (e.g. acid and transition metals) are released to the environment, the destruction of ecosystems, corrosion of infrastructures as well as the water staining can take place. Typical compositions of these waters are collected in **Table 1**. The origin of ALWs can be natural, such as Acid Mine Drainage (AMD) due to the infiltration of water in mines, or industrial, during leaching, electrorefining, pickling or gas scrubbing processes. Such toxicity makes necessary to implement an appropriate treatment to avoid the contamination of ecosystems. Nevertheless, the current management options are not focused on the recovery of added-value products. In this case, circular economic approaches can be implemented for resource recovery.

Table 1. *Mean composition of acidic mining and hydrometallurgical wastewaters*

Origin	Generation	Composition	Ref.
AMD	Oxidation of sulphide minerals	$1<pH<3$ <85 g/L SO_4 <3.5 g/L Fe <3.5 g/L Al <675 mg/L Cu <800 mg/L Zn 80 mM REEs	[1–5]
Leaching	Leaching spent solution, after recovering the elements of interest	<100 g/L H_2SO_4 or HCl <15 g/L Fe $<$ 1g/L Zn, Cu and Ni	[6–9]

Electrorefining	Electrolytic bath to produce Cu 99.99%	140-200 g/L H_2SO_4 40-60 g/L Cu 1-4 g/L Fe	[7,10]
Pickling	Removal of impurities from ferrous and non-ferrous materials	40-200 g/L H_2SO_4 or 80-150 g/L HCl <150 g/L Fe <150 g/LZn	[7,11]
Gas scrubbing	Removal of SO_2(g) and dust	10-500 g/L H_2SO_4 <10 g/L As <2.5 g/L Cu, Zn and Fe <0.05 g/L Hg and Pb <50 mg/L Al, Ni, Cr, Cd, Bi and Sb 0.2-2 g/L HCl 0.1-1g/L HF	[7,12]

One example of ALWs is the AMD, which is generated in the mining industry when sulphide minerals (especially pyrite, FeS_2) are exposed to contact with water and oxygen and then oxidized. AMDs can be generated naturally, but the process can be accelerated because of human activity. Therefore, AMDs can be found in both operating and abandoned poly-sulphide mining sites, including galleries, open pits and mill tailings [13–15]. The oxidation of sulphide minerals produces H_2SO_4, which can dissolve the soil minerals, and finally, an effluent containing mainly metal sulphates (e.g. Fe, Al, Cu and Zn), a low amount of non-metals (e.g. As, Se) and a minor amount of rare earth elements (REEs) is released to the environment [16,17]. REEs, which are included within the list of critical raw materials of the EU, can be found in AMDs, and its recovery is pursued because of their applications in the high-tech industry [18].

Iberian Pyrite Belt is one of the major sources of pyrite worldwide and has been mined from more than 5000 years. Such activity has led to the generation of AMDs, and up to 150 different types of effluents can be found in the Odiel and Tinto basins [1–5]. Usually, REEs are obtained by acidic leaching (mainly with H_2SO_4) of different minerals (bastnaesite, monazite and xenotime), with successive acid neutralisation and solvent extraction stages [19–22]. Nevertheless, the high need for REEs has made necessary to evaluate other secondary resources such as AMDs. For instance, effluents from the Iberian Pyrite Belt discharge watersheds around 1 m^3/s in the dry season, with a mean composition on REEs of 1 mg/L, but it can vary from 0.3 to 11.7 mg/L [3,23,24]. Then AMD can be used for REEs recovery.

The current management option for AMD is the neutralisation/precipitation using an alkali (e.g. lime, caustic lime or limestone). Therefore, acidity is neutralised, and metals precipitate as hydroxides [25,26]. This kind of treatment implies the generation of a voluminous sludge, which is rich in water with a solid content ranging from 2 to 4% and mainly composed of Fe and Al hydroxides, oxyhydroxides and hydroxysulphates (e.g. schwertmannite ($Fe_8O_8(OH)_6SO_4$) at pH>4 or ferrihydrite ($5Fe_2O_3 \cdot 9H_2O$) at pH<4) with minor amounts of other metals (e.g. Zn, Cu, Mn, REEs), which can be adsorbed on or co-precipitate with the precipitated phases. In addition, the sludge should be properly treated in solid-liquid separation units, which can increase the cost of the treatment [16,25–27]. Despite these disadvantages, this method presents a potential recovery of metals by selective precipitation caused by differences in solubilities. For example, Wei et al. [28] evaluated the selective precipitation of Fe and Al using different alkaline reagents (NaOH, Na_2CO_3, NH_4OH, CaO and $Ca(OH)_2$). They were able to recover Fe (98%, purity >93%) at pH 3.5-4.0 and, subsequently, by a further increase of pH to 6.0-7.0, Al precipitated (recovery of 97% with a purity >92%).

Besides, the effectiveness of this method is relatively low with H_2SO_4-rich effluents (10-25%) due to the high alkali consumption. In addition, the presence of non-metals such as As or Se may require a pre-treatment, which usually rely on the use of strong oxidants (O_3, H_2O_2) to oxidise As to As(V) and Se to Se(VI), and their removal by coagulation-precipitation with Al or Fe, ion exchange or electrochemical treatments (for AsH_3 removal) [29–31].

Due to the generation of a water-rich hazardous sludge, which is composed by gypsum, transition metals as hydroxides as well as other impurities (e.g. iron arsenates, Se, Sb, and Bi) [7], that requires an appropriate treatment in addition to the high and continuous consumption of alkalis makes this process not economically viable [16,32]. However, a potential recovery of the acid, although its value is marginal, may imply lower alkali consumption and sludge management costs for its disposal.

For the case of waters with the presence of sulphate, another alternative is the use of Sulphate-reducing bacteria (SBR) under anaerobic for the precipitation of metallic sulphides [33,34]. For example, *Desulfovibrio* and *Desulfotomaculum* are used for such purpose. These bacteria generate sulphide which can precipitate metals, but also at the same time, they lead to an increase in the water alkalinity. Several specific conditions must be present to treat AMDs with SRB, such as: i) pH>5; ii) the presence of an anaerobic media (-200 mV ORP), and; iii) an energy source (organic substrate). SRBs have been mainly studied for in-situ passive remediation of typically small flows of acidic waters for ground-water remediation in the form of permeable reactive barriers [33] or surface bioreactors in wetlands [34].

A reliable management option should consider the subsequent treatment and/or disposal of the generated wastes. The proper management of the generated sludge is, however, one of the main barriers and challenges that require specific consideration and planning. Therefore, a paradigm displacement on the further processing of such hazardous wastes for safe disposal is needed. Efforts could not be allocated to acidity neutralization and should be directed to the development of near-zero liquid and solid waste processes promoting the recovery of water with enough quality for on-site reuse and potential recovery of exploitable by-products from both the ALWs and the resulting residues. In other words, it is necessary to integrate and develop hybrid processes promoting the recovery of industrially profitable by-products.

1.2. The new paradigm of circular management options: the need of integration of concentration and separation technologies

The well-established linear economy model based on a “take-make, consume and dispose of” arrangement in the industry has assumed that there is an unlimited stock of raw materials, which are easy and cheap to obtain and dispose of. Nevertheless, the continuously increasing demand and scarcity of resources, and the consequent environmental degradation, have forced the search for alternative sources of raw materials sought [35].

In the last years, the European Union (EU) has promoted action policies to improve resource efficiency, all of them relying on circular economy models. In comparison to linear economy model, the circular one maintains the added value of products for as long as possible, reducing the need for raw materials and minimising or avoiding the generation of wastes. Nevertheless, in order to implement them is necessary to re-design the value chain, starting from the production until reaching the waste management so the product can be used to create further value at the end of its lifetime. If circular economy schemes are implemented, it is estimated they can bring an economic saving of 630 billion € in the EU industries, by reducing the need for input materials by 17-24% [18,35]. Recently, the EU is promoting circularity through several initiatives, such as the Sustainable Process Industry through Resource and Energy Efficiency (SPIRE) [36]. Furthermore, the EU has identified critical raw materials in terms of their supply risk and economic importance. This first list contained 14 critical raw elements and was enlarged up to 27 in 2017, and it includes REEs, phosphate rock, platinum group metals (PGM) and other elements (e.g. Sb, Bi, Co, In and Mg among others). Mostly, these are important for high-tech products and emerging innovations, and the EU has a lack of primary sources so are mainly imported from China, USA, Russia and Mexico [18]. Therefore, other alternative routes should be found to ensure the supply of critical raw materials.

Despite the application of traditional technologies for the valorisation of ALWs, any of them have not provided solutions regarding the recovery of valuable elements. Nowadays, with the promotion of circular economy and stringent environmental regulations, the recovery of valuable (e.g. Zn, Cu and REEs) and un-valuable (e.g. acid) components from Awls is being pursued.

Ion exchange and adsorption technologies have been applied to treat AMDs by using low-cost sorbents (e.g. natural zeolites) [37–39]. For example, zeolites, with a net negative charge, can be used for the removal of metallic cations from waters. One of the most widely used is the clinoptilolite, which is stable in moderate acidic solutions, but it can suffer degradation ad pH values below 2.0. Blanchard et al. [38] and Zamzow et al. [39] have evaluated the selectivity of zeolites for metal recovery. However, although a large number of studies can be found on the characterization of the equilibrium and kinetics of the metal sorption, there are concerns about the zeolite dissolution along with the sorption and desorption cycles, which limited their study at full scale. In general, most of the developed applications devoted to the treatment of medium to low flow-rate capacities (up to 100 m^3/d) are based on the use of synthetic polymeric ion-exchange resins. Examples of such applications are focused in the metallurgical industry for the recovery of hazardous and/or added-value compounds (e.g. As, Sb, Bi, Se) from strongly acidic solutions. It is worth mentioning the use of highly specific sorbents based on molecular recognition technology and commercialized by IBC (Superlig) [40] for the recovery of Sb and Bi from H_2SO_4 solutions from copper tank house electrolytes, or the use of ion-exchange resins for the same applications commercialized by Koch (BARS, AsRU and SSU) [41].

Acid retardation, based on the sorption of the un-dissociated acid on polymeric ion-exchange resins and its further recovery after water backwashing has been postulated for specific applications in metallurgical and surface treatment industries [12,42,43]. Anion exchange resins (Dowex 1 X8 and Retardation 550WQ2) have been employed for the purification of different acids (e.g. H_2SO_4 and $NiSO_4$, HCl and $FeCl_2$) by Hatch and Dillon [42]. They observed that differences in elution times allowed the separation of the acid and salt. For example, with a mixture containing 176 g/L H_2SO_4 and 38 g/L $NiSO_4$, they were able to recover H_2SO_4 (137 g/L) free of $NiSO_4$. Petkova et al. [43] tested the Wofatit SBW resin for acid recovery from waste plating solutions (H_2SO_4 250-270 g/L, 6-13 g/L Ni, <1 g/L Cu and Fe, <0.5 g/L Zn). They achieved 80% of acid recovery with a low presence of impurities (<2 g/L). Despite the advantages of acid retardation, two disadvantages should be considered: one stage for purifying the acids may be needed, and the regeneration of the resin can increase the cost of the process.

Solvent extraction, typically used in large hydrometallurgical processing stages, is used in specific applications to recover expensive acids and added value metallic ions [44–46]. For example, the extractant Cyanex923 dissolved in toluene can be used for acid recovery (e.g. H_2SO_4, HCl) [44] and its extraction (H^+X^-) by solvating reagents (S_{org}) is explained as a solvation reaction described by equation 1:

$$mH_{aq}^{+} + X_{aq}^{m-} + S_{org} \rightleftarrows HXLS_{org} \qquad (1)$$

Solvent extraction has been applied for treating pickling solutions (10-80 g/L HCl, 80-150 g/L Fe and 5-150 g/L Zn) for the recovery of Zn using tri-octyl-amine or tri-butyl-phosphate extractants [45]. They found that the presence of Fe and pH affected the Zn extraction capacity using solvating extractants. Wisniewski [46] studied the performance of Cyanex 923 (50% diluted in kerosene) for the removal of As from 50-200 g/L H_2SO_4 solutions. The removal of As species (both As(III) and As(V)) was attained, but part of the H_2SO_4 was co-extracted at high acidity levels. As in the previous case, acid can be recovered, but an acid purification unit, as well as regeneration unit for the organic phase, are needed.

1.3. Integration of membrane-based technologies for the recovery of valuable elements from Acidic Liquid Wastes

In the last years, membrane technologies are being preferred in the industry over conventional methods because they can attain similar results as current management options but saving costs. A membrane is a semi-permeable barrier that can separate particles, molecules, solutes or ions regarding their size, charge or diffusivity. As a result, for cross-flow configurations, a permeate (i.e. the stream containing the compounds that have permeated across the membrane) and a concentrate (i.e. the stream containing the compounds that are rejected by the membrane) streams are obtained. Nowadays, membranes are widely applied in many fields, especially for the removal of undesirable compounds from the feed solution such as CO_2(g) from natural gas and salts from seawater for drinking water production. The advantages of membrane processes comprise low to medium energy consumption, medium to high concentration factors, working at mild conditions (pressure and temperature), no need for additives and the easiness to be combined with other separation units. However, membrane fouling, the low lifetime (especially at extreme conditions) and limited selectivity are their main drawbacks [45].

In order to select a suitable membrane technology, it must be taken into account that its performance is affected by the solution composition and its chemical speciation, as well as on the membrane properties. In the scenario of ALWs, and taking into account a circular economy perspective, membrane technologies can be used for: (a) the retention of an added-value solute (either metallic or non-metallic) for its concentration and further separation, and (b) the recovery of a valuable compound (e.g. acid) in the permeate. From the described, properties, the possibility to concentrate streams and to separate given components of interest with a concentration factor are both significant as could reduce in a meaningful way the volumes to be treated and a reduction of the recovery units.

This review is focused on the application of membrane technologies for the valorisation of ALWs within the last 20 years. **Figure 1** shows the growth research activity regarding the application of membrane technologies to valorise acidic effluents. Among the different membrane technologies, nanofiltration (NF), diffusion dialysis (DD), reverse osmosis (RO), electrodialysis (ED), forward osmosis (FO) and membrane distillation (MD) are the most promising ones to tackle these challenges. Other technologies, such as pervaporation, which has proven to be useful for seawater desalination, have not been applied to acidic liquid effluents [47].

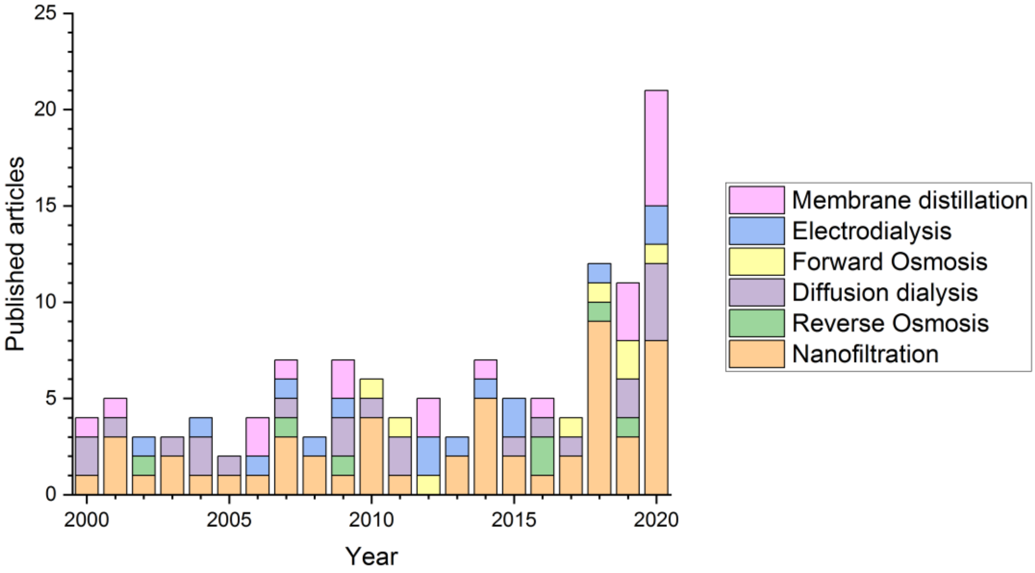

Figure 1. *Articles published involving the treatment of acidic liquid effluents with membrane technologies from 2000 to present. Source: Scopus*

2. Pressure-driven membrane processes

Regarding pressure-driven membranes, they can be classified according to their effective pore size. For instance, Microfiltration (MF) is used to filter colloids and bacteria from 0.1 to 10 µm. Ultrafiltration (UF) allows to remove particles even smaller, such as dissolved macromolecules (e.g. proteins, 2-100 nm). The transport mechanism of these two membrane technologies is the sieving through pores. RO even presents a lower effective pore size (<0.5 nm), allowing only the transport of water. It is assumed that these “pores” are not fixed ones; instead, they are originated due to the movement of polymer chains. NF presents characteristic of both UF and RO. It has an effective pore size between 0.5 and 2.0 nm, allowing the removal of dissolved organic matter and multivalent ions. It remains unclear if the transport mechanism is the one of UF or the one of RO membranes [48,49].

2.1. Nanofiltration

NF is a pressure-driven membrane process that presents characteristics of both UF and RO membranes. NF membranes provide high rejection for multi-charged ionic species (>90%), whereas the single-charged ones can permeate across the membrane (**Figure 2**). There is a current discussion regarding NF membrane structure, as it is suggested that presents a dense structure like RO membranes (not fixed pores, a free-volume instead), or instead that it has fixed pores, similarly to UF membranes. In the first case, the transport of species across the membrane is due to differences in diffusivities across the membrane active layer, whereas in the second case size or steric hindrance is the main exclusion mechanism [50,51].

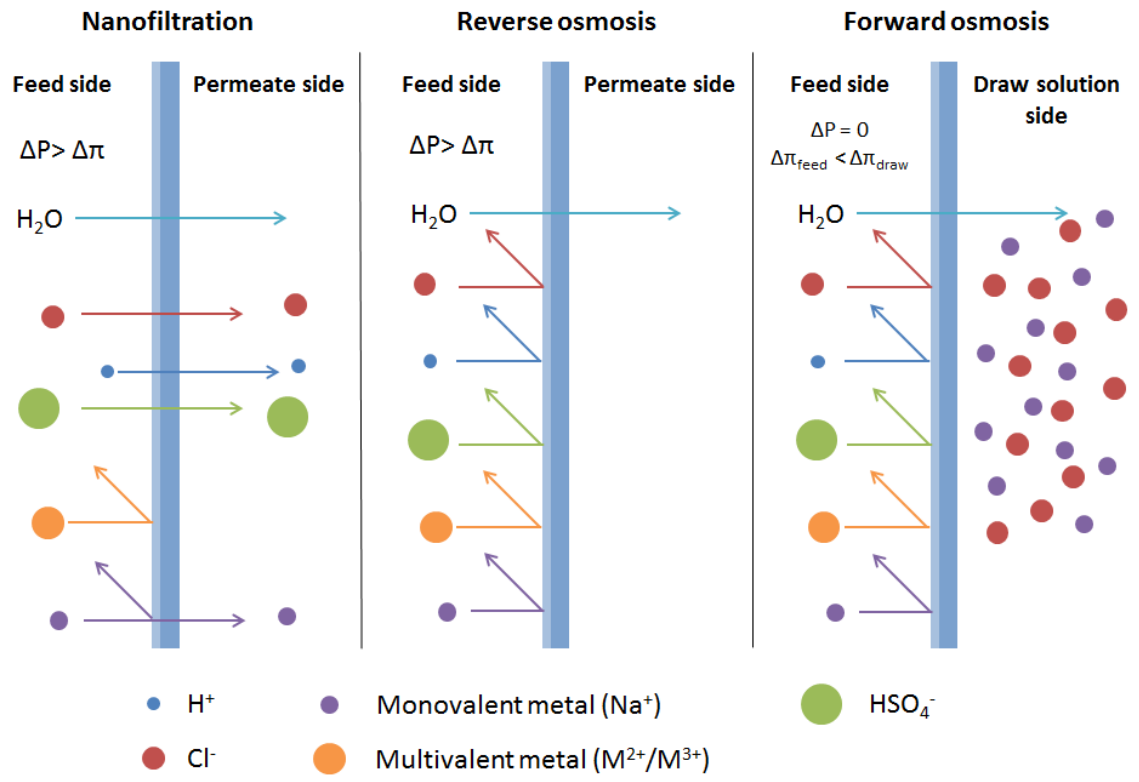

Figure 2. *Schematic representation of nanofiltration, reverse osmosis and forward osmosis membrane processes for the valorisation of acidic waters*

The structure of NF membranes is not fully cross-linked, so functional groups along the surface and inside the active layer are presented. When the membrane is in aqueous solution, these groups can be either protonated or deprotonated. Thus the membrane will present an electric charge. The pH value in which the membrane exhibits no charge is denominated Iso-Electric Point (IEP). If the solution pH is above the IEP, the membrane presents a negative charge and, at pH values below the IEP, the membrane is positively charged [52]. In the case of polyamide-based NF membranes with carboxylic (R-COOH) and amine ($R\text{-}NH_2$) functional groups, at acidic pHs both functional groups will be protonated (R-COOH and $R\text{-}NH_3^+$), conferring the membrane a positively charged surface. Therefore, the anions will be transported across the membrane, whereas anions will be rejected. Instead, at basic pH values, the opposite trend is expected. Carboxylic groups will be deprotonated ($R\text{-}COO^-$) thus, the negatively charged membrane will favour the transport of cations [50,51,53]. Although the selectivity of the NF membranes towards anions or cations, a stoichiometry number of cations or anions should permeate in order to meet the electroneutrality conditions. Then at the acidic pHs of the ALWS, it could be possible to recover purified acids in the permeate.

One issue of importance when treating solutions in NF is the solution speciation, as not all the species are affected in the same way. The main NF membrane exclusion mechanisms are the Donnan and dielectric exclusion. Due to the membrane charge, Donnan exclusion postulates the exclusion of the co-ions (same charge as the membrane). In contrast, the membrane is selective for the ions with opposite charge (counter-ions) [49]. Dielectric exclusion arises due to a difference in the dielectric constant between the solution and the membrane. The higher dielectric constant of the solution than the one of the medium, causes an additional exclusion mechanism for each ion, independently of its sign (positive or negative) [54]. Then, it is expected that multi-charged ions to be better excluded than the monovalent ones. Another exclusion mechanism that should be taken into account is the steric hindrance, especially for those molecules that are not affected by the membrane electric fields, such as neutral species (fully protonated inorganic compounds, H_3PO_4, H_3AsO_4) or organic compounds.

Regarding the effect of speciation, Visser et al. [55] used both aromatic and semi-aromatic polyamide-based NF membranes to study the transport of H_2SO_4. They observed that at $pH>pK_a=1.92$ (predominance of SO_4^{2-} in solution), the acid rejection reached values of 99.9%. However, at lower pH values than the pK_a (predominance of HSO_4^-), rejection dropped to values of 20%. This change in rejection was related to the (1) an inversion of the membrane charge, from negative to positive values, and, (2) the higher amount of HSO_4^-, which according to dielectric exclusion, is less rejected than SO_4^{2-}. H_3PO_4 transport across the NF200 membrane was studied by Ballet et al. [56]. They observed an increase in H_3PO_4 rejection when pH was increased from 40 to 90%, which was related to the lower fraction of $H_2PO_4^-$. Niewersch et al. [57] studied the performance of different NF membranes (Desal DL, DK and NF270) to treat pre-treated sewage and sewage sludge ash at pH ranging from 1 to 4. They observed that acid rejection (H_3PO_4 or H_2SO_4) was minimum at pH 1, which was related to the low degree of acid dissociation and to the membrane positive charge. In recent work, López et al. [58] studied the performance of the NF270 membrane filtering diluted H_2SO_4 from pH 1 to 3 and provided a mathematical model to describe the transport of the acid by means of membrane permeances. The same effect was observed: at pH>pK$_a$ (1.92), the presence of SO_4^{2-} in solution made H_2SO_4 rejections higher (around 80%), whereas at lower pH values these values dropped to 20%.

The speciation of metals should also be considered in the performance of NF membranes. Shang et al. [59] studied the V speciation with the Desal DL and DK membranes at different pH values. They observed that V(V) rejection barely varied from pH 2.5 to 6.5 (98% for DK and 96% DL). In contrast, at higher pHs the shift in equilibrium favoured the presence of lower molecular weight (from $V_{10}O_{28}^{6-}$ to $V_4O_{12}^{4-}$ and $V_3O_9^{3-}$) species, and rejections decreased to 84% for DK and 85% for DL. Hoyer et al. [60] studied the treatment of U-contaminated mining waters with NF, and they observed higher rejections (around 100%) at pH>5 because of the presence of U as high molecular mass species (e.g. $Ca_2UO_2(CO_3)_3$, $UO_2(CO_3)_3^{4-}$).

Additionally, some inorganic solutes can be present in solution as a non-charged species, as is the case of phosphoric acid at pH<2, where H_3PO_4(aq) predominates over $H_2PO_4^-$ [61–66]. Guastalli et al. [62] recovered in the permeate side 56% and 77% of H_3PO_4 from industrial rinsing water containing dissolved Al by using MPF-34 and Desal-DL membranes, respectively. When comparing the rejections of $H_2PO_4^-$ and H_3PO_4 species, the lower rejections of the non-charged species was related to a smaller size than the pores radii. Diallo et al. [63] filtered H_3PO_4 solutions at different concentrations (11.8, 118 and 578 g/L) with the MPF-34 membrane. They observed that rejections varied from 40% at 11.8 g/L to almost zero rejections at 578 g/L due to the higher fraction of the H_3PO_4(aq) species at higher concentrations (i.e. lower pHs). By determining the pore size at these acidic conditions, it was found that the pore size was reduced by a factor of 2 at 578 g/L H_3PO_4. Moreover, the almost zero rejections suggested that there is no size exclusion. Instead, the global rejection of phosphoric acid was governed by the electric effects, such as the interactions between $H_2PO_4^-$ and the membrane. Additionally, Mo and Ge can be presented in solution as neutral species (H_2MoO_4 and $Ge(OH)_4$, respectively) [64,65]. For example, Mo(VI) is found as neutral species (H_2MoO_4) at pH 2, and it was not rejected by the membrane, while the full deprotonation of the molecule (MoO_4^{2-}) at pH 7, increased its rejection (87% for UTC-60 and 75% for NP010). Concerning Ge(IV), which is present in solution as neutral species ($Ge(OH)_4$) in the pH range studied (pH 2-7), rejections were independent of pH and lower than 20%. From the experimental results, the authors determined that the main Mo exclusion mechanism was steric hindrance, whereas the transport for non-charged species was a combination of diffusion and convection. Werner et al. [66] performed a comparative study for In(III) and Ge(IV). They observed similar rejections for Ge(IV) in acidic media (below 15%) because of the presence of $Ge(OH)_4$, whereas In(III) was fully rejected from pH 5 to 12 despite of being present as $In(OH)_3$. At pH of 2, In(III) was mainly found as In^{3+}, which was barely rejected by the membrane (10%) due to its negative charge. The authors related this behaviour to the structure of $Ge(OH)_4$ and $In(OH)_3$. Ge(IV) is coordinated with four OH^- groups in a tetrahedral structure, whereas In(III) is linked to the OH^- groups and surrounded by three water molecules forming a bigger structure. Recently, Boussouga et al. [67] evaluated the influence of both pH (2-12), ionic strength (0.6 – 20 g/L NaCl) and the presence organic matter onto As(V) rejection with NF270 and NF90. They observed that As(V) rejection was dependent of pH for NF270 (10% at pH 2 to 86% at pH 12 for 0.6 g/L NaCl, and from 36% at pH 2 to 78% at pH 12 for 0.6 g/L NaCl), whereas for NF90 it was independent of pH and salinity (93-98%). They related the charge exclusion mechanism for NF270 and size hindrance for NF90. NF has proven to be a suitable technology for the recovery of metals and acids from mining, metallurgical and hydrometallurgical effluents.

The treatment of AMD with NF membranes has already been addressed [52,55,68–71]. Mullet et al. [52] treated an AMD with the NF270 and TriSep TS80 NF membranes, and they observed that at pH values lower than the IEP, the metals were effectively rejected because of the positive membrane charge. Zhong et al. [68] also achieved high metal rejections (>93%) treating a Cu mine effluent (pH 3) with the DK4040F membrane. Al-Zoubi et al. [69] compared the performance of Alfalaval NF99 and Osmonics DK membranes for treating an AMD at pH 2.6. They achieved sulphate rejections higher than 80%, whereas metals were rejected by more than 98%. In a posterior work [70], NF99 and DK showed permeate fluxes of 75 and 60 LMH, respectively and rejections for metals and sulphate higher than 98%. Fornarelli et al. [71] obtained high metal rejections (>95% for Ca, Cu, Mg and Mn(III)) with the NF270 at pH lower than 3. These high rejections were related to the charge exclusion (positively charged membrane). Instead, at higher pH values (above IEP), rejections decreased to 89% due to a negatively charged membrane, which was related to the attraction between the cations and membrane. They observed that sulphate rejections decreased from 97% to 89% due to the lower effect of dielectric exclusion on HSO_4^- than on SO_4^{2-}. Data was not provided regarding the transport of H^+. Visser et al. [55] evaluated the performance of NF70 and NF90 for the treatment of an Au mine effluent (pH 4.1). Both membranes showed a good performance in terms of rejections (>90% for sulphate, Cl, Na and Ca). Rejections of H^+ were not given. López et al. [72,73] evaluated the performance of different NF membranes (NF270, Desal DL and HydraCoRe 70pHT) filtering synthetic AMD solutions. They observed that, at different feed water compositions, the polyamide-based membranes (e.g. NF270 and Desal DL) exhibited high metal rejections (>95%). At the same time, the transport of acid was favoured, achieving even negative H^+ rejections. Recently, Pino et al. [74] evaluated the recovery of Cu from AMD (pH 3.5, 0.5 g/L Cu, 0.4 g/L Al and 4.7 g/L SO_4, among others) by combining NF (NF270) and solvent extraction (LIX 84-IC). NF allowed to concentrate Cu up to 2.4 g/L at 80% of permeate recovery, but gypsum scaling might limit the capacity of recovering water.

The application of NF to industrial ALWs has also been studied. Nÿstrom et al. [75] applied the NF-45 for separating sulphate and nitrate salts from acids, achieving high metal rejections (>95%). Erikson et al. [76] achieved high metal rejections (>99% for Fe, Zn, Cd and Cu) and recovered 50% of the acid with NF for treating a stream containing 330 g/L H_2SO_4. Gonzálet et al. [77] studied the purification of H_2SO_4 solutions. A comparison of NF and RO performances concluded that both achieved similar metal rejections (>95% for Fe, Mg and Al, among others) but NF membranes attained higher fluxes (almost 4 times) and higher acid permeation (80%). Skidmore and Hutter [78] patented a method for purifying H_3PO_4 with NF. They achieved metals rejections higher than 90% (for Al, Fe and Mg). They also reported that working at temperatures below 35°C can increase the membrane lifetime from 300 to 2000 h. Galiana-Aleixandre et al. [79,80] applied NF to treat effluents from the tannery industry achieving high removals for sulphate (>97%) and Cr (not specified). Gherasim and Mikulášek [81] studied the performance of AFC80 membrane for Pb removal (>98%). Tanninen et al. [82–84] carried out studies on the filtration of electrolytes mixtures ($CuSO_4$ or $MgSO_4$) at acidic pH (H_2SO_4). With $CuSO_4$-containing solutions, they observed high Cu rejections (> 95 % for NF45, NF270 and Desal-5DK at 30 g/L) at different H_2SO_4 concentrations (5, 10, 20, 40 and 80 g/L), while acid passed easily across the membrane, also exhibiting negative rejections [82]. Moreover, the effect of the H_2SO_4 dissociation (SO_4^{2-}/HSO_4^-, $pK_a = 1.9$) was observed, especially at high acid concentrations [83]. By adding $MgSO_4$ to the solution instead of $CuSO_4$, the Desal-5DK achieved the also a good performance, with high metal rejections (> 98 % and ~90% for Mg and Cu, respectively) and low H_2SO_4 rejections, varying from 17 to 24% [84]. Manis et al. [85] filtered a solution mimicking an effluent from a copper electroplating plant with the MPF-34 and DK membranes. When H_2SO_4 concentration was increased from 0 to 196 g/L, Cu rejection decreased (from 90 to 80% and from 85 to 45%, for DK and MPF34, respectively at 2 g/L) whereas the acid was more transported across the membrane (rejections from 30 to 10 % and from 20 % to 15 % for DK and MPF34, respectively). Changes in acid rejection were related to higher diffusive transport, while variations in Cu rejection were related to changes in the membrane charge. Ortega et al. [86] treated acid leachate (pH 2, HCl or H_2SO_4-NaCl) of soil with the purpose of extracting metals with the Desal-5 DK membrane. With the HCl leachate, metals were effectively rejected (e.g. >85% for Co, Cr, Fe), while H^+ exhibited negative rejections. However, with the H_2SO_4-NaCl leachate, metals were also effectively rejected, but no H^+ negative rejections were observed. Gomes et al. [87] evaluated the separation of Cr(III) (100 mg/L) from HCl or HNO_3 solutions ($2<pH<2.5$) with Desal 5 DK membrane. Results showed Cr(III) rejections ranging from 77 to 86%, with lower anion (e.g. Cl^- and NO_3^-) rejections (from 25 to 40%) and even negative rejections. Schütte et al. [88] evaluated the recovery of phosphorous from sewage sludge with NF membranes (DL, NF270, AS and Duracid). They observed high metal rejections (around 90% for Cu, Ni, Zn, among others), while phosphorous rejections varied from 20 to 70%. Working by diafiltration model (i.e. by semi-continuously rediluting the feed solution), 84% of phosphate was recovered at 90% of permeate recovery with AS membrane at pH 0.5. López et al. [89] evaluated the performance of NF270 for acid recovery from an effluent of a gas scrubber from a copper smelter. High metals rejections (>80%) were observed, while acid was transported across the membrane. However, As also permeated (<40%) because of its presence as a non-charged species (H_3AsO_4). Recently, López et al. [8] evaluated the Duracid membrane for the treatment of acidic effluents from Cu smelters ($0.6<pH<1.6$, 8-15 g/L Fe and 0.7-1.5 g/L, among others). They obtained a permeate mainly composed of H_2SO_4 with a low content of multivalent metals, whereas the main impurity in the acid was Na and As. They also observed a decrease in rejections with pH due to the equilibrium reactions.

One of the main drawbacks of NF membranes with an active-layer made of polyamide is their low stability working in concentrated acidic media since they are susceptible of suffering hydrolysis at long-term exposition [84,85,90–93]. Plat et al. [90] studied the stability of NF45 and Desal DK membranes in HNO_3 and H_2SO_4 solutions under different conditions (temperature, time exposure and acid concentration). Both membranes exhibited worse stability in 50 g/L HNO_3 than in 200 g/L H_2SO_4 after three months of exposure. The effects of the acid attack were remarkably severe at high temperatures. For example, both membranes exhibited near-zero sucrose and glucose rejections after being immersed at 80°C for one month. Manis et al. [85] aged the Desal DK in 196 g/L H_2SO_4 for two months, and after that, they observed an increase in both permeate flux and Cu transport. Navarro et al. [91] studied how Desal 5DL membrane properties (absolute and volume density charge) and performance (rejection and permeate fluxes) were affected after immersion in H_3PO_4 solutions. They concluded that immersion changed the membrane charge as well as its selectivity. For instance, the treatment with H_3PO_4 solutions implied a decrease in the absolute value of zeta potential but also lowers rejections for cation species. Tanninen et al. [84] evaluated the stability of polyamide-based membranes (NF270, Desal KH and Desal-5DK) in H_2SO_4 (20 g/L) at 60°C. From the membranes mentioned above, the Desal-5DK was the first one on suffering hydrolysis, which resulted in higher permeate fluxes (around the double) and lower Cu rejections (from 96% to 77%) after 3 days of immersion. López et al. [92] evaluated the stability of N270 by immersing the membrane in 98 g/L H_2SO_4 for 30 days. Chemical changes quantified by XPS and FTIR-ATR revealed hydrolysis of amide groups that increased the permanent ionised groups and the size of the free volume, reducing the sieving mechanism controlled by the dielectric exclusion. By filtering AMDs with this membrane, a decrease in metal rejections from 99% to 70% was observed, which was related to the weaker effect of dielectric exclusion caused by the higher free volume. Ricci et al. [93] studied the stability of MPF-34 in acidic media by immersing the membrane in an effluent from a gold mine (pH 1.5) and in 15 g/L H_2SO_4 for 2 months. After exposure, an increase in membrane permeability and a decrease in metal rejection were observed, which were related to the acid attack that led to an increase of pore size (from 0.42 nm to 0.61 and 0.74 for both solutions). Jun et al. [94] studied the effect of acid sulphuric (150 g/L, typical concentration of smelting processes) on polyamide membrane's (NE40, NE70, NE90) physical and chemical properties. Characterisation revealed the membrane degradation by acid-catalyzed hydrolysis, converting amide groups into carboxyl and amine groups. Besides, piperazine polyamide semi-aromatic membranes (NE40, NE70) were more unstable than the aromatic polyamide membrane (NE90).

In order to overcome the stability of membranes in acidic media, researchers are developing a new generation of NF membranes. For example, Zeng et al. [95] developed a poly (amide-s-triazine-amine) NF membrane that showed a similar performance before and after being immersed in 5 g/L H_2SO_4 for 720 h ($MgSO_4$ rejection of 94%). No morphological or chemical changes were observed after immersion. Park et al. [96] prepared acid-resistant membranes using piperazine (1 %wt), sulfonated melamine formaldehyde (0.3 %wt) and sulphanilamide (0.5 %wt) through interfacial polymerization. Results showed $MgSO_4$ rejections higher than 96% that decreased by 6% after soaking the membrane in 150 g/L H_2SO_4 for 30 days. Yun et al. [97] developed an acid-resistant membrane via a water-based coating process by introducing a branched-polyethyleneimine layer onto a loose polyethersulfone in a high-humidity atmosphere. The synthesized membrane achieved 95% of Mg rejection, while acid was transported by 70%. Additionally, the membrane maintained its filtration performance 1 month later after immersion in HCl (pH 1.8). Elshof et al. [98] evaluated different combinations of polyelectrolyte multilayer NF membranes for working in high-acidic media (69 g/L HNO_3). The best results were obtained with the combination of strong polycations (poly(diallyldimethylammonium chloride)) and polyanions (poly(styrenesulfonate)), showing little variations on the polyelectrolyte multilayer NF membrane performance after 2 months (permeate flux of 10.7 L/m^{2}h and rejections of 95.5% $MgSO_4$). Shin et al. [99] developed acid-stable polyamide NF membranes with strong polar aprotic solvents (dimethyl sulfoxide (DMSO), dimethylformamide and N-methyl-2-pyrrolidone). The DMSO activated membrane exhibited the same performance for filtering NaCl (rejection of 85%) after being immersed in 150 g/L H_2SO_4 for 4 weeks because of its higher chemical stability due to their fully-aromatic chemistry. Yu et al. [100] synthesized Janus acid-resistant membranes with an opposite charge with polyethyleneimine and cyanuric chloride. With 0.15 g/L cyanuric chloride in the organic solution, the membrane rejected $MgCl_2$ by 95%, whereas the one for Na_2SO_4 was 45%. After soaking the membrane in 30 g/L HCl for 1800 h, the membrane performance did not show any variation.

Nowadays, acid-stable NF membranes are commercialised offering as good rejections as polyamide membranes, such as Hydracore 70pHT (Hydranautics), MPF-34 (Koch Membrane Systems) and Duracid (GE Osmonics) [62,88,101]. Regarding their stability, for example, MPF-34 kept its performance (permeate flux and rejections) after eight weeks immersion in 196 g/L H_2SO_4 [85]. Despite the composition of the active layer of these membranes to be proprietary, it is expected that is any kind of sulphamide or a sulphonated polyether-sulphone.

As an alternative to polymeric NF membranes, ceramic ones can be employed. The active layer is usually made of zirconia (ZrO_2) or titania (TiO_2) and is supported on alumina (Al_2O_3). These membranes offer a higher chemical, mechanical and thermal stability than polymeric ones. Nevertheless, the fabrication costs and low selectivity of ceramic membranes have limited their application at large scale [102,103]. The literature is scarce regarding the application of ceramic NF membranes [104–108]. Benfer et al. [104] utilized the sol-gel method for synthesizing ZrO_2 and TiO_2 based NF membranes. They observed that the ZrO_2 membrane had smaller pore size and narrower distribution (0.75-1.75 nm) than the TiO_2 one (0.5-2.5 nm). When they evaluated the performance of both membranes, the ZrO_2 showed higher rejections than the TiO_2 membrane (27% NaCl and 66% Na_2SO_4 for the former and 6% NaCl and 11% Na_2SO_4 for the latter). Instead, the TiO_2 membrane exhibited higher permeate flux (3 times higher). Voigt et al. [105] fabricated a ceramic membrane made of TiO_2 with a Molecular

Weight Cut-Off (MWCO) of 450 Da (pore size of 0.9 nm) for decolouring textile wastewater, attaining a colour removal of 70-100%. In a posterior work, a TiO_2 NF membrane was developed by a two-step coating process, characterised by a MWCO of 250 Da and water permeability of 10 L/(m^2·h·bar). Wadekar and Vidic [107] treated a coal mine drainage (pH 7.8) with polymeric (NF270) and ceramic (TiO_2, 500 Da MWCO) membranes. They observed that the polymeric membrane achieved higher multi-charged species rejections (>96%) than the ceramic one (50-70%). Recently, López et al. [108] treated an AMD with both polymeric (MPF-34) and ceramic (TiO_2, 1 nm) membranes. As in the previous case, the polymeric one exhibited higher rejections (80%) than the TiO_2 membrane (<30%).

During the treatment of ALWs with NF, membrane fouling can be present. Fouling directly impacts membrane performance (higher pressure drop, lower permeate fluxes and higher salt passages) and cleanings (chemicals such as acids or bases). Besides, the membrane is usually replaced in cases of severe fouling [109]. Due to the high acidic conditions, organic fouling (algae and biofilms, among others) is not likely to happen. Instead, because of the high metal concentrations in AWLs, the precipitation of inorganic mineral phases (i.e. scaling) can take place. For instance, and despite the low pH of ALWs, the precipitation of Fe(III) as hydroxide ($Fe(OH)_3(s)$) or oxyhydroxide (FeOOH(s)), and gypsum ($CaSO_4·2H_2O(s)$) can occur at the membrane surface. Rieger et al. [110] observed the precipitation of gypsum and metal hydroxides when filtering AMW (pH 2.7). Al-Zoubi et al. [70] also reported gypsum formation during the treatment of AMWs (pH 2.5). Recently, López et al. [8] when treating acidic copper effluents (pH 0.83) observed scaling related to calcium sulphate ($CaSO_4(s)$), iron oxyhydroxide (FeOOH(s)) and iron sulphate ($FeSO_4(s)$). Besides, scorodite ($FeAsO_4·2H_2O(s)$) was also found.

2.2. Reverse osmosis

RO is a pressure-driven process which provides rejections higher than 99.9% for dissolved species (both inorganic and organic). Due to its performance in terms of rejections is widely used for water desalination. However, the high osmotic pressure of the acidic waters and the low stability of RO membranes (mostly made of polyamide) make this technology to be not preferred for the valorisation of acidic effluents. **Figure 2** shows a scheme of a RO operating with ALWs.

RO membranes have been tested to treat AMD either directly or following a NF unit. Rieger et al. [110] treated mine water (pH 2.7, 1.1 g/L Al, 2.3 g/L Cu, 0.6 g/L Fe) with a RO membrane (AlfaLaval RO 98Ht). The membrane exhibited rejections higher than 97% for multivalent species, while Na showed the lowest rejection (95%). After the continuous operation at 30 bar, a decline in permeate flux with time was observed, which was related to membrane scaling caused by the relatively high concentrations of Mg (630 mg/L), Ca (325 mg/L) and SO_4 (14 g/L). Al-Zoubi et al. [69] evaluated the HR98PP membrane for the treatment of AMD at different concentration levels. The membrane exhibited rejections around 94%. However, by comparing its performance with NF membranes (NF99 and DK), these two exhibited rejections even higher (98%). In terms of permeate flux (at 20 bar), the RO membrane had the lowest flux (39 L/m^{2}h), whereas the NF membranes showed permeate fluxes of 67 and 50 L/m^{2}h for the NF99 and DK membranes, respectively. Zhong et al. [68] also studied the performance of an ultra-low pressure RO (ULPRO, RE-4040-BL) with wastewater from a Cu mine (pH 3, 2010 mg/L TDS). The membrane showed rejections higher than 97% for metals (e.g. Ni, Cu, Zn, Pb). Nasir et al. [111] evaluated the performance of a pilot plant for the treatment of AMD (pH 3.9, 1.34 g/L SO_4, 1.65 g/L TDS, 10 mg/L Mn and 0.8 mg/L Fe) consisting on a sand filter, adsorption (rice husk-ash and coal fly-ash), UF and RO. The RO allowed to remove efficiently the SO_4 by more than 98%, whereas the main metals in solution were removed by 94% (Fe) and 95% (Mn). Aguiar et al. [112] studied the effect of different operational variables in the treatment of AMD with TFC-HR and BW30 RO membranes. They observed that RO membranes presented lower permeability (between 4 to 10 times lower) than NF membranes (MPF-34, NF90 and NF270). Additionally, they observed that RO membranes are prone to be fouled in comparison to NF membranes. However, the RO membranes achieved a better quality than NF membranes, especially the TFC-HR as provided an overall rejection of 98% of TS. Ricci et al. [101] integrated NF and RO for the treatment of an Au mining effluent at pH 1.4. The concentrate of the NF membrane (pH 1.3, 535 mg/L metals) was treated with a RO membrane (TFC-HR), which rejected metals by 92% and H_2SO_4 by 98%. In a posterior study, the treatment of this Au mining effluent was evaluated at pilot-scale by Amaral et al. [113]. The RO unit rejected metals by more than 90%, while acid was rejected by 93%.

The performance of RO membranes has been evaluated with other kinds of acidic waters. For example, González et al. [77] employed the SXO1 membrane to purify H_3PO_4 (196 g/L) from Fe (4.9 g/L), Mn (3.4 g/L) and Al (3 g/L), achieving metal rejections higher than 98% with an acid permeation of 46%.

These membranes, usually made of polyamide as NF membranes, present low chemical stability, which makes them susceptible to suffer from acid attack. This has promoted new membranes resistant to acids are being developed. For example, Ricci et al. [93] studied the stability of the TFC-HR membrane in acidic media by immersing the membrane in 7.8 and in 14.7 g/L H_2SO_4 for two months. Over the exposure time, membranes exhibited little increase in their permeability (from 0.92 to 1.22 L/m^{2}hbar) and a slight decrease in their NaCl rejection (from 97% to 94%). Membranes were characterized with ATR-FTIR, SEM, AFM and contact angle. Ishii et al. [114] developed their acid-stable silica-based RO membranes using counter diffusion chemical vapour deposition (CVD) method and diphenyldimethoxysilane as a silica precursor. The membrane rejected H_2SO_4 by 81%, but the γ-alumina substrate dissolved because of acid permeation. Improving the synthesis of the membrane by applying the sol-gel method, the authors developed a modified membrane able to resist at 700 g/L H_2SO_4.

The use of RO membranes is quite limited in this field, mainly because of the characteristics of the solutions to be treated. First of all, the high concentration of metals (implying a high osmotic pressure), makes necessary a large hydraulic pressure to drive needed water transport. Instead, in NF, the difference of osmotic pressure at both membrane sides is noticeably lower due to acid permeation. Besides, RO is also limited by the acidity of the solutions. RO membranes are usually made of polyamide, which makes them susceptible to suffering from acid attack in the long term exposition. Finally, the low salt passage across the membrane (rejections higher than 95%) can cause severe scaling due to the high concentrations at the membrane surface. Therefore, RO is generally implemented to concentrate moderate acidic solutions (2<pH<5) or to produce high-quality water that can be reused on-site.

3. Concentration-driven membrane processes

3.1. Diffusion dialysis

DD is a concentration-driven process used for acid recovery. It employs Anion Exchange Membranes (AEMS), which favour the transport of acid (HX) across the membrane due to its positive charge (given by quaternary ammonium groups). Instead, metals are effectively rejected because of electrostatic repulsions (**Figure 3**) [115]. The transport of the acid anions (X^-) must be accompanied by the one of a cation. Due to the H^+ properties, such as the low ionic radii and high diffusivity in comparison to any other positively charged cation in solution (single or multi-charged) its co-transport is promoted. It was also observed that the acid transport through the AEM was favoured if salts containing the same anion as the one of the acid were added to the solution. This is known as electrolyte-effect [116]. Additionally, water can also be transported across the AEM because of (1) differences in osmotic pressure, and then an osmotic flux takes place from the water to the acid side, and (2) the solvation of acid molecules, which results in water transport from the acid to the water side [117].

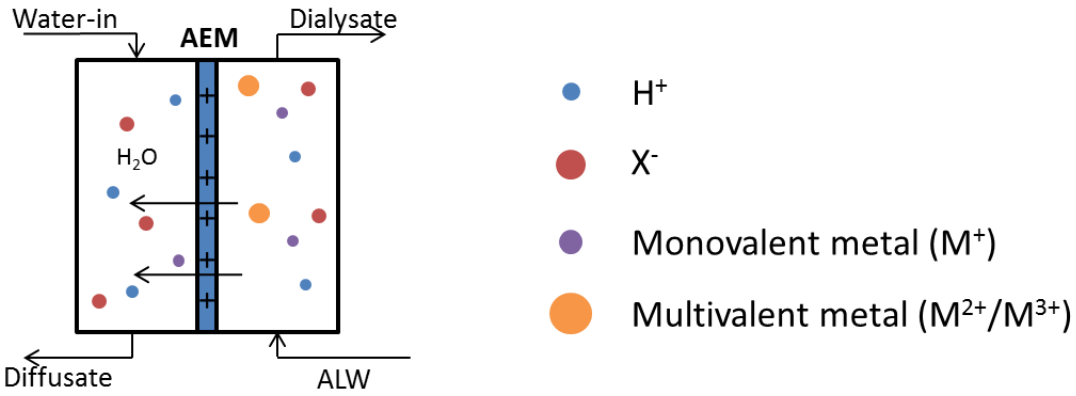

Figure 3. *Schematic representation of a diffusion dialysis unit incorporating an anion exchange membrane(AEM) for the recovery of a strong mineral acid (HX)*

DD has been successfully applied for the purification and recovery of H_2SO_4, HCl or H_3PO_4. Wei et al. [116] used the DF120-I and DF120-III for treating an acidic leaching solution (H_2SO_4). They observed that the addition of $FeSO_4$ and $VOSO_4$ promoted the transport of H^+ across the membrane due to the electrolyte-effect. When they studied the effect of flow rates, they achieved a recovery of 83% of H_2SO_4 with high metal rejections (>93%) at a flow rate ratio of 1. When they increased that ratio to 1.6, rejection of metals decreased to 90%, but higher acid recovery (87%) was attained. Gueccia et al. [117] evaluated HCl recovery from pickling solutions (<105 g/L HCl, <150 g/L Fe(II)) with Fumasep membranes. They observed that the water flux due to ion solvation prevailed at high acid concentrations, whereas osmotic flux predominated at lower concentrations. Additionally, they characterised species transport to determine membrane permeabilities to acid, salt ($FeCl_2$) and water. Li et al. [118] evaluated the performance of the DF120 membrane for acid recovery from leaching solutions (2.4 mol/L H^+, 4.2 g/L V(V), 13.8 g/L Al), achieving values of 84% at feed to water flow rates ratios of 1-1.3. Under the same conditions, metals were rejected by more than 90%. Jeong et al. [119] studied the performance of Selemion DSV for treating a solution containing 440 g/L H_2SO_4, 52 g/L Fe and 18 g/L Ni. They observed that acid recovery depended on operational parameters, such as the flow rates and temperature, but also on initial acid concentration. They achieved acid recoveries of almost 80% with low impurities of metals (<2 g/L). In a recent work, Gueccia et al. [120] evaluated the HCl recovery from pickling solutions (5-20 g/L Zn, 50-150 g/L Fe and 70-100 g/L HCl) in continuous configuration with Fumasep membranes, achieving acid recoveries around 80% with a 30% of Fe and 60% of Zn leakages. The high metal leakages were related to the formation of negatively charged metal-chloride complexes. Xu et al. [121] treated a contaminated acidic solution (1.8 mol/L H^+, 11 g/L Al and 6 g/L Cu) generated in an anoxic oxidation process with the DF120 membrane. By increasing the feed flow rate from $3\cdot10^{-4}$ to $7\cdot10^{-4}$ m^3/h, acid recovery decreased from 76 to 61 %. By increasing the flow rate ratio (feed flow rate was $4.5\cdot10^{-4}$ m^3/h) from 0.3 to 1.2, higher acid recovery was achieved (90%). However, the increase in the ratio led to a higher metal passage (Cu: 4 to 15 %, Al: 3 to 8 %). Pilot-scale tests showed an acid recovery of 85 % and an Al leakage of 5 %. Wang et al. [122] evaluated the DF120-III membrane for the treatment of a stone coal acid leaching solutions (mixture of HF, H_3PO_4 and H_2SO_4). They observed that the F rejection was the highest one (98%), followed by the one for P (90%) and S (68%). Despite of the presence of fluorides, they were effectively rejected because of the presence of AlF^{2+} and AlF_2^+ species. Luo et al. [123] studied the performance of DF120 membrane in a spiral wound module for H_2SO_4 recovery. Best results in terms of acid recovery and concentration were achieved with a series connection in both acid and water side with a counter-current flow pattern. This configuration was compared with a single, double and triple spiral wound membrane module. Triple spiral-wound membrane module allowed to obtain the same acid recovery working at higher flow rates (65% recovery at 6.5 mL/min in the single and 50.5 mL/min with the triple). Lan et al. [124] evaluated the recovery of a spent solution (HNO_3-based) with ED with DF120. Acid recovery increased from 83 to 94% by increasing water to feed ratio from 1.0 to 1.2. The membrane more effectively rejected bivalent cations since they have charges that are strongly rejected by the membrane. The selectivity of the membrane followed the trend: Mg^{2+}> Ca^{2+}> Li^+> Na^+> K^+. By working at low water to acid ratio, the transport of metals is more impeded.

Working at flow rate ratio water to acid of 1.07, and by changing the acid concentration from 6.3 to 189 g/L, a maximum acid recovery at 189 g/L was observed (96.2%). However, at higher concentrations, the mass transfer was controlled by the membrane itself, so the acid recovery started to decrease. Xu et al. [125] studied the potential for acid recovery from a galvanizing waste (110 g/L HCl, 150 g/L Fe(II) and 4.5 g/L Zn) with the DF120 membrane. At flow rate ratio between 2.0 and 3.1 (0.4 L/h of acid), acid recovery was over 88% (>72 g/L). However, both Fe and Zn leakages increased with the flow rate ratio. Fe leakage varied from 11 to 23%, while the one for Zn was higher than 56% because of its presence as an anion ($ZnCl_3^-$, around 85 % of total zinc in solution). It was possible to obtain higher HCl concentrations in the diffusate (i.e. recovered acid stream) at high Fe concentrations because of the salt effect.

Palatý and Žáková have studied and characterised the transport of species across the Neosepta-AFN membrane [126–132]. Their works cover a wide range of acids and salts, and the effect of solution speciation was also investigated. These works are explained in the paragraphs below.

Palatý and Žáková have studied the transport of inorganic acids [131,132]. They employed Fick's first and second laws to determine the apparent diffusivity of H_2SO_4, HCl, HNO_3, H_3PO_4 and HF through the membrane [131]. The highest values were obtained for HCl (<28 g/L) and HNO_3 (<12 g/L), whereas the lowest values were observed for H_3PO_4. Additionally, they detected that H_2SO_4 and HF diffusivities increased with concentration, whereas the ones for HNO_3 and H_3PO_4 showed the opposite trend. The transport of acids (HNO_3 and H_2SO_4) was described taking into account their dissociated forms (i.e. HNO_3 flux was the sum of NO_3^- and HNO_3(aq) fluxes, H_2SO_4 flux was the sum of HSO_4^- and SO_4^{2-} fluxes) using the Nernst-Planck equation [132]. They observed that H_3O^+ had higher mobility than the other species, which could be beneficial for separating acids from salts due to the high proton leakage. Regarding the NO_3^- and SO_4^{2-} ions, both showed similar mobilities at concentrations below 0.5 mol/L, but they increased with acid concentration.

Palatý and Žáková have found that the membrane permeability to H_2SO_4 was dependent on its concentration, and the major resistance to its transport was found in the liquid films at both membrane sides [126]. Working with electrolyte mixtures (H_2SO_4 and $CuSO_4$ or H_2SO_4 and $ZnSO_4$), they observed that metal transport across the membrane was proportionally related to its concentration but inversely to acid concentration. This effect was related to the changes of metal speciation, which shifted the equilibrium towards the presence of the free metal ion form.

Similar studies have been carried out with HCl [129,130]. By studying HCl-$FeCl_3$ mixtures [129], the addition of $FeCl_3$ salts enhanced acid transport, achieving concentrations in the diffusate even higher than in the feed side. Additionally, they observed that the membrane was prone to better transport HCl than H_2SO_4. For HCl-$NiCl_2$ experiments [130], $NiCl_2$ was fully rejected by the membrane. However, higher acid concentrations promoted the transport of $NiCl_2$ across the membrane.

Ersoz et al. [133] characterised the transport of H_2SO_4 and HCl through an aminated polyether-sulphone AEM (SB-6407) and Neosepta AMH membranes. Both membranes showed higher affinity for H_2SO_4 than for HCl, which was reflected in the diffusion dialysis coefficients. They observed that strong basic anion-exchange groups have permeability for mineral acids two orders higher than the corresponding values of electrolytes.

A new generation of AEMs is being developed to enhance acid transport and the separation factor. Khan et al. [134] developed AEMs using brominated poly (2,6-dimethyl-1,4-phenylene oxide) (BPPO) as a polymer backbone and 4-methylpyridine (MP) as an ion exchange element. They studied the effect of the content of 4-methylpyridine onto the membrane's properties. The increase of MP content (from 14% to 35%) resulted in higher ion-exchange capacity (from

1.94 mmol/g to 2.24 mmol/g) and the water uptake (from 17% to 31%). The performance of the AEM was compared with the one of DF-120B using 36.5 g/L HCl and 31.7 g/L $FeCl_2$. The developed AEM with 35% MP showed an acid dialysis coefficient of 0.066 m/h (0.004 m/h for DF-120B) and a separation factor of 78 (23 for DF-120B). Ji et al. [135] functionalized BPPO with tris(2-(2-methoxyethoxy) ethyl) amine (TDA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA) to achieve hydrophilic transport channels and high selectivity. Syntehtised membrane was tested with 36.5 g/L HCl and 33.7 g/L $FeCl_{2,}$ and its performance was compared with a commercial DF-120. The membrane containing a 45% of DMAEMA achieved the best results, with an acid dialysis coefficient of 0.0325 m/h and a selectivity factor of 49. Instead, the DF-120 membrane had lower values for acid dialysis coefficient (0.009 m/h) and separation factor (19). Besides, the membrane kept their properties for 10 cycles. Ji et al. [136] prepared an AEM by introducing quaternary ammonium groups with long hydrophilic side chains into BPPO (namely QPPO). After that, membranes were also put in an oven at 90 °C for 2 h (namely TQPPO) to enhance crosslinking. Consequently, QPPO membranes had a higher ion-exchange capacity than TQPPO membranes, but a lower water uptake. When authors evaluated the membrane performance with 36.5 g/L HCl and 33.7 g/L $FeCl_2$, they observed that the BPPO-1.75 membrane had higher acid dialysis coefficient (0.059 m/h) than TQPPO-1.75 membrane (0.047 m/h). However, the BPPO-1.75 membrane had lower separation factor (19) than the TQPPO-1.75 one (33). Yadav et al. [137] synthesised graphene quantum dot quaternized polysulfone membranes to enhance both acid recovery and separation factor. Synthesised membranes had a water uptake ranging from 22% to 32%, without and with 1% of graphene quantum dots, respectively. Besides, graphene quantum dots' presence increased the ion exchange capacity, from 1.52 meq/g to 1.81 meq/g for the above conditions. When evaluating the membrane performance with 73 g/L HCl and 30 g/L $FeCl_2$, the AEM containing 1% of graphene quantum dots showed the best performance, in terms of acid dialysis coefficient (0.006 m/h) and separation factor (39).

3.2. Forward osmosis

The application of FO in desalination and wastewater treatment has attracted the attention of researchers. In comparison to RO, no external pressure is needed to drive the separation process in FO, and only a high osmotic pressure difference is needed to drive the transport of water. In order to achieve that, the feed solution is separated from the draw solution (high osmotic pressure) by a semi-permeable membrane. Therefore, water flows from the feed to the draw solution to equalize salinity [138,139]. **Figure 2** shows a scheme of a FO operating with ALWs. The FO membrane can be operated either with the active layer facing the draw solution (AL-DS) or the feed solution (AL-FS). Jin et al. [140] observed higher permeate fluxes facing the active layer the draw solution, whereas Tang et al. [141] reported higher organic fouling in the AL-DS mode. Nevertheless, in the case of ALWs, low content of dissolved organic matter is typically reported, but the main concern with ALWs is associated with the formation of Al and Fe hydroxides at even low pH values. Phuntsho et al. [142] reported that temperature and pH are also key factors in mass transfer in FO, as the increase of temperature promotes both solvent and solute transport.

Nevertheless, only a few studies regarding the application of FO in the treatment of ALWs can be found in the literature. You et al. [143] tested an inorganic membrane to remove metals (Cu, Zn, Cd and Pb with a total concentration of 200 mg/L) from AMD at pH 4.5. By using 117 g/L NaCl as draw solution, they were able to remove metals by 94% and a permeate flux of 69 LMH. Vital et al. [144] evaluated the application of FO for the treatment of AMD using a thin-film composite membrane (*FOMEM-0415* – Hayward), using 58.5 g/L NaCl or NH_4HCO_3 as draw solution. Metals from AMD were rejected by more than 97% using both draw solutions. However, the salts of the draw solution were also transported and, and metal precipitation occurred working with NH_4HCO_3. Pramanik et al. [145] evaluated flat-sheet polyamide membranes supported on polysulphone (Porífera) and studied how orientation (AL-DS or AL-FS), temperature and pH (from 3 to 7) affects the permeate flux and the rejection of three

REEs (Ce, La and Dy) mimicking an AMD. They obtained higher fluxes at high pH and temperatures with the AL-DS mode. REEs rejection in the AL-FS (89-96%) was slightly higher than in the AL-DS mode (83-88%). In addition, the REEs rejection was influenced by the solution pH and temperature. For example, rejections increased with the temperature of feed and draw solution as well as with the pH. Choi et al. [146] evaluated the metal recovery from AMD by the integration of FO and NF. Two different draw solutions were evaluated, EDTA-4Na and PSS-Na for the FO unit. Some metals (e.g. Mn, As, Cd and Pb) were completely rejected by the membrane, while Fe, Cu and Zn exhibited lower rejections (80-85%). Baena-Moreno et al. [147] evaluated the effect of draw solution (NaCl, KCl, $CaCl_2$, and $MgCl_2$ from 1 to 5 mol/L) in the water recovery and metal rejection from AMD (pH 2.7, 11.7 g/L SO_4, 1.1 g/L Mg, 1 g/L Zn and 0.7 g/L Fe). They observed that the water flux increased with concentration in the order $KCl<NaCl<CaCl_2<MgCl_2$, whereas metal rejections were higher than 99.5%. In all cases, working with 475 g/L $MgCl_2$ as draw solution, 90% of water was recovered (around 5 L/m^2h), but scaling was observed, mainly a mixture of metallic sulphates and carbonates.

4. Electrically-driven membrane processes

ED is an electrically-driven membrane process which uses ion-exchange membranes to drive the transport of ions under the application of an external electric field. Functional groups from ion-exchange membranes provide the membrane a charge, which allows them to exclude fully or partially ionic species with the same charge of the membrane (co-ions). Therefore, the stack is formed by intercalating Anion and Cation Exchange membranes (AEMs and CEMs, respectively), and each set of AEM and CEM form a cell pair. By applying an external electric field, cations will migrate towards the cathode, and in their path, cations pass through CEM (negatively charged) but are retained by AEM (positively charged). Anions in solutions will migrate towards the anode and experience the opposite trend. Finally, two streams are produced, one with a higher ion concentrations than feed solution, and another depleted of them [148–150].

4.1. Conventional electrodialysis

Conventional ED has been applied to purify and concentrate industrial ALWs. Most of the works published in the literature are for H_2SO_4-based streams, ranging from 50 to 200 g/L. For example, Cifuentes et al. [151] studied the separation of species from Cu electrorefining electrolytes (50 g/L H_2SO_4, 3-9 g/L Cu, 3 g/L As (As(III) or As(V)), 0.025 g/L Sb) with the Ionac AEM MA-3745 and CEM MC-3470. The separation of sulphate from Cu and As was achieved and the transport rates were determined (0.2-0.6 mol Cu/m^2 h, 0.65-2.8 mol SO_4/m^2 h, 0.016-0.03 mol As/m^2 h). Both As and Sb form cations, anions and uncharged species in H_2SO_4 media (e.g. H_3AsO_3 and $H_4AsO_3^+$ for As(III); $H_2AsO_4^-$ and H_3AsO_4 for As(V), $H_2Sb_2O_2^+$ and H_3SbO_3 for Sb(II)), which can be transported towards the anode and cathode according to their charge. At lab-scale operations with recirculation, the further separation of Cu from As can be achieved because of the high transport rate ratio (12.5 for Cu(II)/As(III) and 20 for Cu(II)/As(V)), whereas the transport of sulphate was the highest one (2.8 mol/m^{2}h). Therefore, it could be possible to obtain a stream containing Cu with traces of As in the cation concentrate compartment. By working at higher temperatures (44 °C) in the semi pilot cell, the transport rate of Cu increased a 38% (0.52 mol Cu/m^{2}h) in comparison to the operation at 22°C (0.38 mol Cu/m^2·h). At the same acidity level, Cifuentes et al. [152] studied the system $CuSO_4$-H_2SO_4-Fe from a copper electrowinning bath (9 g/L Cu, 50 g/L H_2SO_4 and 0.5 g/L Fe(II)). The removal rates for metals increased linearly with cell current, and its transport rates at 250 A/m^2 were between 0.5-1.1 mol Cu/m^2·h and 0.035-0.071 mol Fe/m^2·h. By moving from a laminar to a turbulent flow regime (Re=8200), the transport rate of Cu increased by 15%. Moreover, Cu and Fe were removed by 96.6 and 99.5 %, respectively after 24h of operation. Besides, the fact that anions (SO_4^{2-} and HSO_4^-) were transported towards the anode made feasible the recovery of water with a specific energy consumption of 1 kWh/kg. Chekioua and Delimi [153] evaluated the treatment of acid pickling bath (150 g/L H_2SO_4 and 26 g/L Fe(II)) with ED using different membranes (AEM: AMX; CEM: CMX, Nafion 117 and CMV). Working with the CMX, the best results were obtained in terms of Fe(II) rejection (66%) and energy consumption (1.85 kWh/kg). The rejection of Fe(II) improved from 7.4% to 66.4% when the current density increased from 1 to 20 mA/cm^2. However, further increases in the current density (30 mA/cm^2) resulted in lower rejections (60.5%) due to Fe(II) scaling. Moreover, they observed that, by increasing Fe(II) concentration up to 52 g/L, the membrane performance improved (Fe(II) rejection of 70%), which was related to the higher pH, and then, the lower amount of the competitive H^+ in solution. The addition of Fe(II) also promoted a higher recovery of H_2SO_4 in the anodic compartment (from 14 g/L to 25 g/L H_2SO_4 when Fe(II) increased from 1 to 52 g/L). Boucher et al. [148] evaluated the recovery of H_2SO_4 from solutions coming from Zn industry (200 g/L) polluted with metals (10 g/L Zn, 10 g/L Mg and 1 g/L Mn). Finally, they recovered 69% of H_2SO_4 with a low passage of metals (<8%). Sistat et al. [154] evaluated the recovery of H_2SO_4 from a contaminated effluent (200 g/L H_2SO_4, 10 g/L Zn and Mg, 5 g/L Mn) with a Nafion CEM modified by electrodeposition of polyethyleneimine on one side of the membrane. Acid recoveries between 58 to 67% were achieved with energy consumptions ranging between 1.0 and 1.2 kWh/kg H_2SO_4. The total metal leakage was below 0.5% for each metal, without implying any additional cost. Recently, Melnikov et al. [155] evaluated ED for concentrating H_2SO_4 and HNO_3. The ED allowed to concentrate H_2SO_4 from 49 to 137 g/L and HNO_3 from 19 to 132 g/L at a current density of 4.3 A/dm^2. Current efficiency was quite low (27% for H_2SO_4 and 22% for HNO_3), which was related to the proton leakage across the AEMs.

The treatment of other streams containing another kind of acids has also been studied. For instance, Sun and Xu [156] evaluated the treatment of waste H_3PO_4 solutions (196 g/L H_3PO_4, 0.5 g/L Al, 0.5 g/L Mo) with ED. Experiments were carried at a voltage of 15V in order to achieve higher removals of Al and Mo. They observed that at higher H_3PO_4 concentrations, the transport of Al and PO_4 decreased (7% and 15%, respectively), whereas it accelerates the ones of Mo due to its presence as an anion, $Mo_2O_4^{2-}$. They also evaluated different membranes: CMX/AMX, CM1/AM1 and CMX-SB/ACS and at least 30% and 7% of Al and Mo were removed from the acidic solution. Zhang et al. [157] studied the recovery of HCl from Al foils wastewaters (49 g/L HCl and 20 g/L $AlCl_3$) by the integration of DD and ED. By working with a feed flow rate of 0.60 L/m^2h in the DD unit and 2 A in the ED stack, the average acid recovery and Al leakage ratios were 75% and 12% respectively, while the energy consumption was only 0.41kWh.

Conventional ED has also been applied for the treatment of AMD. For example, Buzzi et al. [149] treated an AMD at pH 2.4 polluted with Na, Mg, Ca and Fe(III). Finally, water at pH 3 was recovered with a low content of metal (removal of 97%), with their concentrations below detection limits. Martí-Calatayud et al. [150] studied the H_2SO_4 recovery from synthetic AMD (pH 1.68, 8 g/L $Fe_2(SO_4)_3$, 1.5 g/L Na_2SO_4). After 10h of operation, they were able to concentrate H_2SO_4 in a factor of 2.6, 3.4 and 4.0 for 5, 10 and 15 mA/cm^2, respectively. During the experiments, it was observed that AEMs with high ion-exchange capacities originated a stronger Donnan exclusion of co-ions, which led to the dissociation of HSO_4^- ions in the membrane and then reduced the efficiency for H_2SO_4 recovery. With regard to Fe(III), at the beginning of the experiments its concentration in the cathodic compartment increased, but at a certain time reached a value lower than the initial one. Moreover, Fe(III) concentration in the central compartment was the same at 10 and 15 mA/cm^2 (1.2 g/L), which was related to the formation of $Fe(OH)_3$ precipitates in the anodic side of the CEM as a result of surpassing the limiting current density (16 mA/cm^2). In addition, more of the half of the imposed current density was used to drive the transport of SO_4^{2-} ions across the membrane. In terms of specific energy consumption, it increased drastically with the increase of the current density from 6 kWh/kg) at 5 mA/cm^2 to 20 kWh/kg 15 mA/cm^2 because of the precipitation at the membrane surface.

4.2. Advanced electrodialysis

A continuous effort on improving the performance of conventional ED has promoted the development of enhanced configurations such as: i) Selectrodialysis (SED) with the integration of mono-selective and standard ion-exchange membranes to promote the separation of monovalent ions from multivalent ions; ii) Bipolar ED (BMED) by the integration of bipolar membranes with AEM and CEM, and; iii) reactive ED (RED) where metallic ions with redox properties could be reduced. Details of such configurations are described schematically in **Figure 4**. From the described configuration, the possibility to concentrate streams and to separate a compound of interest provides the option to reduce the volume to be treated and, therefore, the number or recovery units.

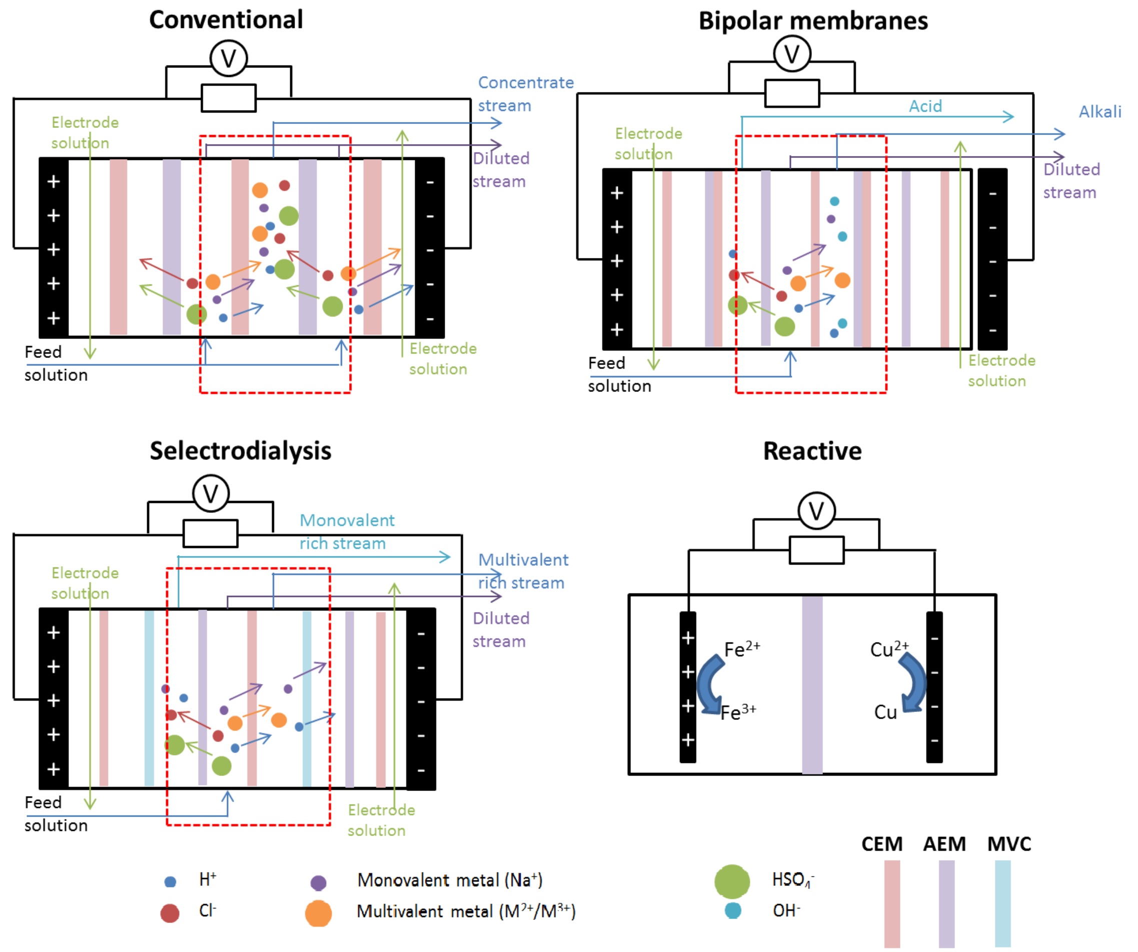

Figure 4. *Schematic representation of electrical-driven membrane processes for the valorisation of acidic waters: conventional ED, bipolar membrane ED, selectrodialysis and reactive ED*

Bipolar membranes are formed by an anion exchange layer overlapped with a cation exchange layer, where water split occurs, and then acid and alkaline solutions are produced [158]. Melnikov [155] evaluated BMED for concentrating different salts and acids (e.g. 14.7 and 29.4 g/L H_2SO_4, and 18.9 g/L HNO_3). The current efficiency for both acids was lower than 25%, which was related to the transfer of protons across the AEM. The concentration of the acid can be limited by the osmotic and electroosmotic transport of water across the membrane. Liu et al. [159] treated the raffinate from a Cu ore hydrometallurgical processing (pH 1.4, 45 g/L SO_4^{2-}, 11.8 g/L Fe, 336 mg/L Zn and 135 mg/L Cu, among others) with BMED. The optimum current density and the volume raffinate to transition metal chamber ratio were 3 mA/cm^2 and 1:15, respectively. Moreover, by increasing the number of chambers from one to three, the energy consumption decreased from 0.160 to 0.089 kWh/L of raffinate. After 40 h of operation of the BMED, it was possible to recover the 86% of the total sulphate, mainly as H_2SO_4 (39 g/L), whereas the metal impurities were rejected (99.3% Fe, 99.1% Zn, 99% Cu, 84.9% Ni, 70.6% Cr, 96% Cd and 95% As) and its amount in the recovered acid was below 100 mg/L. Then, this acid can be reused as leaching influent.

SED incorporates a monovalent selective ion-exchange membrane in the stack, usually a monovalent selective cation membrane (MVC) to remove metals. Reig et al. [160] studied the performance of SED with a MVC in order to separate As(V) from Cu and Zn from an acidic metallurgical process stream (pH 2.3, 2 g/L Cu, 9.6 g/L Zn and 2.4 g/L As). The SED configuration showed it was possible to obtain a Cu/Zn-rich (80% of Cu, 87% of Zn and 0.02% of As) and As-rich stream (95% of As) with a specific energy consumption of 2.6 kWh/kg $CuSO_4$ and $ZnSO_4$.

The main purpose of ED is to separate or concentrate species, but when the main objective is the production of chemicals at the electrodes, it is named as RED. Cifuentes et al. [161] evaluated the recovery of Cu with RED. The system consisted of anolyte (180 g/L H_2SO_4, 56 g/L Fe(II)) and catholyte (180 g/L H_2SO_4, 40 g/L Cu) solutions separated by an AEM (Ionac MA-3475 Tokuyama, Tokuyama ACS) at a current density of 300 A/m^2 to achieve the electrodeposition of Cu in the cathode. The transport of Cu and Fe decreased around 80% with two membranes instead of one, at the expenses of increasing the cell voltage by 20%. However, if another membrane was placed, the transport of metals across the membranes barely varied. Two ACS membranes exhibited better performance, with the lower transport rates for Cu ($4 \cdot 10^{-4}$ mol/m^2h) and Fe ($17 \cdot 10^{-4}$ mol/m^2h) at 0.77 V. The higher transport rate for Fe was related to its presence as an anion in H_2SO_4 media ($Fe(SO_4)_2^-$) and its higher concentration. In a posterior work, with the Ionac MA-3475 membrane under the same conditions, Cifuentes et al. [162] studied the effect of temperature (30-60 °C) and applied cell current (0.4-0.8 A) on the RED performance. At a constant cell current, by increasing the temperature, the voltage of the two-compartment cell decreased because of the higher diffusivities and lower electrical resistance. In the three-compartment cell, the cathodic current efficiency was quite high (98-99%) with an energy consumption between 0.94 to 1.39 kWh/kg Cu at current densities ranging from 200 to 600 A/m^2. In comparison to conventional electrowinning, these values were quite lower (2 kWh/kg Cu at 350 A/m^2). In a latter work, they were able to model the data with deviations between experimental data and model prediction lower than 3% [163,164].

The integration of liquid membranes inside the ED stack has also been studied to separate metals selectively. Sadyrbaeva [165] integrated a liquid membrane in an ED stack for the treatment of a solution containing 110-146 g/L HCl, 0.6 g/L Co(II) and 0.6 g/L Ni(II). At such acidity, Ni(II) is present as Ni^{2+} and $NiCl^+$, whereas Co(II) can be found either as Co^{2+} or $CoCl_4^{2-}$. The removal of Co(II) increased with the current density and HCl and Co(II) concentration, whereas it barely varied with Ni(II) concentration and the carrier concentration in the liquid membrane. They were able to separate selectively Co(II) and Ni(II) with a separation factor $\beta_{Co/Ni}$ of 145, which could be improved at higher Ni(II) ($\beta_{Co/Ni}$ of 330) and Co(II) ($\beta_{Co/Ni}$ of 400) concentrations. They also evaluated whether the type of acid (e.g. H_2SO_4, HNO_3 or $HClO_4$) affects the separation, but no effect was observed.

5. Thermally-driven membrane processes

5.1. Membrane distillation

MD is a thermally-driven process which uses a micro-porous non-wetted hydrophobic membrane to drive the transport of vapours and volatile compounds (e.g. water, HCl) due to a difference of vapour pressure, and then they condensate at the surface of the membrane [166,167]. MD presents some advantages, such as: i) high rejection of non-volatile and dissolved species (>99%); ii) lower operation conditions (temperature and pressure) than conventional processes, and; iii) low fouling due to solution/membrane surface interactions. Nevertheless, they present some drawbacks such as lower permeate flux than RO, mass transfer resistance due to air trapped and heat lost due to conduction [168,169]. During operation, the applied hydrostatic transmembrane pressure must be lower than the membrane liquid entry pressure. If not, the liquid will enter the pores due to surface tension force [166]. A review on the application of MD for the recovery of valuable-added components from acidic waters has recently been published [168].

Different models have been proposed for describing mass transfer across MD membranes. Generally, it takes place by a combination of convection and diffusion through membrane structure. In the absence of air, the membrane resistance can be described either by the Knudsen diffusion model or Poiseuille (viscous) flow model, while molecular diffusion model is used in the presence of air [166].

Figure 5 shows a scheme of the different operation configuration of MD for HCl effluents. The direct contact membrane distillation (DCMD) is the most employed configuration, which puts the feed solution at high temperatures in contact through the membrane with a cold solution. Therefore, the vapour pressure gradient promotes the transport of vapours and volatile compounds. Other configurations, such as the air gap MD (AGMD) and water gap MD (WGMD) are based on putting a space filled with air (or water) between the membrane and the cold solution, so the molecules in the gap condense and can be recovered. Another configuration of interest is the vacuum MD (VMD), which consists of applying vacuum in the permeate side to enhance the vapour pressure gradient [168].

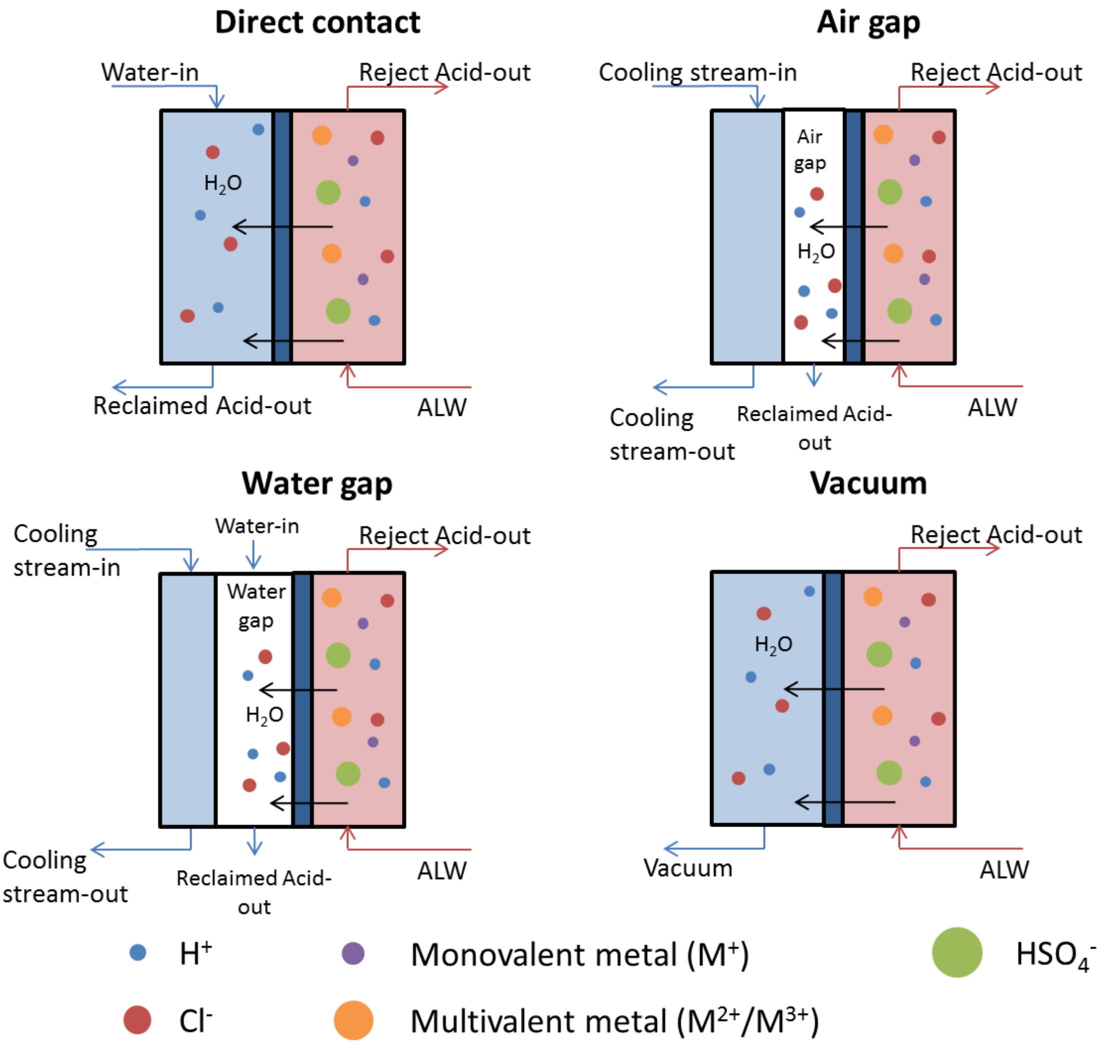

Figure 5. *Schematic representation of thermal-driven membrane processes for the valorisation of acidic waters: direct contact, air gap, water gap and vacuum MD*

The application of MD has been studied for the recovery of different kind of acids [170–174]. Zhang et al. [170] evaluated the permeation of H_2SO_4 in MD, observing an acid transport below 2% through the membrane. Additionally, the authors noticed that the acid flux decreased at higher acid concentrations, but increased with temperature. Caputo et al. [171] evaluated the concentration of HI or H_2SO_4 for $H_2(g)$ production from the sulphur–iodine (S–I) process using DCMD at 58°C feed temperature with a polypropylene (PP) capillary membrane and AGMD at 80°C with a PTFE flat-sheet membrane. Better results were obtained with the AGMD configuration, achieving higher permeate fluxes (16.97-7.8 L/m^{2}h for HI and 5.0-0.7 L/m^{2}h for H_2SO_4) than with the DCMD configuration (2.0 L/m^{2}h for HI and 1.3 L/m^{2}h for H_2SO_4). Moreover, the former also achieved higher concentration factors, from 88 to 980 g/L H_2SO_4 with a negligible concentration in the reclaimed acid-out, and from 38 to 1024 g/L HI, which was higher than the azeotrope concentration (973 g/L). However, part of the HI permeated across the membrane (666 g/L). Recently, Si et al. [174] evaluated the combination of VMD (PTFE membrane) and mechanical vapour recompression for the treatment of H_2SO_4 solution (100 g/L). The solution was concentrated up to values of 500 g/L, assuming an energy saving of 65.5%. Thiruvenkatachari et al. [173] studied the performance of AGMD for HNO_3-water mixtures with a PTFE membrane. They observed that by increasing the concentration of the acid from 126 to 378 g/L, the permeate flux decreases. However, an increase in the permeate flux was observed at concentrations higher than the azeotrope (680 g/L) due to the permeation of HNO_3. They were able also to concentrate 126 g/L HNO_3 at 80 °C, achieving a final concentration of 346 g/L (below the azeotrope). Nevertheless, part of the acid was lost in the permeate (31.5 g/L). The performance of MD has also been evaluated for acid mixtures. For instance, Tomaszewska and Mientka [172] evaluated the separation of HCl from HCl-H_2SO_4 solutions with capillary PP membranes. Working at the same acid concentration (51 g/L HCl and H_2SO_4) at 60 °C, the permeation of HCl across the membrane was very small, while the H_2SO_4 was rejected. At higher HCl concentrations (111 g/L HCl and 61 g/L H_2SO_4), the acid permeated in a greater extent. In the opposite case, with higher concentrations of H_2SO_4, the transport of HCl was enhanced. Moreover, it was also favoured working at higher temperatures (70 °C). Kim et al. [175] evaluated the potential concentration and purification of H_3PO_4 from a stream containing 702 g/L H_3PO_4, 82 g/L HNO_3, 69 g/L acetic acid and 2.36 mg/L Al with VMD. Working at a vacuum of 730 mmHg at 125 °C, the desired concentration was achieved and also the acetic acid and HNO_3 were separated from H_3PO_4. However, impurities of 3.68 mg/kg were found in the purified acid.

As in the case of DD, the addition of salts to the solution promoted the transport of acid across the membrane (“salt-effect”) [176–178]. For example, Tomaszewska et al. [177] evaluated the concentration and recovery of HCl with PP membranes at different concentrations (50-300 g/L) and temperatures (60 and 70 °C). At low acid concentration (<150 g/L, 60 °C) the permeate was practically pure water. However, at higher acid concentrations and temperature, the flux of acid across the membrane increased because of its higher vapour pressure. The addition of $FeCl_3$ to the solution improved the HCl flux because of the salt effect, allowing the recovery of pure HCl as permeate ($FeCl_3$ rejected more than 99.9%). Experiments performed with a pickle liquor (8.9 g/L Fe(III) and 101 g/L HCl) showed that at concentrations below 150 g/L HCl and 28 g/L Fe(III) it was possible to obtain pure water as permeate. Beyond this point, pure acid was obtained instead, with Fe(III) being rejected by 100%. Tomaszewska et al. [178] evaluated the transport of HCl across PTFE and Polyvinylidene fluoride (PVDF) flat-sheet and PP capillary membranes. They observed that the PP membrane exhibited the lowest water and permeate fluxes within a wide range of HCl concentrations (50-260 g/L) and temperatures (40-70 °C). Within the range 140-200 g/L HCl was transported across the membrane. At high concentrations (>200 g/L), they observed that it was possible to obtain even higher concentrations in the permeate than in the feed side. The presence of $FeCl_3$ favoured the transport of the HCl, yielding an acid-rich permeate with a low amount of metals (Fe rejection >99.5%). Feng et al. [176] evaluated the concentration of titanium white waste acid by DCMD with self-prepared PVDF hollow fibres. By working only with 200 g/L H_2SO_4, they were able to concentrate the acid to values between 360-390 g/L with acid rejections higher than 99.9%. Experiments containing also 30 g/L $FeSO_4$ exhibited rejections higher than 99%, but a considerable flux decline was observed. Supersaturation of the solution in the membrane occurred, leading to pore blocking. After HCl cleaning for $FeSO_4$ crystals removal, the flux was partially restored without seeing any chemical or physical deterioration of the membrane.

The applicability of MD has been studied for treating different acidic effluents. For example, the MD performance has been evaluated for the treatment of AMD [179–181]. Amaya-Vías et al. [179] evaluated WGMD and AGMD using polytetrafluoroethylene (PTFE) membranes at different temperatures (50-80 °C) with AMD from the Tinto River (pH 2.1 and composed mainly by 10.5 g/L SO_4^{2-}, 0.81 g/L Mg^{2+} and 0.73 g/L Fe). Both MD configurations allowed to obtain high permeate fluxes (up to 16.8 L/m^2h for WGMD and 10.2 L/m^2h for AGMD) achieving rejections higher than 99% for the metals in solution, whereas the permeate pH was close to one of the natural waters. Ryu et al. [180] integrated adsorption on zeolite with DCMD for the recovery of water from AMD (pH 2, 340 mg/L Fe, 220 mg/L Mg, 170 mg/L Ca, 150 mg/L Al and 120 mg/L Cu). Zeolite achieved transition metal removals between 26 to 31%. The DCMD was fed with effluent from the zeolite unit, which contained 6.4 g/L TDS and, after recovering 50% of the water, its total concentration was 12.9 g/L TDS. The TDS concentration in the permeate remained below 0.01 g/L. Membrane fouling by Fe and Al was avoided by a pH adjustment to 4, and a high-quality freshwater was obtained, while H_2SO_4 and metals were concentrated in solution. In a latter work, Ryu et al. [181] integrated DCMD (PTFE membrane) with adsorption (amine grafted SBA-15) for Cu recovery from AMD (pH 2.0, 4.3 g/L SO_4 and 92 mg/L Cu). They were able to achieve a permeate flux of 14.5 L/m^2h and a final Cu concentration of 233 mg/L at a water recovery of 80%.

The treatment of H_2SO_4-based solutions (e.g. leaching or mining effluents) has been also addressed [182,183]. Kesieme et al. [182] employed MD for treating H_2SO_4 leaching solutions (1.08 mol/L H^+, 15.7 g/L Fe, 4.4 g/L Al). They were able to recover water by more than 80%, with a low presence of acid (<0.1 g/L). Finally, acid and metals were concentrated with a factor of 4, except for Ca, which caused scaling. Jimenez and Ulbricht [183] evaluated the water recovery and concentration of the acid (H_2SO_4) and metals from a Cu mining effluent (pH 2, 300 mg/L Fe, 50 mg/L Cu) with DCMD. With a feed temperature of 60 °C, D845 and 3M membranes exhibited average water fluxes of 5.9 and 6.2 L/m^{2}h, respectively. Moreover, salt rejections higher than 99.9% were achieved. Concerning the acid, it was barely transported across the membrane and was concentrated by 40%.

Besides, the MD has also been applied to HCl-based solutions contaminated with metals [184–187]. For example, Cai and Guo [184] evaluated the application of MD (PTFE membrane) for the treatment of wastewaters from the hot-dip galvanising industry, which was characterised by the presence of HCl ($0.5<pH<1.5$), $FeCl_2$ (50-300 g/L) and $FeCl_3$ (4-35 g/L). The increase in the acidity in the feed solution (0-200 g/L) resulted in a lower permeate flux across the membrane (from 8 to 6 kg/m^{2}h at 75°C). However, a more acidic permeate was obtained at higher acid feed concentrations. By the addition of $FeCl_2$, the acidity in the permeate was increased, with high metal rejections (>99.99%). Nevertheless, the permeate flux decreased because of the lower H_2O activity. Chen et al. [185] evaluated the recovery of PGMs from refining_wastewater (pH 0.03, 48 g/L Cl^-, 11.4 g/L Na, 10 g/L K, among others) at 60 °C using DCMD. The increase in feed pH from 0.03 to 7 resulted in a lower permeate flux because of the lower partial vapour pressure or membrane scaling. Membrane analysis revealed silica scaling when pH was adjusted to 5 and 7, and Cr(III) scaling at pH 3. During operation, the permeate was mainly composed of HCl with low amounts of metals (<5 mg/L). Tang and Zhou [186] evaluated the recovery of HCl from a solution containing REEs using VMD. At batch experiments (60 °C), from a feed solution composed of 190 g/L HCl and 0.3 mol/L REEs, it was possible to recover 84% of the acid, with very low concentrations of REEs (3 mmol/L). Working at continuous VMD experiments, the potential of VMD for concentrating REEs was observed, achieving concentrations 3 to 4 times higher than the feed solution. Tomaszewska et al. [187] applied MD for treating pickling solutions with capillary PP membranes at 70 °C. After operation with synthetic solutions (106 g/L HCl and 94 g/L Fe(III)), it was possible to recover all of the HCl in the permeate while Fe was completely rejected. Water rinse in the feed side was needed to prevent the formation of salt crystals in the membrane pores. By treating the pickling effluent (86-135 g/L HCl, 361 g/L metals (Cu, Fe, Zn and Mg)), the permeate was richer in HCl than the feed side (165 g/L), whereas metals were rejected and their concentration in the feed stream rose to 600 g/L. Moreover, crystals $CuCl_2{\cdot}2H_2O$ crystals were found in that stream. Recently, Chen et al. [188] evaluated DCMD (PTFE-PVDF/PET membrane, 20°C and 60°C for permeate and feed solutions, respectively) from refining wastewater produced for the recovery of precious metals in spent catalysts (pH 0.03, 490 g/L Cl^-, 11 g/L Na, 10 g/L K, 537 mg/L Zn, 6 mg/L and 1 mg/L Ag). Flux decreased from 15 to 5 kg/m^2 h when recovery reached 60%. Permeate was composed of HCl (545 mg/L) with low presence of metals (<6 mg/L). Working at higher pH values led to membrane scaling, mainly by silica and Cr (III) species.

6. Comparison of membrane technologies for the valorisation of acidic liquid wastes

As can be seen in the previous sections, membrane technology covers a wide range of applications, from the treatment of AMD to different metallurgical and hydrometallurgical effluents. **Tables 2-4** collect some examples of the performance of the above-explained membrane technologies for the treatment of AMD, industrial with a moderate (<0.5 mol/L) and high (>0.5 mol/L) acidity.

Regarding the treatment of AMD (**Table 2**), NF membranes offer an alternative to the valorisation of acidic effluents, since the acid can be recovered as permeate, while metals are rejected effectively (>90%). Their use for AMD treatment is recommended; because they would allow lower alkali consumption to recover the metals selectively [68,92]. The other membrane technologies (ED, FO, MD and RO) are more focused on the purification and recovery of water. All of them can reject metals effectively (>95%). ED seems not to be the preferred one if Fe(III) is present, because at higher water recoveries, the precipitation of Fe on the membranes as $Fe(OH)_3$ can increase the specific energy consumption [150]. Among the others, FO is a promising technology (instead of RO) because it does not require an external hydraulic force to achieve water recovery. However, the selection of an appropriate draw solution can be difficult because of scaling issues [144]. Another kind of draw solutions may be useful, such as NaCl [145] or even chelating agents (PSS-Na or EDTA-4Na) [146]. Due to the low acidity of these waters, DD is not a suitable option for the treatment of AMD.

Concerning the applicability of membrane technologies to the treatment of industrial effluents, they were grouped depending on the acidity of the stream: those for moderate (<0.5 mol/L, **Table 3**) and high (>0.5 mol/L, **Table 4**) acidities.

For moderate acidity streams, ED (with different configurations as shown in **Figure 2**), MD and NF are currently researched. BMED has proved to be effective at producing a stream rich in H_2SO_4 with a low content of metal impurities [159]. Instead, the application of SED has been more focused on the separation of different components by the use of selective ion-exchange membranes (MVC) (e.g. separation of As from Cu/Zn) [160]. MD distillation, when applied for the treatment of AMD, can be useful for concentrating the different compounds in solution, and if HCl is present, its recovery and purification can be achieved [184]. Regarding NF membranes, acid can be purified. However, weak electrolytes as non-charged species (e.g.

H_3AsO_4 or H_3AsO_3) are not rejected by the membrane, and then contaminate the obtained acid [89]

If a higher acidity is present in the solution (>0.5 mol/L), then DD may be the preferred option, because of the presence of an AEM that favours the transport of anions while most metals are successfully rejected. With this technology, more than 70% of the acid can be recovered with a low amount of metal impurities. ED can also be applied for acid recovery, but the high concentration of acid makes necessary to provide a higher voltage to increase the acid transport rate. As in the previous case, MD can be used for the recovery of volatile compounds (HCl or HNO_3) [172,173]. Moreover, it can be used for purifying acids (e.g. H_3PO_4) from volatile compounds (acetic acid, HNO_3) [175]. The driven-pressure membrane technologies (i.e. NF and RO) are not suitable for the valorisation of acidic effluents. RO membranes are not suitable because of the need for high pressure and low acid permeation and subsequent recovery [77]. Instead, NF membranes can provide the recovery of acid in the permeate and concentrated metal stream in the concentrate [77,85]. However, the fact that both kinds of membranes are usually made of polyamide makes them susceptible to acid attack [85,91,93].

In relation to an economic point of view, no data comparing operational expenditures (OPEX) and capital expenditures (CAPEX) among the different membrane technologies to treat acidic liquid effluents have been reported. However, it is estimated that membrane treatment can imply a CAPEX of 500-1000 US $\$/m^3$ and an OPEX of 0.5-1.0 US $\$/m^3$. Instead, the current management options, such as chemical precipitation, has a CAPEX of 300-1250 US $\$/m^3$ and an OPEX of 0.2-1.5 US $\$/m^3$, whereas biological sulphate removal has a CAPEX of 800-1500 US $\$/m^3$ and an OPEX of 0.7-1.5 US $\$/m^3$ [189].

Figure 6 sums up the potential uses of the streams obtained from the above-mentioned membrane separation processes. All of them produce a concentrate stream, which is very rich in metals, and can be used for: i) selective precipitation for metal recovery, whereas the supernatant (i.e. water) can be discharged to the natural receiving bodies or be reused internally; ii) solvent extraction; iii) ion-exchange for the selective recovery of a target metal (e.g. REEs, Cu, Zn), and; iv) electrowinning for the electrodeposition of one specific metal (e.g. Cu). With some technologies, such as NF, DD and MD (the latter depending on the acid, mainly HCl), the recovery of a purified acid stream is quite feasible. This one can be used for: i) leaching processes to dissolve the raw minerals; ii) pickling processes to remove impurities from the metal surface; iii) regeneration of the solvent extractant; iv) regeneration of the ion-exchange resin, and; v) electrolyte in the electrowinning baths. Nevertheless, other technologies obtain a stream containing water instead of acid, as it is the case of ED, FO, RO and MD. In this case, water can be either reused internally or discharged to the natural water receiving bodies.

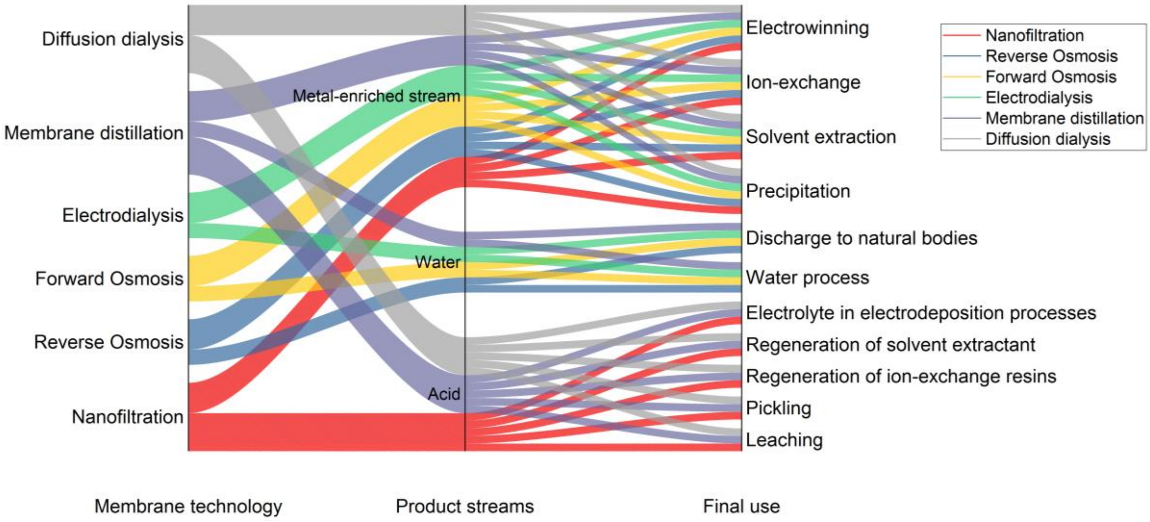

Figure 6. *Schematic representation of the membrane processes for the valorisation of acidic waters, the product streams obtained and their potential use.*

As already stated, most of the described ALWs are characterised by elevated concentrations of acids and dissolved metallic species, which can be recovered as valuable by-products and used to balance the cost of the treatment. When the value of the by-products and the treated water exceeds the cost of the treatment train, it is feasible to design valorisation routes that provide economic benefits as well as to solutions to the associated environmental problem. Generally, the above-described membrane processes will not provide a single treatment stage for the recovery of by-products, but their integration could be beneficial for:

i) Reduction of the generated waste sludge and concentrated streams, which require a long-term handling and disposal with associated long-term environmental liabilities.
ii) Creation of a revenue from the rich acid or metallic streams to partly or fully offset the treatment costs.
iii) Selective separation of target components taking benefit of the species and membrane properties.
iv) Contribution to the long-term sustainability of industrial and mining ALWs, as the on-site recovery of acids and metals is promoted.

Table 2. *Performance of membrane technologies treating AMD. Details on feed composition and operation conditions are provided.*

Membrane technology	Water composition (mg/L)		Membrane used	Operation conditions	Results	Ref.
ED	pH 2.8 Na: 296 Mg: 71 Ca: 230	Fe(III): 80 Cl: 194 SO_4: 1570	CEM: HDX100 AEM: HDX200	5 compartments with recirculation Current density: 2.6 mA/m^2 55 h operation	pH 2.92 Extraction efficiency: >97%	Buzzi et al. [149]
	pH 1.7 Na: 460	Fe(III): 2230 SO_4: 6720	CEM: HDX100 AEM: HDX200	3 compartments with recirculation Current density: 5-15 mA/m^2 10h of operation	Concentration factor for H_2SO_4: 2.64 (5), 3.36 (10) and 4.00 (15) Specific energy consumption: 6(5)-20(15) kWh/kg $Fe(OH)_3$ precipitation at 15 mA/m^2	Martí-Calatayud et al. [150]
FO	pH: n.a. Cu: 615 Al: 293 Ca: 313	Mg: 436 Mn: 203 SO_4: 8250	FOMEM-0415 – Hayward	Draw solution: 58.5g/L NaCl or 78 g/L NH_4CO_3	NaCl as draw solution Average permeate flux: 12 L/m^2 h Rejection: >97% NH_4CO_3 as draw solution Experiments not completed because of scaling (carbonates)	Vital et al. [144]
	pH 3.0 La: 1.2 Ce: 3.3 Dy: 0.4 Na: 120	Ca: 250 Mg: 100 K: 20 Mn: 4.2 Al: 8.8	Polyamide-based	80% of water recovery Draw solution: 279 g/L NaCl	Permeate flux: 12 – 9 L/m^{2}h REEs rejections: from 84 to 90%	Pramanik et al. [145]
	pH 3.1 Mn: 4.2 Fe: 19.2 Cu: 5.6	Zn: 3.6 As: 0.24 Pb: 0.45	Polyamide-based	Draw solution (π=8.9 bar): PSS-Na: 100 g/L EDTA-4Na: 42 g/L	Permeate flux: 7.5 L/m^{2}h (PSS-Na) 9.8 L/m^{2}h (EDTA-4Na) Rejections: Mn, As, Cd and Pb: >99% Fe, Cu and Zn: 80%	Choi et al. [146]

MD	pH 2.1 Fe: 735 Zn: 202 Cu: 185 Mn: 49 K: 30	NO_3^-: 50 Na: 54 Cl: 54 Ca: 170 Mg: 809 SO_4: 10418	PTFE membrane	AGMD WGMD Feed solution: 50, 60, 70, 80 °C Cooling water: 15 °C	Permeate flux WGMD: 4.0 (50 °C) to 16.8 (80 °C) L/m^2h Permeate flux AGMD: 2.8 (50 °C) to 10.1 (80 °C) L/m^2h Rejections: Cu, Fe, Zn, Mn, Mg, NO_3 ,SO_4: >99.9% Na, K, Ca, Cl: >95%	Amaya-Vías et al. [179]
	pH 2.0 Ca: 170 Mg: 220 Na: 50 Fe: 340	Zn: 120 Cu: 90 Al: 150 SO_4: 4300	PVDF membrane	DCMD Feed solution: 55 °C Permeate solution: 22 °C 50% water recovery	Permeate flux: 2.5 L/m^2h Permeate solution: <10 mg/L TDS SO_4 concentration in the permeate: 50 mg/L Feed solution concentration factor: 2	Ryu et al. [180]
NF	pH 3 Na: 653 K: 173 Cu: 79 Zn: 18	Ni: 17 Pb: 10 SO_4: 375 Cl: 530 NO_3: 107	DK-4040F	2-12 bar	Permeate flux: 12 to 60 L/m^2 h Rejections: Ni: >91% Cu: >91.5% Zn: >92.5% Pb: >93.5% H^+, Na, K: n.a.	Zhong et al. [68]
	pH: 4.5 Ca: 480 Cu: 410 K: 310 Mg: 770	Mn(III): 440 Na: 2000 Cl: 2300 SO_4: 6900	NF270	5-8 bar Permeate flux: 25-35 L/m^2 h	Rejections: Mn(III),Mg: 95% Ca: 92% Cu: 88% SO_4: 96% H^+, K, Na, Cl: n.a.	Fornarelli et al. [71]
	pH 1.0 Al: 560 Zn: 44 Cu: 40	Ca: 24 REEs: 140 SO_4: 9410	NF270	4-20 bar	Permeate flux: 18-90 L/m^2 h Rejections: Metals: >98% SO_4: 40% H^+: -5 to 5%	López et al. [92]

RO	pH 2.7 Al: 1139 Ca: 326 Mg: 630	Mn_{tot}: 225 Cu_{tot}: 2300 Fe_{tot}: 628 SO_4: 14337	AlfaLaval RO 98Ht	15 bar	Permeate flux: 50 L/m^2 h Rejections: Multicharged metals and SO_4: >98% Na: 96% Membrane scaling (Mg-Ca-SO_4) at twofold concentrated AMD	Rieger et al. [110]
	pH 2.5 Al: 1290 Ca: 395 Cu: 2735 Fe(III): 446	Mn(III): 295 Mg: 776 SO_4: 20400 CO_3: 1320	HR98PP	5-20 bar	Permeate flux: 3-32 L/m^2h Rejections: Cu, Fe(III), Mn(III), Ca, Mg, Al: >97% SO_4: 80% H^+, CO_3: n.a.	Al-Zoubi et al. [69]
	* pH 1.3 Cu: 32 Ni: 24 Co: 5 Al: 25	As: 28 Ca: 90 Mg: 277 Fe: 44 Mn: 10	TFC-HR	10 bar 50% water recovery	RO initial permeate flux: 11.4 L/m^2h pH 2.5 Rejection: Cu: 99.3% Ni: 94.8% Co: 98.2% Al: 97.4% As: 92.7% Ca: 98.2% Mg: 95.7% Fe: 98.7% Mn: 98.8%	Ricci et al. [101]

n.a. not available

*The solution composition refers to the NF permeate of an AMD

Table 3. *Performance of membrane technologies treating effluents with a moderate acidity (<0.5 M). Details on feed composition and operation conditions are provided.*

Membrane technology		**Water composition (mg/L)**		**Membrane used**	**Operation conditions**	**Results**	**Ref.**
ED	Conventional	H_2SO_4: 50000 Cu: 9000	As (V): 3000 Sb: 25	CEM: MC-3470 AEM: MA-3475	Lab-scale with recirculation Current density: 225 A/m^2	Cu transport rate: 0.61 mol/m^2h SO_4 transport rate: 2.8 mol/m^2h As(III) transport rate: 0.03 mol/m^2h	Cifuentes et al. [151]
	BMED	pH 1.4 SO_4: 45200 Fe: 11800 Zn: 336	Cu: 135 As: 64 Cd: 5	CEM: NRE212 AEM: IONSEP EDI BPM: BP-1E	Three membrane pairs 40 h operation Current density: 3.0 mA/cm^2	H_2SO_4 recovery: 85.9% (39 g/L) Removal rate: Cu, Zn, Fe: >95% Ni: 78% Cr: 68% Specific energy consumption: 0.09 kWh/L Cell voltage: 8.5 V	Liu et al. [159]
	SED	pH 2.3 Cu: 2920	Zn: 9417 As: 2250	Fujifilm MVC, CEM and AEM Type 2	Three membrane pairs 300 min of operation	Specific energy consumption: 2.34 kWh/(kg $CuSO_4$+$ZnSO_4$) Cu/Zn-rich stream: pH 1.3 Cu: 2133 mg/L Zn: 8109 mg/L As: 9 mg/L As-rich stream: pH 0.7 Cu: 911 mg/L Zn: 2753 mg/L As: 2832 mg/L	Reig et al. [160]
MD		pH 2 Fe: 300 Cl: 50	SO_4: 590 Cu: 50	D845 (PTFE) or 3M PVDF	5 h operation Feed temperature: 60°C Cold water: 20°C	Permeate flux D845: 5.9 L/m^2h Permeate flux 3M: 6.2 L/m^2h Salt rejection: 99.9%	Jimenez and Ulbricht [183]

	50 g/L HCl 95 g/L $FeCl_2$		PTFE	Feed temperature: 75°C Cold water: 20°C	Permeate flux: 6.5 kg/m^2 h HCl concentration in the permeate: 7 g/L Fe(II) rejection: 99.99%	Cai and Guo [184]
NF	pH 2.2 Al: 12.4 Ca: 1574 Cu: 9.8 K: 298 Mg: 238	Mn: 85 Na: 77744 Pb: 475 SO_4: 5739 Si: 34	Desal DK	17 bar	Rejections: H: 36% Al: 92% Ca: 42% Cu: 12% K: 0% Mg: 79% Mn: 66% Na: -3% Pb: 36% SO_4: 89% Si: 3%	Ortega et al. [86]
	pH 2 – 2.5 Cr(III): 500		Desal DK	4 – 18 bar	Cr(III): 70 – 85% Cl: 40 – 58% H^+: -40 – -30 % (theoretical)	Gomes et al. [87]
	pH 0.28 As(V): 610 Na: 170 Fe(III): 29 Zn: 100	K: 40 Ca: 20 Cu: 13 SO_4: 40510 Cl: 9040	NF270	4.5 – 20 bar	H^+, As(V): 5–25% Na, K: 45–80% Fe(III), Ca, Cu: >85% Zn: >85% SO_4: 10–40% Cl: -5 – -20%	López et al. [89]

Table 4. *Performance of membrane technologies treating effluents with a high acidity (>0.5 M). Details on feed composition and operation conditions are provided.*

Membrane technology	Water composition (g/L)		Membrane used	Operation conditions	Results	Ref.
DD	H_2SO_4: 450 Fe: 52 Ni: 18	Na: 0.61 Mg: 0.10	Asahi Type T-0b Dialyzer	Flow rate ratio: 1 Flow rate: $0.26 \cdot 10^{-3}$ m^3/m^2h	Acid recovery: 80% Rejection: Ni (96%), Fe (99%) Concentration in the diffusate: 421 g/L H_2SO_4 and metals impurities (<2 g/L)	Jeong et al. [119]
	HCl: 76 g/L Fe: 150 g/L		Fumasep type FAD	Batch configuration 7h operation	Acid recovery: 75% (due to salt-effect) Fe leakage: 7% Prevalence of drag flux (t<0.5 h) Prevalence of osmotic flux (t>0.5 h)	Gueccia et al. [117]
	H^+: 1.75 V: 2.1 Al: 17.6 Fe: 5.8 Mg: 4.5	K: 6.8 F: 11.2 P: 1.4 S: 185	DF120-III	Flow rate ratio: 1 – 1.1 Flow rate: 12 mL/min	H_2SO_4 acid recovery: 71% (1.5 g/L H^+) Rejections: V: 95% Al: 99% Fe: 97% Mg: 98% K: 85% F: 98% P: 91%	Wang et al. [122]
ED	H_2SO_4: 150 $FeSO_4$: 26		CEM: CMX AEM: AMX	7h operation Current density: 20 mA/cm^2	Acid concentration factor: 13% Fe removal: 66% Specific energy consumption: 1.8 kWh/kg	Chekioua and Delimi [153]
	H_3PO_4: 196 Al: 13.5 Mo: 48		CEM: CMX-SB AEM: ACS	15 V	P removal: 15% Al removal: 45% Mo removal: 7%	Sun and Xu [156]
MD	HCl: 52	H_2SO_4: 183	PP capillary membrane (Accurel PP S6/2)	5 h operation Feed temperature: 70°C Cold water: 20°C	Feed side: 280 g/L H_2SO_4 60 g/L HCl	Tomaszewska and Mientka [172]

	HNO_3: 252		PTFE	AGMD Feed temperature: 80°C Cooling water: 15°C	Permeate side: 8 g/L HCl Permeate flux: 2 L/m^2 h Membrane selectivity: 0.17	Thiruvenkatachari et al. [173]
	* H_3PO_4: 702 HNO_3: 82	Al: 0.023 Acid acetic: 69		VMD: 730 mm Hg Feed temperature: 125°C	H_3PO_4: 850 g/L Al concentration: 1mg/kg Separation efficiency: 100% HNO_3, HAc	Kim et al. [175]
NF	H_2SO_4: 200 Cu: 2		DK MPF-34	Permeate recovery: 10% Membrane immersion in 196 g/L H_2SO_4 for 8 weeks	Permeate flux: 50 (DK) and 10 (MPF-34) L/m^2 h Rejections DK: H_2SO_4 (10%), Cu (85%) Rejections MPF-34: H_2SO_4 (10%), Cu (45%) After 8 weeks immersion Permeate flux: 360 (DK) and 50 (MPF-34) L/m^2 h Cu Rejections: DK (5%), MPF-34 (35%)	Manis et al. [85]
	H_3PO_4: 200 Fe: 0.71 Mg: 0.50	Al: 0.44 V: 0.06 Zn: 0.10	DL DK MPF-34	35 bar	Permeate flux: 17.1 (DL), 11.3 (DK) and 4.5 (MPF-34) L/m^2 h Acid permeation: 83.3 (DL), 80.2 (DK) and 90.8 (MPF-34) % Acid purification: 92.3 (DL), 83.3 (DK) and 19.6 (MPF-34) %	González et al. [77]
RO	H_3PO_4: 200 Fe: 0.71 Mg: 0.50	Al: 0.44 V: 0.06 Zn: 0.10	SX01 ESPA SW30HR	125 bar	Permeate flux: 13.7 (SX01), 20.0 (ESPA) and 5.6 (SW30HR) L/m^2 h Acid permeation: 46.3 (SX01),2.5 (ESPA) and 4.2 (SW30HR) % Acid purification: 98.4 (SX01), 34.4 (ESPA) and 76.8 (SW30HR) %	González et al. [77]

* After being pre-treated with DD

7. Application of membrane technologies at industrial scale for the valorisation of acidic liquid effluents

Mining and hydrometallurgical industries play an essential role in the sustainable management of water resources, especially in its balance (e.g. water discharge and consumption). Despite the high water volumes of mining and hydrometallurgical industries needed to be treated, literature is scarce in relation to the industrial application of membrane technologies to valorise acidic effluents. Several examples can be found related to acidic mine water treatment, but no data were found regarding the hydrometallurgical industry (**Table 5**).

Chesters et al. [190] reported more than 363 mines (69% of them are copper and gold sites) that generate waters that can be potentially treated with membrane technology. They also reported to be 67 operational membrane plants by 2016. One of the first large scale applications is at Mexicana de Cananea Mine (Mexico) to remove and treat water from the pit. A RO plant designed to treat 900 m^3/h (50% recovery) allows to concentrate copper to 1.6 g/L (which is fed to a SX/EW process) and to generate a clean permeate. Another example is located in Minera Yanacocha (Perú). The RO plant treats the pregnant liquor solution during the rainy season to concentrate them and to make the gold extraction process viable [190]. In another example, AMD from a coal mine is treated to produce potable water in South Africa. The influent is characterised by a pH of 2.7 with a TDS content of 4930 mg/L. The AMD also presents 660 mg/L Ca, 230 mg/L Mg, 3090 mg/L SO_4 and 210 mg/L Fe, among others. The treatment consists of a neutralization and precipitation step using limestone/lime followed by a three-stage membrane process combining UF and RO in series. The treatment process allows to recover more than 97% of water, obtaining 25 ML/d of potable water. The capacity of the plant was increased to 50 ML/d in 2014. The purified water is characterised by a pH 6.0-9.0 with an electrical conductivity below 70 mS/cm and a TDS content lower than 450 mg/L. The treatment cost is 1.50 US $\$/m^3$, whereas the municipality pays 1.00 $\$/m^3$ for the water. The plant consums an average value of 2500 kWh/m^3. Initially, problems related to membrane blockage due to suspended solids and presence of foams were observed [191,192]. Another study case can be found at the Bingham Canyon Mine of the Kennecott Utah Copper company, where mining activities have resulted in two groundwater plumes. The big one (247 million m^3) has a sulphate concentration ranging from 500 to 5000 mg/L, whereas waters from the other plume (62 million m^3) are characterised by elevated concentrations of heavy metals (including lead, arsenic and cadmium, among others), low pH ($2.9<pH<3.4$) and a high concentration of sulphate (>20 g/L). A RO treatment plant (using Hydronautics ESPA2) was built for the treatment of waters from both plumes, which presented a mean concentration of 1200 mg/L and a TDS of 2000 mg/L. Along the six years of operation of the RO plant, the water recovery was around 70-75%. Permeate was send to the district distribution system, whereas the concentrate was sent back to the plumes [193]. NF was also tested to treat the water from the Bingham Canyon Mine after the suspended solid removal stage. In this case, the raw water contained a 92 g/L TDS (mainly 73.8 g/L SO_4, 9.9 g/L Mg and 5.9 g/L Al) and the NF membrane allowed to remove metals and sulphate by more than 97%. Antiscalants were dosed to avoid gypsum precipitation inside the pressure vessels and concentrate lines [194,195]. Another example is the on-site water treatment of the complex of Ulan Coal Mines (Australia) (with both underground and open-pit mining sites). An on-site water treatment scheme allows to produce a clean permeate blended with on-site waters, generating a flow of 30000 m^3/d that is discharged into surface water bodies. The plant incorporates a pre-treatment based on the oxidation of Fe(II) and Mn(II) and its subsequent removal. This is achieved by combining chlorine oxidation and a sand filter with $MnO_2(s)$ that catalyses their oxidation. Therefore, scaling is avoided in the UF and RO units. The RO has a capacity of 12 ML/d [196]. Mine water from a coal mine in Queensland is being treated with a system containing MF followed by RO with a water capacity of 500 m^3/h. Prior to the treatment with MF, several dissolved contaminants are removed by oxidation, coagulation or precipitation [197]. Another plant was built in Tweefontein (South Africa) to treat mine water. The plant can treat 15000 m^3/d producing 10000 m^3/d of potable water. The treatment contains 2-stage of RO membrane processes with an inter-stage softening, and the RO permeate is sent to mineralizing and chlorinating units [198,199]. One example of Zero Liquid Discharge can be found in Collahuasi Copper Mine in Chile. Most of the Chilean Copper mine industry is located up to 150 km from the sea, which implies pumping seawater at a cost of 3.00 US \$/m^3, whereas the desalination cost of the mining waste waters is sensitively lower. The treatment plant can treat 5000 m^3/d (80% recovery) and incorporates UF/RO membranes with an extensive pretreatment [200,201].

Table 5. *Examples of full-scale membrane plants for the treatment of acidic waters*

Location	Feedwater	Membrane process	Treatment capacity (%recovery)	Ref.
Mexicana de Cananea (Mexico)	Water from pit	RO	900 m^3/h (50%)	[190]
Minera Yanacocha (Perú)	Pregnant liquour	RO	2750 m^3/h	[190]
eMalahleni (South Africa)	AMD	UF+RO	26000 m^3/d (97%)	[191,192]
Bingham Canyon Mine (USA)	Acidic groundwater	RO	n.d. (75%)	[193]
Bingham Canyon Mine (USA)	Acidic groundwater	NF	n.d.	[194,195]
Ulan Coal Mines	On-site water	UF + RO	30000 m^3/d	[196]

(Australia)				
Queensland's coal mine (Australia)	Mine water	MF+RO	500 m^3/h	[197]
Tweefontein (South Africa)	Mine water	RO	15000 m^3/d (66%)	[198,199]
Collahuasi Copper Mine (Chile)	n.d.	UF + RO	5000 m^3/d (80%)	[200,201]

n.d.: no data

8. Market perspectives for membranes in acidic mine waters processing technologies

Membrane market analysis projected a growth from 4.4 billion € in 2019 to 6.7 billion € by 2024, at a compound annual growth rate (CAGR) of 9.0%. The highest growth is expected to be in the Asian Pacific, including some large and rapidly growing economies (China, India, Indonesia), because of the increasing demand for physical water treatment. This is related to modifications in regulations concerning water treatment and wastewater discharge. The major drivers are found in the rising awareness about wastewater reuse, rapid industrialization and increasing populations. Besides, the strict regulations regarding water treatment and discharge, the shift from chemical to physical water treatments as well as the variation in the climate, which is related to rains are also driving the membrane market. Accordingly, membranes can be classified concerning their application: food and beverages, water and wastewater (including mining and hydrometallurgical effluents) [202]. Limited reports are found in relation to acidic effluents, and most of the data are related to the global market on membranes.

One of the main characteristics of mining and hydrometallurgical operations are the high volumes of water needed for processing stages and the wastewater generated (e.g. typically higher than 500 m^3/h). Consequently, the membrane suppliers can found a market opportunity in these industries. Besides, a second group of drivers can be found on the changing regulations regarding discharge limits, the increasing investment for water treatment, and the industrialization and automatization of mining sites.

Regarding the membrane type, the polymeric ones are currently leading the market. They can be classified according to the presence of natural (e.g. wool, rubber, and cellulose) or synthetic (e.g. polyamide, PTFE, polysulfone and polyethersulfone, among others) polymers. The last ones are the most promising to be used in the mining and hydrometallurgical field, as they provide a cost-effective solution, achieving a good selectivity, efficiency and they are easy to operate [203]. In relation to the technology, NF is widely applied to both chemical and mining processing stages, and it is projected to register the highest CAGR between 2019 and 2024 [202]. Its application is expected to grow because of its ability to transport mono-charged species (e.g. main strong acids or bases used in the mineral processing stages), while rejecting multi-charged metallic species (e.g. transition metal as precious metals and rare earth elements). This specific separation provides advantages in mining applications, especially during pre-treatment or enrichment. Besides, the use of NF provides lower discharge volumes than RO membranes, also reducing the salinity content. The key market players are DuPont (USA), Toray (Japan), Hydranautics (US), Koch Separation Solutions (USA) and Pentair (UK) with a substantial market share [202]. In the case of mining and hydrometallurgical applications, the development of acid-stable membranes has called for major efforts by most of the key providers. In order to meet the growing demand, the market players have launched new membranes and stabilised new collaborations with research centres to improve the performance of their membranes [203]. The requirements of membranes with high stability in acidic media in industrial and mining applications have made the ceramic membranes market to increase significantly in the next seven years. Among the key market players, TAMI

Industries, Pall Corporation, Ceram Hyd Ltd., Atech Innovations GmbH, Hyflux Ltd., Siva and Jiangsu Jiuwu Hi-Tech Co. Ltd. can be found [204].

9. Conclusions

The exhaustion of mining sites has made necessary to promote circular schemes in order to valorise residual effluents. Along the whole production chain, the mining and hydrometallurgical industries produce acidic waters with a relatively high amount of dissolved metals and non-metals that require an appropriate treatment before their discharge. Conventional treatments of such streams rely on neutralisation-precipitation, solvent extraction or ion-exchange, which require a high amount of chemicals and generate a waste difficult to handle. Nowadays, membrane technologies are emerging as an alternative to conventional treatments, because they offer the possibility of recovering valuable components and can be easily integrated with other treatment units. Among them, the following ones are the most promising to promote circularity:

- Diffusion dialysis. It is suitable for treating streams with high acid concentrations (>1 mol/L) because its AEM allows the recovery of acid (>70%) with a low transport of metals (<5%). However, due to the low flow rates to achieve the separation, high membrane area may be needed.
- Electrodialysis. It is useful for desalination since it allows to obtain a purified water stream. However, the presence of Fe(III) may produce scaling on the membrane surface, which will increase the need for electric current to achieve the separation. Despite this disadvantage, other kinds of configurations such as BMED or SED are promising. The BMED can be useful for the production of a purified acid stream, whereas the SED may remove any undesirable compound from the feed solution.

- Forward osmosis. It is under development for the valorisation of acidic effluents. Promising results are being achieved for water recovery from AMD. The main drawback is associated with the selection of an appropriate draw solution to avoid membrane scaling.
- Membrane distillation. Different kinds of acids can be concentrated with MD. Moreover, volatile acids (e.g. HCl, HNO_3) can be transported across the membrane and purely obtained in the permeate.
- Nanofiltration. It is widely used for acidities lower than 1 mol/L as it allows the transport of the acid, while metals are rejected. However, its performance is affected by the solution composition, especially by pH.
- Reverse osmosis. The use of RO is discarded at high acidity levels because of the high need for hydraulic pressure and the lower acid recovery.

As can be seen, membrane technologies are able to treat acidic effluents. Nevertheless, the stability of the membranes at acidic media must be studied. Commercial ion-exchange membranes for DD and ED operation are stable under acidic media, as well as MD membranes (PP, PTFE or PVDF). Nonetheless, most of the NF and RO membranes (usually those made of polyamide) are not stable at acidic media and suffer from hydrolysis in the long term exposure. Nowadays, acid-resistant membranes (both polymeric and ceramic) are emerging as an alternative for the treatment of acidic waters. However, some of them still show poor performance, and research must be towards improving their performance in terms of selectivity. One issue that must be studied is the ways to improve the separation factor for NF and ion-exchange membranes. The transport of non-charged species (e.g. $H_3AsO_4(aq)$) across them may be a limitation regarding the re-use of the purified acid internally. In addition, despite low pH values, scaling can occur. In fact, the low pH of the ALWs and the presence of dissolved metals can cause the precipitation of iron, aluminium and calcium mineral phases, which can limit the applicability of membranes-based systems.

The review on full-scale treatment of AWLs at several mining sites over the last years indicates that recycling such waters by mechanical purification systems (e.g. UF, NF and RO) is preferable than adding chemicals to wastewater (i.e. neutralisation/precipitation).

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References

[1] 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.

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

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

[4] S.A. Welch, A.G. Christy, L. Isaacson, D. Kirste, Mineralogical control of rare earth elements in acid sulfate soils, Geochim. Cosmochim. Acta. 73 (2009) 44–64. doi:10.1016/j.gca.2008.10.017.

[5] D. Merten, J. Geletneky, H. Bergmann, G. Haferburg, E. Kothe, G. Büchel, Rare earth element patterns: A tool for understanding processes in remediation of acid mine drainage, Chemie Der Erde - Geochemistry. 65 (2005) 97–114. doi:10.1016/j.chemer.2005.06.002.

[6] Ma. Nicolle, M. Lampi, K. Valkama, J. Karonen, Leaching of Copper Sulphides, in: Copp. Cobalt Africa, Inc. 8th South. African Base Met. Conf., Southern African Institute of Mining and Metallurgy, Livingstone, Zambia, 2015: pp. 183–194. doi:10.1533/9781845694616.341.

[7] European IPPC Bureau, Reference Document on Best Available Techniques for the Non-Ferrous Metals Industries, 2017. doi:10.2760/8224.

[8] J. López, O. Gibert, J.L. Cortina, Evaluation of an extreme acid-resistant sulphonamide based nanofiltration membrane for the valorisation of copper acidic effluents, Chem. Eng. J. (2020) 127015. doi:10.1016/j.cej.2020.127015.

[9] M. Regel, A.M. Sastre, J. Szymanowski, Recovery of zinc(II) from HCl spent pickling solutions by solvent extraction, Environ. Sci. Technol. 35 (2001) 630–635. doi:10.1021/es001470w.

[10] M.E. Schlesinger, M.J. King, K.C. Sole, Electrowinning, in: Extr. Metall. Copp., Elsevier Ltd, 2011: pp. 349–372. doi:10.1016/b978-0-08-096789-9.10017-4.

[11] A. Culcasi, R. Gueccia, S. Randazzo, A. Cipollina, G. Micale, Design of a novel membrane-integrated waste acid recovery process from pickling solution, J. Clean. Prod. 236 (2019) 117623. doi:10.1016/j.jclepro.2019.117623.

[12] A. Agrawal, K.K. Sahu, An overview of the recovery of acid from spent acidic solutions from steel and electroplating industries, J. Hazard. Mater. 171 (2009) 61–75.

doi:10.1016/j.jhazmat.2009.06.099.

[13] A.S. Sheoran, V. Sheoran, Heavy metal removal mechanism of acid mine drainage in wetlands: A critical review, Miner. Eng. 19 (2006) 105–116. doi:10.1016/j.mineng.2005.08.006.

[14] D.B. Johnson, K.B. Hallberg, Acid mine drainage remediation options: A review, Sci. Total Environ. 338 (2005) 3–14. doi:10.1016/j.scitotenv.2004.09.002.

[15] D.W. Blowes, C.J. Ptacek, J.L. Jambor, C.G. Weisener, D. Paktunc, W.D. Gould, D.B. Johnson, The Geochemistry of Acid Mine Drainage, in: Treatise on Geochemistry, Elsevier, 2014: pp. 131–190. doi:10.1016/B978-0-08-095975-7.00905-0.

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

[17] E. Macingova, A. Luptakova, Recovery of metals from acid mine drainage, Chem. Eng. Trans. 28 (2012) 109–114. doi:10.3303/CET1228019.

[18] European Commission, Report on Critical Raw Materials and the Circular Economy PART 3/3, 2018. doi:10.1097/PPO.0b013e3181b9c5d5.

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

[20] R.D. Abreu, C.A. Morais, Study on Separation of Heavy Rare Earth Elements by Solvent Extraction with Organophosphorus Acids and Amine Reagents, Miner. Eng. 61 (2014) 82–87. doi:10.1016/j.mineng.2014.03.015.

[21] J. Kulczycka, Z. Kowalski, M. Smol, H. Wirth, Evaluation of the recovery of Rare Earth Elements (REE) from phosphogypsum waste - Case study of the WIZÓW Chemical Plant

(Poland), J. Clean. Prod. 113 (2016) 345–354. doi:10.1016/j.jclepro.2015.11.039.

[22] L. Wang, Y. Yu, X. Huang, Z. Long, D. Cui, Toward greener comprehensive utilization of bastnaesite: Simultaneous recovery of cerium, fluorine, and thorium from bastnaesite leach liquor using HEH(EHP), Chem. Eng. J. 215–216 (2013) 162–167. doi:10.1016/j.cej.2012.09.126.

[23] J. Sánchez España, E. López Pamo, E. Santofimia, O. Aduvire, J. Reyes, D. Barettino, Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications, Appl. Geochemistry. 20 (2005) 1320–1356. doi:10.1016/j.apgeochem.2005.01.011.

[24] M. Olías, C.R. Cánovas, J.M. Nieto, A.M. Sarmiento, Evaluation of the dissolved contaminant load transported by the Tinto and Odiel rivers (South West Spain), Appl. Geochemistry. 21 (2006) 1733–1749. doi:10.1016/j.apgeochem.2006.05.009.

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

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

[27] G. Lee, J.M. Bigham, G. Faure, Removal of trace metals by coprecipitation with Fe, Al and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee, Appl. Geochemistry. 17 (2002) 569–581. doi:10.1016/S0883-2927(01)00125-1.

[28] X. Wei, R.C. Viadero, K.M. Buzby, Recovery of iron and aluminum from acid mine drainage by selective precipitation, Environ. Eng. Sci. 22 (2005) 745–755. doi:10.1089/ees.2005.22.745.

[29] M. Bissen, F.H. Frimmel, Arsenic - A review. Part II: Oxidation of arsenic and its removal in water treatment, Acta Hydrochim. Hydrobiol. 31 (2003) 97–107. doi:10.1002/aheh.200300485.

[30] T.S.Y. Choong, T.G. Chuah, Y. Robiah, F.L. Gregory Koay, I. Azni, Arsenic toxicity, health hazards and removal techniques from water: an overview, Desalination. 217 (2007) 139–166. doi:10.1016/j.desal.2007.01.015.

[31] V.K. Sharma, M. Sohn, Aquatic arsenic: Toxicity, speciation, transformations, and remediation, Environ. Int. 35 (2009) 743–759. doi:10.1016/j.envint.2009.01.005.

[32] F. Fu, Q. Wang, Removal of heavy metal ions from wastewaters: A review, J. Environ. Manage. 92 (2011) 407–418. doi:10.1016/j.jenvman.2010.11.011.

[33] O. Gibert, J. de Pablo, J.L.L. Cortina, C. Ayora, Treatment of acid mine drainage by sulphate-reducing bacteria using permeable reactive barriers: A review from laboratory to full-scale experiments, Rev. Environ. Sci. Biotechnol. 1 (2002) 327–333. doi:10.1023/A:1023227616422.

[34] C.-M. Neculita, G.J. Zagury, B. Bussière, Passive Treatment of Acid Mine Drainage in Bioreactors using Sulfate-Reducing Bacteria: Critical review and research needs, J. Environ. Qual. 36 (2007) 1–16. doi:10.2134/jeq2006.0066.

[35] European Commission, Communication from the Commission - Towards a circular economy: A zero waste programme for Europe, 2014.

[36] Spire, SPIRE 2050 Vision. Towards the Next Generation of European Process Industries, (2019). https://www.spire2030.eu/what/walking-the-spire-roadmap/spire-2050-vision.

[37] U. Wingenfelder, C. Hansen, G. Furrer, R. Schulin, Removal of heavy metals from mine waters by natural zeolites, Environ. Sci. Technol. 39 (2005) 4606–4613.

doi:10.1021/es048482s.

[38] G. Blanchard, M. Maunaye, G. Martin, Removal of heavy metals from waters by means of natural zeolites, Water Res. 18 (1984) 1501–1507. doi:10.1016/0043-1354(84)90124-6.

[39] M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren, D.E. Shanks, Removal of Heavy Metals and Other Cations from Wastewater Using Zeolites, Sep. Sci. Technol. 25 (1990) 13–15. doi:10.1080/01496399008050409.

[40] IBC Advanced Technologies, Superlig Products, (n.d.). http://www.ibcmrt.com/products/superlig/ (accessed November 16, 2020).

[41] Koch Separation Technologies, BARS, AsRU and SSU Ion Exchange, (n.d.). https://www.kochseparation.com/technologies/ion-exchange/bars-asru-and-ssu-ion-exchange/ (accessed November 16, 2020).

[42] M.J. Hatch, J.A. Dillon, ACID RETARDATION A Simple Physical Method for Separation of Strong Acids from Their Salts, I&EC Process Des. Dev. 2 (1963) 253–263.

[43] E. Petkova, H. Vassilev, V. Shkodrova, Separation of waste plating solution sulphuric acid from metal cations by anion exchange, Hydrometallurgy. 6 (1981) 291–297.

[44] F.J. Alguacil, F.A. López, The extraction of mineral acids by the phosphine oxide Cyanex 923, Hydrometallurgy. 42 (1996) 245–255. doi:10.1016/0304-386X(95)00101-L.

[45] U. Kerney, Treatment of spent pickling acids from hot dip galvanizing, Resour. Conserv. Recycl. 10 (1994) 145–151. doi:10.1016/0921-3449(94)90047-7.

[46] M. Wisniewski, Extraction of arsenic from sulphuric acid solutions by Cyanex 923, Hydrometallurgy. 46 (2003) 235–241. doi:10.1016/s0304-386x(97)90003-7.

[47] R. Castro-Muñoz, Breakthroughs on tailoring pervaporation membranes for water desalination: A review, Water Res. 187 (2020) 116428. doi:10.1016/j.watres.2020.116428.

[48] M. Mulder, Basic Principles of Membrane Technology, Springer Netherlands, 1996. doi:10.1007/978-94-009-1766-8.

[49] R.W. Baker, Membrane Technology and Applications, 2nd ed., John Wiley & Sons, 2004.

[50] A.W. Mohammad, Y.H. Teow, W.L. Ang, Y.T. Chung, D.L. Oatley-Radcliffe, N. Hilal, Nanofiltration membranes review : Recent advances and future prospects, Desalination. 356 (2015) 226–254. doi:10.1016/j.desal.2014.10.043.

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

[52] M. Mullett, R. Fornarelli, D. Ralph, Nanofiltration of mine water: impact of feed pH and membrane charge on resource recovery and water discharge, Membranes (Basel). 4 (2014) 163–180. doi:10.3390/membranes4020163.

[53] D.L. Oatley-Radcliffe, M. Walters, T.J. Ainscough, P.M. Williams, A.W. Mohammad, N. Hilal, Nanofiltration membranes and processes: A review of research trends over the past decade, J. Water Process Eng. 19 (2017) 164–171. doi:10.1016/j.jwpe.2017.07.026.

[54] S. Bandini, D. Vezzani, Nanofiltration modeling: The role of dielectric exclusion in membrane characterization, Chem. Eng. Sci. 58 (2003) 3303–3326. doi:10.1016/S0009-2509(03)00212-4.

[55] T.J.K. Visser, S.J. Modise, H.M. Krieg, K. Keizer, The removal of acid sulphate pollution by nanofiltration, Desalination. 140 (2001) 79–86.

[56] G.T. Ballet, A. Hafiane, M. Dhahbi, Influence of operating conditions on the retention of

phosphate in water by nanofiltration, J. Memb. Sci. 290 (2007) 164–172. doi:10.1016/j.memsci.2006.12.046.

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

[58] J. López, M. Reig, A. Yaroshchuk, E. Licon, O. Gibert, J.L. Cortina, Experimental and theoretical study of nanofiltration of weak electrolytes: SO 4 2– /HSO 4 – /H + system, J. Memb. Sci. 550 (2018) 389–398. doi:10.1016/j.memsci.2018.01.002.

[59] G. Shang, G. Zhang, C. Gao, W. Fu, L. Zeng, A novel nanofiltration process for the recovery of vanadium from acid leach solution, Hydrometallurgy. 142 (2014) 94–97. doi:10.1016/j.hydromet.2013.11.007.

[60] M. Hoyer, D. Zabelt, R. Steudtner, V. Brendler, R. Haseneder, J.U. Repke, Influence of speciation during membrane treatment of uranium contaminated water, Sep. Purif. Technol. 132 (2014) 413–421. doi:10.1016/j.seppur.2014.05.044.

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

[62] A.R. Guastalli, J. Labanda, J. Llorens, Separation of phosphoric acid from an industrial rinsing water by means of nanofiltration, Desalination. 243 (2009) 218–228. doi:10.1016/j.desal.2008.04.024.

[63] H. Diallo, M. Rabiller-Baudry, K. Khaless, B. Chaufer, On the electrostatic interactions in the transfer mechanisms of iron during nanofiltration in high concentrated phosphoric acid, J. Memb. Sci. 427 (2013) 37–47. doi:10.1016/j.memsci.2012.08.047.

[64] K. Meschke, B. Daus, R. Haseneder, J.U. Repke, Strategic elements from leaching solutions by nanofiltration – Influence of pH on separation performance, Sep. Purif. Technol. 184 (2017) 264–274. doi:10.1016/j.seppur.2017.04.048.

[65] K. Meschke, N. Hansen, R. Hofmann, R. Haseneder, J.U. Repke, Characterization and performance evaluation of polymeric nanofiltration membranes for the separation of strategic elements from aqueous solutions, J. Memb. Sci. 546 (2018) 246–257. doi:10.1016/j.memsci.2017.09.067.

[66] A. Werner, A. Rieger, M. Mosch, R. Haseneder, J.U. Repke, Nanofiltration of indium and germanium ions in aqueous solutions: Influence of pH and charge on retention and membrane flux, Sep. Purif. Technol. 194 (2018) 319–328. doi:10.1016/j.seppur.2017.11.006.

[67] Y.A. Boussouga, H. Frey, A.I. Schäfer, Removal of arsenic(V) by nanofiltration: Impact of water salinity, pH and organic matter, J. Memb. Sci. 618 (2021) 118631. doi:10.1016/j.memsci.2020.118631.

[68] C.-M. Zhong, Z.-L. Xu, X.-H. Fang, L. Cheng, Treatment of Acid Mine Drainage (AMD) by Ultra-Low-Pressure Reverse Osmosis and Nanofiltration, Environ. Eng. Sci. 24 (2007) 1297–1306. doi:10.1089/ees.2006.0245.

[69] H. Al-Zoubi, A. Rieger, P. Steinberger, W. Pelz, R. Haseneder, G. Härtel, Optimization Study for Treatment of Acid Mine Drainage Using Membrane Technology, Sep. Sci. Technol. 45 (2010) 2004–2016. doi:10.1080/01496395.2010.480963.

[70] H. Al-Zoubi, A. Rieger, P. Steinberger, W. Pelz, R. Haseneder, G. Härtel, Nanofiltration of Acid Mine Drainage, Desalin. Water Treat. 21 (2010) 148–161. doi:10.5004/dwt.2010.1316.

[71] R. Fornarelli, M. Mullett, D. Ralph, Factors influencing nanofiltration of acid mine drainage, Reliab. Mine Water Technol. (2013) 563–568.

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

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

[74] L. Pino, E. Beltran, A. Schwarz, M.C. Ruiz, R. Borquez, Optimization of nanofiltration for treatment of acid mine drainage and copper recovery by solvent extraction, Hydrometallurgy. 195 (2020) 105361. doi:10.1016/j.hydromet.2020.105361.

[75] M. Nyström, J. Tanninen, M. Mänttäri, Separation of metal sulfates and nitrates from their acids using nanofiltration, Membr. Technol. 2000 (2000) 5–9. doi:10.1016/S0958-2118(00)86633-1.

[76] P.K. Eriksson, L.A. Lien, D.H. Green, Membrane technology for treatment of wastes containing dissolved metals, in: V. Ramachandram, C.C. Nesbitt (Eds.), Second Int. Symp. Extr. Process. Treat. Minimization Wastes, 1996: pp. 649–658.

[77] M.P. González, R. Navarro, I. Saucedo, M. Avila, J. Revilla, C. Bouchard, Purification of phosphoric acid solutions by reverse osmosis and nanofiltration, Desalination. 147 (2002) 315–320. doi:10.1016/S0011-9164(02)00558-1.

[78] H.J. Skidmore, K.J. Hutter, Methods of purifying phosphoric acid, US 5945000 A, 1999. https://www.google.es/patents/US5945000?dq=purification+of+aqueous+phosphoric+

acid+by+hot+filtration+using+a+polyamide+nanofilter&hl=es&sa=X&ved=0ahUKEwiA8Z2CxKfLAhWDVRQKHYXxCm4Q6AEIHDAA (accessed March 4, 2016).

[79] M. V. Galiana-Aleixandre, A. Iborra-Clar, A. Bes-Piá, J.A. Mendoza-Roca, B. Cuartas-Uribe, M.I. Iborra-Clar, Nanofiltration for sulfate removal and water reuse of the pickling and tanning processes in a tannery, Desalination. 179 (2005) 307–313. doi:10.1016/j.desal.2004.11.076.

[80] M. V. Galiana-Aleixandre, J.A. Mendoza-Roca, A. Bes-Piá, Reducing sulfates concentration in the tannery effluent by applying pollution prevention techniques and nanofiltration, J. Clean. Prod. 19 (2011) 91–98. doi:10.1016/j.jclepro.2010.09.006.

[81] C.-V. Gherasim, P. Mikulášek, Influence of operating variables on the removal of heavy metal ions from aqueous solutions by nanofiltration, Desalination. 343 (2014) 67–74. doi:10.1016/j.desal.2013.11.012.

[82] J. Tanninen, M. Mänttäri, M. Nyström, Nanofiltration of concentrated acidic copper sulphate solutions, Desalination. 189 (2006) 92–96. doi:10.1016/j.desal.2005.06.017.

[83] J. Tanninen, M. Mänttäri, M. Nyström, Effect of electrolyte strength on acid separation with NF membranes, J. Memb. Sci. 294 (2007) 207–212. doi:10.1016/j.memsci.2007.02.042.

[84] J. Tanninen, S. Platt, M. Nyström, Nanofiltration of sulphuric acid from metal sulphate solutions, Proc. Imstec 2003, Sydney. (2003) 1–6.

[85] A. Manis, K. Soldenhoff, E. Jusuf, F. Lucien, Separation of copper from sulfuric acid by nanofiltration, in: Fifth Int. Membr. Sci. Technol. Conf., 2003.

[86] L.M. Ortega, R. Lebrun, J.F. Blais, R. Hausler, P. Drogui, Effectiveness of soil washing, nanofiltration and electrochemical treatment for the recovery of metal ions coming

from a contaminated soil, Water Res. 42 (2008) 1943–1952. doi:10.1016/j.watres.2007.11.025.

[87] S. Gomes, S.A. Cavaco, M.J. Quina, L.M. Gando-Ferreira, Nanofiltration process for separating Cr(III) from acid solutions: Experimental and modelling analysis, Desalination. 254 (2010) 80–89. doi:10.1016/j.desal.2009.12.010.

[88] T. Schütte, C. Niewersch, T. Wintgens, S. Yüce, Phosphorus recovery from sewage sludge by nanofiltration in diafiltration mode, J. Memb. Sci. 480 (2015) 74–82. doi:10.1016/j.memsci.2015.01.013.

[89] J. López, M. Reig, O. Gibert, J.L. Cortina, Increasing sustainability on the metallurgical industry by integration of membrane nanofiltration processes: Acid recovery, Sep. Purif. Technol. 226 (2019) 267–277. doi:10.1016/j.seppur.2019.05.100.

[90] S. Platt, M. Nyström, A. Bottino, G. Capannelli, Stability of NF membranes under extreme acidic conditions, J. Memb. Sci. 239 (2004) 91–103. doi:10.1016/j.memsci.2003.09.030.

[91] R. Navarro, M.P. González, I. Saucedo, M. Avila, P. Prádanos, F. Martínez, A. Martín, A. Hernández, Effect of an acidic treatment on the chemical and charge properties of a nanofiltration membrane, J. Memb. Sci. 307 (2008) 136–148. doi:10.1016/j.memsci.2007.09.015.

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

[93] B.C. Ricci, C.D. Ferreira, L.S. Marques, S.S. Martins, B.G. Reis, M.C.S. Amaral,

Assessment of the chemical stability of nanofiltration and reverse osmosis membranes employed in treatment of acid gold mining effluent, Sep. Purif. Technol. 174 (2017) 301–311. doi:10.1016/j.seppur.2016.11.007.

[94] B.M. Jun, S.H. Kim, S.K. Kwak, Y.N. Kwon, Effect of acidic aqueous solution on chemical and physical properties of polyamide NF membranes, Appl. Surf. Sci. 444 (2018) 387–398. doi:10.1016/j.apsusc.2018.03.078.

[95] Y. Zeng, L. Wang, L. Zhang, J.Q. Yu, An acid resistant nanofiltration membrane prepared from a precursor of poly(s-triazine-amine) by interfacial polymerization, J. Memb. Sci. 546 (2018) 225–233. doi:10.1016/j.memsci.2017.10.022.

[96] H.M. Park, H. Takaba, Y.T. Lee, Preparation and characterization of TFC NF membrane with improved acid resistance behavior, J. Memb. Sci. 616 (2020) 118620. doi:10.1016/j.memsci.2020.118620.

[97] T. Yun, S.Y. Kwak, Recovery of hydrochloric acid using positively-charged nanofiltration membrane with selective acid permeability and acid resistance, J. Environ. Manage. 260 (2020) 110001. doi:10.1016/j.jenvman.2019.110001.

[98] M.G. Elshof, W.M. de Vos, J. de Grooth, N.E. Benes, On the long-term pH stability of polyelectrolyte multilayer nanofiltration membranes, J. Memb. Sci. 615 (2020) 118532. doi:10.1016/j.memsci.2020.118532.

[99] M.G. Shin, S.J. Kwon, H. Park, Y.I. Park, J.H. Lee, High-performance and acid-resistant nanofiltration membranes prepared by solvent activation on polyamide reverse osmosis membranes, J. Memb. Sci. 595 (2020) 117590. doi:10.1016/j.memsci.2019.117590.

[100] L. Yu, Y. Zhang, L. Xu, Q. Liu, B. Borjigin, D. Hou, J. Xiang, J. Wang, One step prepared

Janus acid-resistant nanofiltration membranes with opposite surface charges for acidic wastewater treatment, Sep. Purif. Technol. 250 (2020) 117245. doi:10.1016/j.seppur.2020.117245.

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

[102] S.M. Samaei, S. Gato-Trinidad, A. Altaee, The application of pressure-driven ceramic membrane technology for the treatment of industrial wastewaters – A review, Sep. Purif. Technol. 200 (2018) 198–220. doi:10.1016/j.seppur.2018.02.041.

[103] V. Gitis, G. Rothenberg, Ceramic Membranes. New opportunities and Practical Applications, 1st ed., Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2016. doi:10.1002/9783527696550.

[104] S. Benfer, U. Popp, H. Richter, C. Siewert, G. Tomandl, Development and characterization of ceramic nanofiltration membranes, Sep. Purif. Technol. 22–23 (2001) 231–237. doi:10.1016/S1383-5866(00)00133-7.

[105] I. Voigt, G. Fischer, P. Puhlfürß, M. Schleifenheimer, M. Stahn, TiO2-NF-membranes on capillary supports, Sep. Purif. Technol. 32 (2003) 87–91. doi:10.1016/S1383-5866(03)00064-9.

[106] I. Voigt, M. Stahn, S. Wöhner, A. Junghans, J. Rost, W. Voigt, Integrated cleaning of coloured waste water by ceramic NF membranes, Sep. Purif. Technol. 25 (2001) 509–512. doi:10.1007/978-3-642-54734-2.

[107] S.S. Wadekar, R.D. Vidic, Comparison of ceramic and polymeric nanofiltration membranes for treatment of abandoned coal mine drainage, Desalination. 440 (2018)

135–145. doi:10.1016/j.desal.2018.01.008.

[108] J. López, M. Reig, X. Vecino, O. Gibert, J.L. Cortina, Comparison of acid-resistant ceramic and polymeric nanofiltration membranes for acid mine waters treatment, Chem. Eng. J. 382 (2020) 122786. doi:10.1016/j.cej.2019.122786.

[109] M. Jafari, M. Vanoppen, J.M.C. van Agtmaal, E.R. Cornelissen, J.S. Vrouwenvelder, A. Verliefde, M.C.M. van Loosdrecht, C. Picioreanu, Cost of fouling in full-scale reverse osmosis and nanofiltration installations in the Netherlands, Desalination. 500 (2021) 114865. doi:10.1016/j.desal.2020.114865.

[110] A. Rieger, P. Steinberger, W. Pelz, R. Haseneder, G. Härtel, Mine water treatment by membrane filtration processes - Experimental investigations on applicability, Desalin. Water Treat. 6 (2009) 54–60. doi:10.5004/dwt.2009.644.

[111] S. Nasir, E. Ibrahim, A.T. Arief, Design and experimental testing of small-scale acid mine drainage treatment plant, J. Mater. Environ. Sci. 7 (2016) 3004–3010.

[112] A.O. Aguiar, L.H. Andrade, B.C. Ricci, W.L. Pires, G.A. Miranda, M.C.S. Amaral, Gold acid mine drainage treatment by membrane separation processes: An evaluation of the main operational conditions, Sep. Purif. Technol. 170 (2016) 360–369. doi:10.1016/j.seppur.2016.07.003.

[113] M.C.S. Amaral, L.B. Grossi, R.L. Ramos, B.C. Ricci, L.H. Andrade, Integrated UF–NF–RO route for gold mining effluent treatment: From bench-scale to pilot-scale, Desalination. 440 (2018) 111–121. doi:10.1016/j.desal.2018.02.030.

[114] K. Ishii, A. Ikeda, T. Takeuchi, J. Yoshiura, M. Nomura, Silica-based ro membranes for separation of acidic solution, Membranes (Basel). 9 (2019). doi:10.3390/membranes9080094.

[115] J. Luo, C. Wu, T. Xu, Y. Wu, Diffusion dialysis-concept, principle and applications, J. Memb. Sci. 366 (2011) 1–16. doi:10.1016/j.memsci.2010.10.028.

[116] C. Wei, X. Li, Z. Deng, G. Fan, M. Li, C. Li, Recovery of H2SO4 from an acid leach solution by diffusion dialysis, J. Hazard. Mater. 176 (2010) 226–230. doi:10.1016/j.jhazmat.2009.11.017.

[117] R. Gueccia, S. Randazzo, D. Chillura Martino, A. Cipollina, G. Micale, Experimental investigation and modeling of diffusion dialysis for HCl recovery from waste pickling solution, J. Environ. Manage. 235 (2019) 202–212. doi:10.1016/j.jenvman.2019.01.028.

[118] W. Li, Y. Zhang, H. Jing, X. Zhu, Y. Wang, Separation and recovery of sulfuric acid from acidic vanadium leaching solution by diffusion dialysis, J. Environ. Chem. Eng. 4 (2016) 1399–1405. doi:10.1016/j.jece.2015.11.038.

[119] J. Jeong, M.S. Kim, B.S. Kim, S.K. Kim, W.B. Kim, J.C. Lee, Recovery of H2SO4 from waste acid solution by a diffusion dialysis method, J. Hazard. Mater. 124 (2005) 230–235. doi:10.1016/j.jhazmat.2005.05.005.

[120] R. Gueccia, A.R. Aguirre, S. Randazzo, A. Cipollina, G. Micale, Diffusion dialysis for separation of hydrochloric acid, iron and zinc ions from highly concentrated pickling solutions, Membranes (Basel). 10 (2020) 1–17. doi:10.3390/membranes10060129.

[121] J. Xu, D. Fu, S. Lu, The recovery of sulphuric acid from the waste anodic aluminum oxidation solution by diffusion dialysis, Sep. Purif. Technol. 69 (2009) 168–173. doi:10.1016/j.seppur.2009.07.015.

[122] K. Wang, Y. Zhang, J. Huang, T. Liu, J. Wang, Recovery of sulfuric acid from a stone coal acid leaching solution by diffusion dialysis, Hydrometallurgy. 173 (2017) 9–14. doi:10.1016/j.hydromet.2017.07.005.

[123] F. Luo, X. Zhang, J. Pan, A.N. Mondal, H. Feng, T. Xu, Diffusion dialysis of sulfuric acid in spiral wound membrane modules: Effect of module number and connection mode, Sep. Purif. Technol. 148 (2015) 25–31. doi:10.1016/j.seppur.2015.04.033.

[124] S. Lan, X. Wen, Z. Zhu, F. Shao, C. Zhu, Recycling of spent nitric acid solution from electrodialysis by diffusion dialysis, Desalination. 278 (2011) 227–230. doi:10.1016/j.desal.2011.05.031.

[125] J. Xu, S. Lu, D. Fu, Recovery of hydrochloric acid from the waste acid solution by diffusion dialysis, J. Hazard. Mater. 165 (2009) 832–837. doi:10.1016/j.jhazmat.2008.10.064.

[126] Z. Palatý, A. Žáková, Transport of sulfuric acid through anion-exchange membrane NEOSEPTA-AFN, J. Memb. Sci. 119 (1996) 183–190.

[127] Z. Palatý, A. Žáková, Separation of H2SO4 + CuSO4 mixture by diffusion dialysis, J. Hazard. Mater. 114 (2004) 69–74. doi:10.1016/j.jhazmat.2004.06.023.

[128] Z. Palatý, A. Žáková, Separation of H2SO4 + ZnSO4 mixture by diffusion dialysis, Desalination. 169 (2004) 277–285. doi:10.1016/j.desal.2004.01.001.

[129] Z. Palatý, A. Žáková, P. Doleček, Modelling the transport of Cl- ions through the anion-exchange membrane NEOSEPTA-AFN systems HCl/membrane/H2O and HCl-FeCl3/membrane/H2O, J. Memb. Sci. 165 (2000) 237–249. doi:10.1016/S0376-7388(99)00239-2.

[130] Z. Palatý, A. Žková, Separation of HCl+NiCl2 mixture by diffusion dialysis, Sep. Sci. Technol. 42 (2007) 1965–1983. doi:10.1080/15363830701313362.

[131] Z. Palatý, A. Žáková, Apparent diffusivity of some inorganic acids in anion-exchange membrane, J. Memb. Sci. 173 (2000) 211–223. doi:10.1016/S0376-7388(00)00363-X.

[132] Z. Palatý, A. Žáková, Transport of some strong incompletely dissociated acids through anion-exchange membrane, J. Colloid Interface Sci. 268 (2003) 188–199. doi:10.1016/j.jcis.2003.07.034.

[133] M. Ersoz, I.H. Gugul, a. Sahin, Transport of Acids through Polyether-Sulfone Anion-Exchange Membrane., J. Colloid Interface Sci. 237 (2001) 130–135. doi:10.1006/jcis.2001.7487.

[134] M.I. Khan, M. Khraisheh, F. Almomani, Fabrication and characterization of pyridinium functionalized anion exchange membranes for acid recovery, Sci. Total Environ. 686 (2019) 90–96. doi:10.1016/j.scitotenv.2019.05.481.

[135] W. Ji, X. Ge, N.U. Afsar, Z. Zhao, B. Wu, W. Song, Y. He, L. Ge, T. Xu, In-situ crosslinked AEMs with self-assembled nanostructure for acid recovery, Sep. Purif. Technol. 247 (2020) 116927. doi:10.1016/j.seppur.2020.116927.

[136] W. Ji, B. Wu, Y. Zhu, M. Irfan, N. Ul Afsar, L. Ge, T. Xu, Self-organized nanostructured anion exchange membranes for acid recovery, Chem. Eng. J. 382 (2020) 122838. doi:10.1016/j.cej.2019.122838.

[137] V. Yadav, S.K. Raj, N.H. Rathod, V. Kulshrestha, Polysulfone/graphene quantum dots composite anion exchange membrane for acid recovery by diffusion dialysis, J. Memb. Sci. 611 (2020) 118331. doi:10.1016/j.memsci.2020.118331.

[138] T.Y. Cath, A.E. Childress, M. Elimelech, Forward osmosis: Principles, applications, and recent developments, J. Memb. Sci. 281 (2006) 70–87. doi:10.1016/j.memsci.2006.05.048.

[139] S. Zhao, L. Zou, C.Y. Tang, D. Mulcahy, Recent developments in forward osmosis: Opportunities and challenges, J. Memb. Sci. 396 (2012) 1–21.

doi:10.1016/j.memsci.2011.12.023.

[140] X. Jin, C.Y. Tang, Y. Gu, Q. She, S. Qi, Boric acid permeation in forward osmosis membrane processes: Modeling, experiments, and implications, Environ. Sci. Technol. 45 (2011) 2323–2330. doi:10.1021/es103771a.

[141] C.Y. Tang, Q. She, W.C.L. Lay, R. Wang, A.G. Fane, Coupled effects of internal concentration polarization and fouling on flux behavior of forward osmosis membranes during humic acid filtration, J. Memb. Sci. 354 (2010) 123–133. doi:10.1016/j.memsci.2010.02.059.

[142] S. Phuntsho, S. Vigneswaran, J. Kandasamy, S. Hong, S. Lee, H.K. Shon, Influence of temperature and temperature difference in the performance of forward osmosis desalination process, J. Memb. Sci. 415–416 (2012) 734–744. doi:10.1016/j.memsci.2012.05.065.

[143] S. You, J. Lu, C.Y. Tang, X. Wang, Rejection of heavy metals in acidic wastewater by a novel thin-film inorganic forward osmosis membrane, Chem. Eng. J. 320 (2017) 532–538. doi:10.1016/j.cej.2017.03.064.

[144] B. Vital, J. Bartacek, J.C. Ortega-Bravo, D. Jeison, Treatment of acid mine drainage by forward osmosis: Heavy metal rejection and reverse flux of draw solution constituents, Chem. Eng. J. 332 (2018) 85–91. doi:10.1016/j.cej.2017.09.034.

[145] B.K. Pramanik, L. Shu, J. Jegatheesan, K. Shah, N. Haque, M.A. Bhuiyan, Rejection of rare earth elements from a simulated acid mine drainage using forward osmosis: The role of membrane orientation, solution pH, and temperature variation, Process Saf. Environ. Prot. 126 (2019) 53–59. doi:10.1016/j.psep.2019.04.004.

[146] J. Choi, S.J. Im, A. Jang, Application of volume retarded osmosis – Low pressure

membrane hybrid process for recovery of heavy metals in acid mine drainage, Chemosphere. 232 (2019) 264–272. doi:10.1016/j.chemosphere.2019.05.209.

[147] F.M. Baena-Moreno, M. Rodríguez-Galán, F. Arroyo-Torralvo, L.F. Vilches, Low-Energy Method for Water-Mineral Recovery from Acid Mine Drainage Based on Membrane Technology: Evaluation of Inorganic Salts as Draw Solutions, Environ. Sci. Technol. (2020). doi:10.1021/acs.est.0c03392.

[148] M. Boucher, N. Turcotte, V. Guillemette, G. Lantagne, A. Chapotot, G. Pourcelly, R. Sandeaux, C. Gavach, Recovery of spent acid by electrodialysis in the zinc hydrometallurgy industry : performance study of different cation-exchange membranes, Hydrometallurgy. 45 (1997) 137–160.

[149] D.C. Buzzi, L.S. Viegas, M.A.S. Rodrigues, A.M. Bernardes, J.A.S. Tenório, Water recovery from acid mine drainage by electrodialysis, Miner. Eng. 40 (2013) 82–89. doi:10.1016/j.mineng.2012.08.005.

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

[151] L. Cifuentes, G. Crisóstomo, J.P. Ibez, J.M. Casas, F. Alvarez, G. Cifuentes, On the electrodialysis of aqueous H2SO4-CuSO4 electrolytes with metallic impurities, J. Memb. Sci. 207 (2002) 1–16. doi:10.1016/S0376-7388(01)00733-5.

[152] L. Cifuentes, I. García, P. Arriagada, J.M. Casas, The use of electrodialysis for metal separation and water recovery from CuSO4-H2SO4-Fe solutions, Sep. Purif. Technol. 68 (2009) 105–108. doi:10.1016/j.seppur.2009.04.017.

[153] A. Chekioua, R. Delimi, Purification of H2SO4 of Pickling Bath Contaminated by Fe(II)

Ions Using Electrodialysis Process, Energy Procedia. 74 (2015) 1418–1433. doi:10.1016/j.egypro.2015.07.789.

[154] P. Sistat, G. Pourcelly, C. Gavach, N. Turcotte, M. Boucher, Electrodialysis of acid effluents containing metallic divalent salts: Recovery of acid with a cation-exchange membrane modified in situ, J. Appl. Electrochem. 27 (1997) 65–70. doi:10.1023/A:1026419000089.

[155] S.S. Melnikov, O.A. Mugtamov, V.I. Zabolotsky, Study of electrodialysis concentration process of inorganic acids and salts for the two-stage conversion of salts into acids utilizing bipolar electrodialysis, Sep. Purif. Technol. 235 (2020) 116198. doi:10.1016/j.seppur.2019.116198.

[156] G. Sun, J. Xu, Treatment of waste phosphoric acid containing metal ions by electrodialysis, Adv. Mater. Res. 455–456 (2012) 1228–1231. doi:10.4028/www.scientific.net/AMR.455-456.1228.

[157] X. Zhang, C. Li, X. Wang, Y. Wang, T. Xu, Recovery of hydrochloric acid from simulated chemosynthesis aluminum foils wastewater: An integration of diffusion dialysis and conventional electrodialysis, J. Memb. Sci. 409–410 (2012) 257–263. doi:10.1016/j.memsci.2012.03.062.

[158] A. Campione, L. Gurreri, M. Ciofalo, G. Micale, A. Tamburini, A. Cipollina, Electrodialysis for water desalination: A critical assessment of recent developments on process fundamentals, models and applications, Desalination. 434 (2018) 121–160. doi:10.1016/j.desal.2017.12.044.

[159] Y. Liu, X. Ke, H. Zhu, R. Chen, X. Chen, X. Zheng, Y. Jin, B. Van der Bruggen, Treatment of raffinate generated via copper ore hydrometallurgical processing using a bipolar membrane electrodialysis system, Chem. Eng. J. 382 (2020) 122956.

doi:10.1016/j.cej.2019.122956.

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

[161] L. Cifuentes, C. Mondaca, J.M. Casas, The effectiveness of membrane systems for the separation of anolyte and catholyte in a lab-scale copper electrowinning cell based on reactive electrodialysis, Miner. Eng. 17 (2004) 803–809. doi:10.1016/j.mineng.2004.01.010.

[162] L. Cifuentes, M. Grágeda, G. Crisóstomo, Electrowinning of copper in two- and three-compartment reactive electrodialysis cells, Chem. Eng. Sci. 61 (2006) 3623–3631. doi:10.1016/j.ces.2006.01.008.

[163] L. Cifuentes, J.M. Casas, J. Simpson, Modelling the effect of temperature and time on the performance of a copper electrowinning cell based on reactive electrodialysis, Chem. Eng. Sci. 63 (2008) 1117–1130. doi:10.1016/j.ces.2007.11.004.

[164] L. Cifuentes, J.M. Castro, G. Crisóstomo, J.M. Casas, J. Simpson, Modelling a copper electrowinning cell based on reactive electrodialysis, Appl. Math. Model. 31 (2007) 1308–1320. doi:10.1016/j.apm.2006.02.016.

[165] T.Z. Sadyrbaeva, Separation of cobalt(II) from nickel(II) by a hybrid liquid membrane-electrodialysis process using anion exchange carriers, Desalination. 365 (2015) 167–175. doi:10.1016/j.desal.2015.02.036.

[166] M. Khayet, Membranes and theoretical modeling of membrane distillation: A review, Adv. Colloid Interface Sci. 164 (2011) 56–88. doi:10.1016/j.cis.2010.09.005.

[167] E. Drioli, A. Ali, F. Macedonio, Membrane distillation: Recent developments and

perspectives, Desalination. 356 (2015) 56–84. doi:10.1016/j.desal.2014.10.028.

[168] A.F.S. Foureaux, V.R. Moreira, Y.A.R. Lebron, L.V.S. Santos, M.C.S. Amaral, Direct contact membrane distillation as an alternative to the conventional methods for value-added compounds recovery from acidic effluents: A review, Sep. Purif. Technol. 236 (2020) 116251. doi:10.1016/j.seppur.2019.116251.

[169] A. Alkhudhiri, N. Darwish, N. Hilal, Membrane distillation: A comprehensive review, Desalination. 287 (2012) 2–18. doi:10.1016/j.desal.2011.08.027.

[170] G. Zhang, Q. Zhang, K. Zhou, Study on concentrating sulfuric acid solution by vacuum membrane distillation, J. Cent. South Univ. Technol. 6 (1999) 99–102. doi:10.1007/s11771-999-0007-5.

[171] G. Caputo, C. Felici, P. Tarquini, A. Giaconia, S. Sau, Membrane distillation of HI / H2 O and H2 SO4 / H2 O mixtures for the sulfur-iodine thermochemical process, Int. J. Hydrogen Energy. 32 (2007) 4736–4743. doi:10.1016/j.ijhydene.2007.07.011.

[172] M. Tomaszewska, A. Mientka, Separation of HCl from HCl-H2SO4 solutions by membrane distillation, Desalination. 240 (2009) 244–250. doi:10.1016/j.desal.2007.10.093.

[173] R. Thiruvenkatachari, M. Manickam, T. Ouk Kwon, I. Shik Moon, J. Woo Kim, Separation of water and nitric acid with porous hydrophobic membrane by air gap membrane distillation (AGMD), Sep. Sci. Technol. 41 (2006) 3187–3199. doi:10.1080/01496390600854651.

[174] Z. Si, D. Han, J. Gu, Y. Song, Y. Liu, Exergy analysis of a vacuum membrane distillation system integrated with mechanical vapor recompression for sulfuric acid waste treatment, Appl. Therm. Eng. 178 (2020) 115516.

doi:10.1016/j.applthermaleng.2020.115516.

[175] J.Y. Kim, C.H. Shin, H. Choi, W. Bae, Recovery of phosphoric acid from mixed waste acids of semiconductor industry by diffusion dialysis and vacuum distillation, Sep. Purif. Technol. 90 (2012) 64–68. doi:10.1016/j.seppur.2012.02.013.

[176] X. Feng, L.Y. Jiang, Y. Song, Titanium white sulfuric acid concentration by direct contact membrane distillation, Chem. Eng. J. 285 (2016) 101–111. doi:10.1016/j.cej.2015.09.064.

[177] M. Tomaszewska, M. Gryta, A.W. Morawski, The influence of salt in solutions on hydrochloric acid recovery by membrane distillation, Sep. Purif. Technol. 14 (1998) 183–188. doi:10.1016/S1383-5866(98)00073-2.

[178] M. Tomaszewska, M. Gryta, A.W. Morawski, Mass transfer of HCl and H2O across the hydrophobic membrane during membrane distillation, J. Memb. Sci. 166 (2000) 149–157. doi:10.1016/S0376-7388(99)00263-X.

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

[180] S. Ryu, G. Naidu, M.A. Hasan Johir, Y. Choi, S. Jeong, S. Vigneswaran, Acid mine drainage treatment by integrated submerged membrane distillation–sorption system, Chemosphere. 218 (2019) 955–965. doi:10.1016/j.chemosphere.2018.11.153.

[181] S.C. Ryu, G. Naidu, H. Moon, S. Vigneswaran, Selective copper recovery by membrane distillation and adsorption system from synthetic acid mine drainage, Chemosphere. 260 (2020) 127528. doi:10.1016/j.chemosphere.2020.127528.

[182] U.K. Kesieme, N. Milne, C.Y. Cheng, H. Aral, M. Duke, Recovery of water and acid from leach solutions using direct contact membrane distillation, Water Sci. Technol. 69 (2014) 868–875. doi:10.2166/wst.2013.788.

[183] Y.P. Jimenez, M. Ulbricht, Recovery of Water from Concentration of Copper Mining Effluents Using Direct Contact Membrane Distillation, Ind. Eng. Chem. Res. 58 (2019) 19599–19610. doi:10.1021/acs.iecr.9b02499.

[184] J. Cai, F. Guo, Mass transfer during membrane distillation treatment of wastewater from hot-dip galvanization, Sep. Purif. Technol. 235 (2020) 116164. doi:10.1016/j.seppur.2019.116164.

[185] G. Chen, L. Tan, M. Xie, Y. Liu, Y. Lin, W. Tan, M. Huang, Direct contact membrane distillation of refining waste stream from precious metal recovery: Chemistry of silica and chromium (III) in membrane scaling, J. Memb. Sci. 598 (2020) 117803. doi:10.1016/j.memsci.2019.117803.

[186] J. Tang, K. Zhou, Hydrochloric acid recovery from rare earth chloride solutions by vacuum membrane distillation, Rare Met. 25 (2006) 287–292. doi:10.1016/S1001-0521(06)60055-7.

[187] M. Tomaszewska, M. Gryta, A.W. Morawski, Recovery of hydrochloric acid from metal pickling solutions by membrane distillation, Sep. Purif. Technol. 22–23 (2001) 591–600. doi:10.1016/S1383-5866(00)00164-7.

[188] G. Chen, L. Tan, M. Xie, Y. Liu, Y. Lin, W. Tan, M. Huang, Direct contact membrane distillation of refining waste stream from precious metal recovery: Chemistry of silica and chromium (III) in membrane scaling, J. Memb. Sci. 598 (2020) 117803. doi:10.1016/j.memsci.2019.117803.

[189] URS Infrastructure & Environment UK Limited, The Coal Authority-Metal Mine Water Treatment Review, (n.d.). https://www.gov.uk/government/collections/metal-mine-water-treatment.

[190] S.P. Chesters, P. Morton, M. Fazel, Membranes and minewater – waste or revenue stream, in: Proc. IMWA 2016, 2016: pp. 1310–1322.

[191] Pentair, Pentair - Case study BHP Billiton & Anglo American, (n.d.). https://xflow.pentair.com/en/case-studies/witbank (accessed February 4, 2021).

[192] E. Merta, eMalahleni water treatment plant, (n.d.). https://mineclosure.gtk.fi/emalahleni-water-treatment-plant/ (accessed February 5, 2021).

[193] Interstate Technology and Regulatory Council, Mining Waste Treatment Technology Selection. Pressure-driven membrane separation technologies, (2010) 1–33. https://www.itrcweb.org/miningwaste-guidance/to_membrane_sep.htm#case_study.

[194] H. Bayer, Sludge Management and Treatment of Weak Acid or Neutral pH Drainage, in: Proc. 2004 Ontario MEND Work., Sudbury, Ontario, 2004.

[195] S. Mortazavi, Application of Membrane Separation Technology to Mitigation of Mine Effluent and Acidic Drainage, 2008. http://mend-nedem.org/wp-content/uploads/2013/01/3.15.1.pdf.

[196] E. Cséfalvay, V. Pauer, P. Mizsey, Recovery of copper from process waters by nanofiltration and reverse osmosis, Desalination. 240 (2009) 2–6. doi:10.1016/j.desal.2007.11.070.

[197] Pall Corporation, Mine Water Treatment. Filtration and Separation Technologies for Mine Water Treatment, (n.d.).

https://www.google.com/url?sa=t&rct=j&q=&esrc=s&source=web&cd=&ved=2ahUKEwjcjbWm-tLuAhXTtXEKHV_9DjEQFjABegQIAhAC&url=https%3A%2F%2Fru.pall.com%2Fpdfs%2FIndustrial-Manufacturing%2FMEMWTEN_Pall_Mine_Water_Treatment.pdf&usg=AOvVaw2CehYFcONWeaaE8ZM5Yyqi.

[198] DRA Global, Tweefontein water reclamation plant, (n.d.). https://draglobal.com/projects/tweefontein-water-reclamation-plant/ (accessed February 5, 2021).

[199] Mining News, From waste to resource, (n.d.). https://miningnews.co.za/2019/10/21/from-waste-to-resource/ (accessed February 5, 2021).

[200] Mining Technology, Collahuasi Copper Mine, Northern Chile - Mining Technology | Mining News and Views Updated Daily, (n.d.). https://www.mining-technology.com/projects/collahuasi/ (accessed February 5, 2021).

[201] Water Online, Inseparable dependence, (n.d.). http://www.waterafrica.co.za/index.php/features/effluent-industrial-waste/35-inseparable-dependence (accessed February 5, 2021).

[202] Markets and Markets, Membranes Market by Material (Polymeric, Ceramic), Technology (RO, UF, MF, NF), Application (Water & Wastewater Treatment, Industrial Processing), Region (North America, APAC, Europe, MEA, South America) - Global Forecast to 2024 , (n.d.). https://www.marketsandmarkets.com/Market-Reports/membranes-market-1176.html (accessed February 8, 2021).

[203] Transparency Market Research, Membrane Filtration Market - Global Industry Analysis,

Size, Share, Growth, Trends and Forecast 2017 - 2026, (n.d.). https://www.transparencymarketresearch.com/membrane-filtration-market.html (accessed February 8, 2021).

[204] The Courier, Ceramic Membranes Market Analysis With Key Players, Applications, Trends And Forecasts 2027 || TAMI Industries, Pall Corporation, Atech Innovations GmbH, (n.d.). https://www.mccourier.com/ceramic-membranes-market-analysis-with-key-players-applications-trends-and-forecasts-2027-tami-industries-pall-corporation-atech-innovations-gmbh/ (accessed February 8, 2021).

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: