![BIOMOre - An Alternative Mining Concept]

A new mining concept for extraction metals from deep ore deposits by using biotechnology

D4.4
PLS pre-concentration, product recovery and effluent treatment

Hatch

With review by

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D4.4 Report on "Results of PLS pre-concentration, product recovery and effluent treatment"

Due date of Deliverable	2017-01-31
Actual Submission Date	2017-03-30
Start Date of Project	2015-02-01
Duration	36 months
Deliverable Lead Contractor	Hatch Associates Ltd
Revision	Version 1.2
Last Modifications	2017-03-30
Nature	R
Dissemination level	PU
Public Summary enclosed	No
Reference / Workpackage	WP4
Digital File Name	De-170330-0033 - D4.4 Report on 'Results of PLS preconcentration, product recovery and effluent treatment'
Document reference number	De-170330-0033
No of pages	66 (incl. cover and annexes)
Keywords	membrane; PLS; reverse osmosis; nano filtration; RO; NF; pre-concentration;
In bibliography, this report should be cited as follows:	n/a

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amsul	ammonium sulfate
CF	concentration factor
NF	nanofiltration
PLS	pregnant leach solution
RO	reverse osmosis
MF	microfiltration
UF	ultrafiltration
IEP	iso-electric point

Note: This document adopts the 'f' spelling of the element sulfur and of all other names containing the 'sulf-' root. This is aligned with the implementation of the IUPAC ruling that 'sulfur' is the only acceptable English spelling for this element, its compounds, and derivative words.

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Executive summary

The BIOMOre project aims to develop a new mining concept for extracting metals from deep ore deposits using economic, sustainable, and environmentally acceptable technologies. The objective of BIOMOre project is to develop new technological concepts for in-situ recovery of copper via bioleaching and hydrofracturing, as well as to determine the most cost effective technologies for metal separation and marketable product generation.

Pressure-driven membrane separation technologies and their application in hydrometallurgical operations for the pre-concentration of pregnant leach solutions (PLS) are reviewed in this report. Membrane separation, namely nanofiltration (NF) and reverse osmosis (RO), is investigated as the lead technology to pre-concentrate a PLS in order to upgrade the concentration of copper, thus to improve the efficiency of the copper extraction process.

Particular focus has been given to NF applications as NF has been shown to be the most suitable amongst pressure-driven membrane technologies, due to its process flexibility as well as cost advantages over RO. A review of NF operations in hydrometallurgical applications is presented. Particular focus is given to the ability of NF for PLS pre-concentration, product recovery and effluent treatment by: i) selectively separation of sulfates from chlorides, ii) recovering clean undiluted acid from metals extraction operations (e.g. copper, or uranium), iii) pre-concentration of metal containing streams, recover acid as well as clean water production for reuse when coupled with RO.

A thorough review of membrane fouling is given in the report, with particular attention to gypsum scaling prevention, minimisation and management strategies. Gypsum scaling is expected to be the major factor limiting the efficiency of NF for PLS pre-concentration. Due to the low pH of the PLS and its complex chemistry, minimisation and management of gypsum via traditional means (e.g. feed softening, addition of antiscalant) are not effective. Novel cleaning strategies (e.g. microbubbles, ultrasonic and magnetic fields) and original flowsheet options (e.g. incremental recoveries by NF coupled with forced precipitation in seeded reactors) have been suggested as potential solutions to manage gypsum scaling.

The performance of NF on a typical BIOMOre PLS has been assessed in terms of ion rejection and system recovery. The objective of the modelling exercise is to determine the ability of NF to upgrade the PLS by concentrating valuable metals. The copper concentration factor resulting from NF filtration ranges from three to ten depending on the PLS composition and volumetric recovery. Note that these results are subject to an appropriate management of gypsum scaling. A PLS composition representative of the BIOMOre conditions is based on the composition of the laboratory leach tests of consortium partners, mass balance information, and available data from published literature. The work on this report was completed before the availability of PLS samples from continuous leaching.

Content

1. Introduction

The shortage of technology metals in modern economies together with the rising demand and the more challenging and hard-to-access low-grade deposits call for more efficient technologies for mining and metal extraction. The BIOMOre project aims to develop a new mining concept for extracting metals from deep ore deposits using economic, sustainable, and environmentally acceptable technologies. The objective of BIOMOre project is to develop new technological concepts for in-situ recovery of copper via bioleaching and hydrofracturing, as well as to determine the most cost-effective technologies for metal separation and marketable product generation.

Hydrometallurgy has a key role in determining the most suitable process technology solution for metal recovery. The traditional method normally considered for high-grade copper deposits of solvent extraction and ion exchange followed by electrowinning, might not be the optimal solution for low-grade deposits that are becoming the prevalent resource of copper.

Membrane separation technologies have become more and more prominent in the mining and mineral processing industry due to their high efficiency, easy operation, small footprint and modular construction. While membrane filtration has been the leading technology in the field of desalination and wastewater treatment, its application in hydrometallurgical operations has been evolving at a slower rate. Promising results have been shown in the mineral extraction industry in the last two decades. Membrane separation offers many potential benefits such as clean water recovery, reduction of volume requiring conventional treatments, and decreased usage of reagents. This translates into smaller and more efficient plants with lower capital and operating costs, as well as lower environmental impacts. With increasingly stringent environmental regulations and the desire for low and zero discharge, a joint effort of research bodies and industries is required to promote and optimize the application of membrane separation technologies in the mining sector.

Membrane technologies nanofiltration (NF) and reverse osmosis (RO) are reviewed in this report with a view to pre-concentrating the pregnant leach solution (PLS) prior to solvent extraction.

2. Membrane separation technologies

2.1. Pressure-driven membrane processes

In a membrane separation process, the membrane acts as a thin barrier that permits selective mass transport splitting a stream into the material that passes through the membrane (i.e., the permeate or product), and the material that is rejected by the membrane (i.e., the retentate or reject), as depicted in Figure 1. The membrane systems most commonly adopted in mineral processing operations are pressure-driven processes where pressure is exerted uniformly on the membrane surface that drives the flux of solution through the membrane. In the applications considered in this review, the membrane system operates in cross-flow configuration where the feed solution flows tangentially to the membrane surface. This mode of operation minimizes the build-up of particles and colloids on the membrane surface, thus maximizing the separation efficiency.
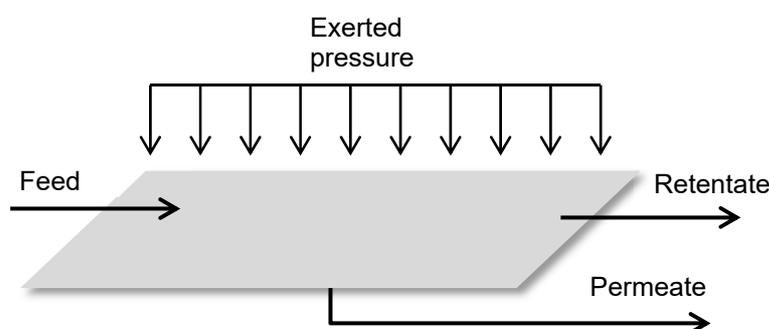
Figure 1: Schematic representation of a pressure-driven membrane process.

Different chemical species have different transport rates through the membrane matrix (Cameron and Edwards, 2012). The rate of mass transfer across a membrane depends on driving forces, such as i) the shape, size, and ionic charge of the permeating species, ii) the membrane material properties and composition, iii) the necessity for charge balance either side of the membrane, iv) the interaction between the permeating species and the membrane material.

Pressure-driven membrane processes are normally classified in terms of i) the size range of rejected species, ii) the mechanisms of rejection and driving forces, and iii) the chemical structure and composition of the membrane material. A summary of the pressure-driven membrane processes and their characteristic properties are given in Table 1.

Table 1: Pressure-driven membrane process classification.

	Microfiltration	**Ultrafiltration**	**Nanofiltration**	**Reverse osmosis**
Rejection of	Particles, clay, bacteria	Macromolecules, proteins	High molecular weight compounds, multi-valent ions	High and low molecular weight compounds, multi- and mono-valent ions
Driving force	Sieving	Sieving	Sieving, Electromigration	Sieving, Electromigration
Pore size	0.1 - 4 µm	0.002 - 0.1 µm	0.001 - 0.002 µm	< 0.002 µm
Operating pressure	< 2 bar	< 10 bar	< 40 bar	< 60 bar

Microfiltration (MF) and ultrafiltration (UF) are commonly used for the removal of suspended solids from water and wastewater. UF is also capable of removing a range of high molecular weight dissolved molecules and colloids (Table 1 and Figure 2). The driving force of both MF and UF is sieving and separation occurs based on particle size. Particles which are bigger in size and shape than the membrane pores are rejected by the membrane. MF and UF are commonly used as a pre-treatment to nanofiltration and reverse osmosis.

Cut-offs of different liquid filtration techniques

Micrometer logarithmic scaled	0,001	0,01	0,1	1	10	100	1000
Angstroms logarithmic scaled	1	10	100	1000	10^4	10^5	10^6	10^7
Molecular weight (Dextran in kD)		0,5	50	7.000			

Size ratio of substances to be separated: Solved salts, Sugar, Atomic radius, Pyrogens, Albumin (66 kD), Viruses, Bacteria, Red blood cells, Yeast, Pollen, Human hair, Sand

Separating process: Reverse osmosis, Nano filtration, Ultra filtration, Micro filtration, Particle filtration

MICROFILTRATION — Water, Monovalent Ions, Multivalent Ions, Viruses, Bacteria, Suspended Solids

ULTRAFILTRATION — Water, Monovalent Ions, Multivalent Ions, Viruses, Bacteria, Suspended Solids

NANOFILTRATION — Water, Monovalent Ions, Multivalent Ions, Viruses, Bacteria, Suspended Solids

REVERSE OSMOSIS — Water, Monovalent Ions, Multivalent Ions, Viruses, Bacteria, Suspended Solids

Figure 2: Characterisation of pressure-driven membranes based on rejected species.

Due to the overlap in pore size of NF and RO membranes (Table 1 and Figure 2), NF is often, erroneously, referred to as a "loose" RO membrane. However, it has been

recognized that the rejection mechanisms of RO and NF, as well as their potential applications, are somewhat different (Cameron and Edwards, 2012). In theory, water is the only material that would pass through the RO membrane whilst the vast majority of ions, particles, organics and salts are rejected (Figure 2). On the contrary, NF membranes tend to strongly reject multi-valent ions, while allowing the passage of mono-valent ions. This fundamental difference gives NF its own unique advantages within the field of membrane separation.
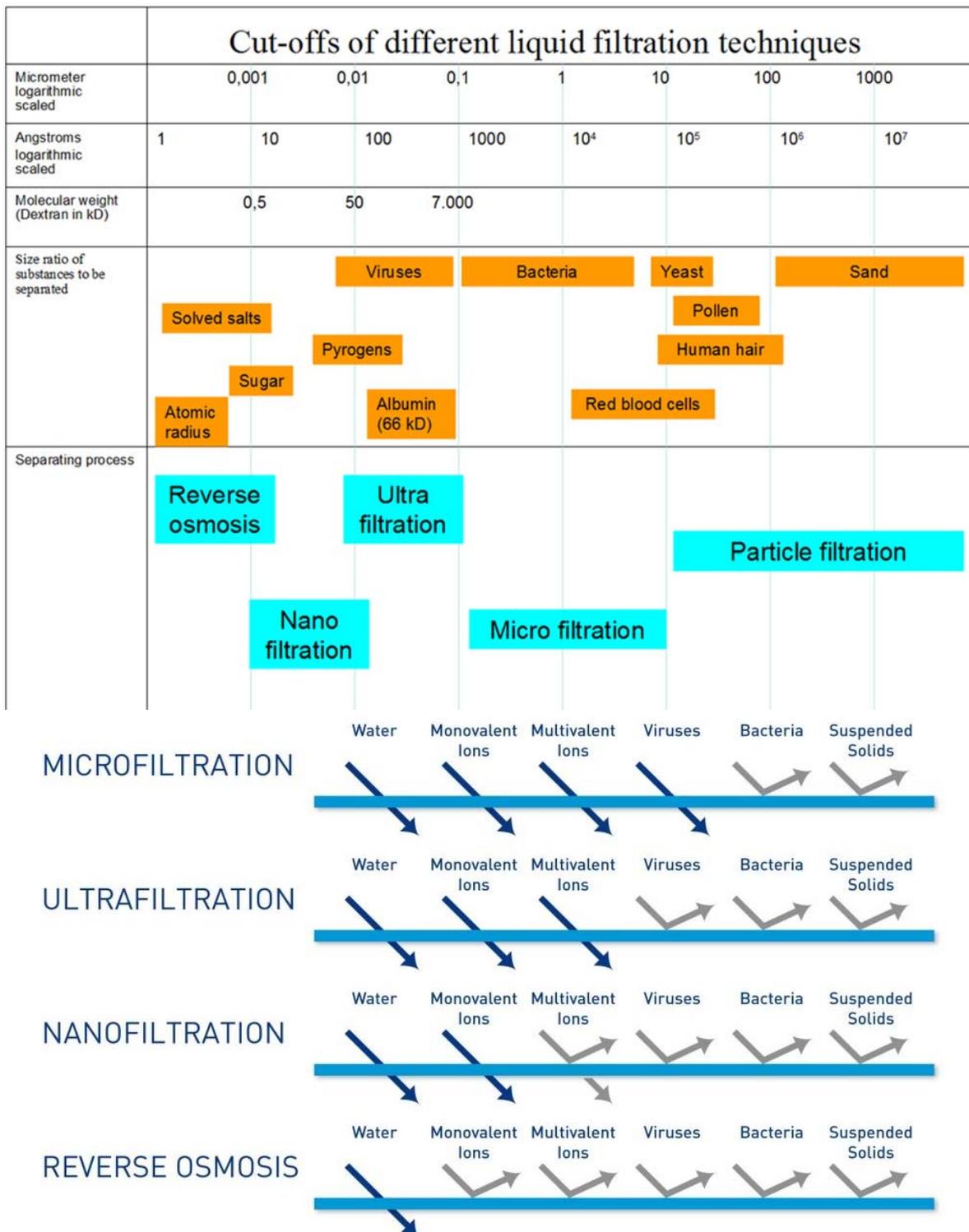
The NF, and to a lesser extent, RO too, separation mechanism can be identified as a sum of convection and diffusion transport mechanisms, i.e. sieving effects, together with electromigration which results from membrane charge density and charge polarity (Childress and Elimelech, 2000; Qin et al., 2004). Convective transport of ions with the water flux through the membrane is caused by the pressure gradient between the feed side and the permeate side. Diffusive transport is a consequence of the concentration gradient as achieved by the rejection of solutes. Electromigration is caused by a streaming potential difference across the membrane. This streaming potential is caused by the electric current generated by the convective flow of a fluid that is necessarily charged, through the pores of a charged membrane. For uncharged molecules, sieving or size exclusion is primarily responsible for separation and is controlled by molecular size and shape in solute form. For ionic species, both sieving and electromigration are responsible for separation.

The unique separation characteristics of NF membranes permit the high selectivity of multi-valent versus mono-valent ions. Multi-valent metal ions are highly rejected by the membrane while mono-valent ions like bisulfate, chloride, sodium and strongly dissociated acids such as hydrochloric, sulfuric and nitric acids, are poorly rejected. This uniquely allows to selective separation of metals from acid species, producing an undiluted and purified acid in the permeate stream. This property makes NF membranes particularly appealing for use in mineral processing operations and has led to the development of experimental, pilot and industrial scale plants in hydrometallurgical applications (Soldenhoff et al., 2005; Cameron and Edwards, 2012).

The inherent difference of rejection characteristics between RO and NF gives a niche application. RO has largely been considered as an end-of-pipe technology in water and wastewater treatment, desalination and water purification. NF has the potential to be applied as an in-process technology in the field of reagent recovery and in combination with existing technologies such as ion exchange resins and chemical treatments (Mortazavi, 2008; Cameron and Edwards, 2012).

The large development of RO together with the poorly understood separation dynamics of NF has hindered the development of NF systems. Only in the last two decades has the potential of NF started to be recognized, and research as well as industrial applications have flourished (Manis et al., 2003; Soldenhoff et al., 2005; Tanninen et al., 2006; Mortazavi, 2008; Ortega et al., 2008; Ahmad and Ooi, 2010; Al-Rashdi et al., 2012; Cameron and Edwards, 2012). RO and NF are known to

provide similar rejection performances for heavy metals. NF is the preferable in-process technology because it shows a higher flux at lower pressure, leading to lower capital investment, lower cost of operation and maintenance (Al-Zoubi et al., 2010a). NF also has the ability to selectively concentrate and recover commodity metals and multi-valent ions without concentrating the full total dissolved ions of the solution. The potential benefits of NF include process water recovery (optimizing water balance and reducing the volume required for conventional treatment), decreased usage of reagents by acid recovery, and higher permeate production at reduced capital and operating costs comparing to traditional RO systems. This could translate to smaller and more efficient plants with lower capital and operating costs and lower environmental impacts (Al-Zoubi et al., 2010a; Fornarelli et al., 2013).

2.2. Principles of membrane processes

The following terminology and principles refer to pressure-driven membrane processes that will be used extensively in this report.

2.2.1. Permeate flow and flux

The passage of water through the semi-permeable membrane is defined by the following equation:

$$Q = k * (\Delta P - \Delta \pi) * A$$

Where:

Q is the permeate flow through the membrane,

k is the membrane permeability coefficient for water,

ΔP is the applied pressure differential (difference between pressure on feed side and pressure on the permeate side),

$\Delta \pi$ is the osmotic pressure differential (difference between osmotic pressure of feed and osmotic pressure of permeate), and

A is the membrane area.

The solution flow through the membrane is proportional to the difference between the applied pressure differential and the osmotic pressure differential across the membrane. This is often referred to as the driving pressure.

The permeate flux indicates the amount of product (i.e. permeate) produced by the membrane system per unit area. It is calculated as the ratio of permeate flow and membrane area. Typical permeate fluxes of NF and RO operations are in the range of 15–25 L $h^{-1}m^{-2}$, although this varies between applications.

The osmotic pressure of a solution is a function of the concentration of dissolved ions and the temperature. An estimate of osmotic pressure is obtained by the following equation:

$$\pi = 1.12 * (273 + T) * \sum m_i$$

Where:

π is the osmotic pressure of the solution,

T is the solution feed temperature, and

m_i is the molar concentration of dissolved species i.

2.2.2. System Recovery

System recovery represents the percentage of solution that is recovered in the permeate stream relative to the feed rate. System recovery is often referred to as volumetric recovery and is defined by the following equation:

$$R = \frac{Q_p}{Q_f} * 100$$

Where:

R is the volumetric recovery (%),

Q_p is the permeate flow rate, and

Q_f is the feed flow rate.

In simple terms, if a system is said to operate at 75% recovery from 100 L h⁻¹ of feed flow, then a permeate stream of 75 L h⁻¹ and a retentate stream of 25 L h⁻¹ are produced. The retentate stream contains the concentrated dissolved salts which, at a volumetric recovery of 75%, are approximately four times more concentrated than in the initial feed. This is referred to as the Concentration Factor (CF).

Typical recovery values vary between 50% and 85%. The maximum achievable recovery differs for each application and its value is a function of many factors, namely the system hydraulics, the onset of fouling on the membrane surface and the osmotic pressure of the feed solution.

The system hydraulics are determined by the crossflow rates of feed solution along the membrane. Higher crossflow rates produce shear and turbulence and therefore reduce the potential for fouling on the membrane surface. Crossflow rates should be kept as constant as possible throughout the entire membrane system to ensure minimal fouling on the membrane surface. Typical crossflow rates through membrane plants ranges between 8 to 12 m³ h⁻¹. Although feasible in practice, high

recovery values (> 85%) often pose challenges in designing membrane systems with a consistent and acceptable crossflow.

The osmotic pressure of the feed solution is often regarded as a limiting factor for the maximum achievable recovery. As the recovery increases, so does the osmotic pressure of the feed solution which leads to a higher required operating pressure to maintain an acceptable permeate flux. The operating pressure however cannot exceed the maximum allowable pressure of the membrane element, thus limiting the maximum attainable volumetric recovery. The maximum allowable operating pressure of standard, conventional NF and RO membranes is approximately 41 bar and 60 bar, respectively.

The onset of fouling on the membrane surface is often regarded as the major limitation of membrane processes. This can be due to supersaturation of rejected species or the buildup of organic layers on the membrane surface. Fouling inevitably leads to increased feed pressure, reduced volumetric recovery, and reduced membrane life.

2.2.3. Ion rejection

Ion rejection represents the ability of the membrane to reject a specific ion and concentrate its mass in the retentate stream. Opposite to ion rejection is ion transmission, which defines the ability of the membrane to let that specific ion permeate through. Ion rejection is defined by the following equation:

$$\text{Rej} = \left(1 - \frac{C_p}{C_f}\right) * 100$$

Where:

Rej is the ion rejection (%),

C_p is the ion concentration in the permeate, and

C_f is the ion concentration in the feed.

Note that ion rejection is defined as a ratio of ion concentrations in the permeate and in the feed and not as a ratio of the mass flow deportments. An ion rejection equal to zero implies that the same ion concentration is found in the feed and in the permeate.

When the ion is preferentially transmitted through the membrane, its rejection results in a negative value. Negative rejections imply that the ion concentration is higher in the permeate than in the feed. In other words, a mass transfer from feed to permeate occurs and the feed stream is depleted of that specific ion. Negative ion rejections are attributed to the Donnan effect and are a function of membrane charge and electromigration.

3. Fouling of membrane systems

Fouling of membrane surfaces by suspended solids, organic material, biofilm growth, and precipitation of supersaturated inorganic salts represents a major limitation of pressure-driven membrane processes. Fouling inevitably leads to increased feed pressure and energy consumption, reduced permeate flux and permeate quality, and reduced membrane life. All of these effects contribute to a decrease in process performance, resulting in increased operating cost. Fouling can often be mitigated by the use of Clean-In-Place (CIP) techniques. There is however an incremental buildup of residual refractory foulants that leads to the application of continually higher pressures and eventually membrane replacement.

3.1. Fouling classification

Fouling is classified into five different categories according to its origin, the impacts on the membrane performance and the preventative measures.

3.1.1. Membrane scaling

Membrane scaling is caused by the precipitation of dissolved salts from the feed stream. Since the salts from the feed stream are usually concentrated by a factor of two to five times in the NF and RO processes, their solubility limits can be exceeded and thus precipitation can occur. Even though the retentate solutions are usually supersaturated, scale formation on the membrane is predominantly governed by the availability of sufficient nucleation sites. Therefore, induction time, i.e. the time to induce formation of detectable nucleation crystals, is crucial for scale formation.

Scale formation has always been a serious limitation in designing and operating NF and RO systems since scaling causes flux decline, membrane degradation, loss of production and elevated operating costs (Antony et al., 2011). Types of scale encountered on NF and RO membranes includes calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, silicates, calcium phosphate and aluminosilicates (Antony et al., 2011).

Scale formation is influenced by various operating conditions such as pH, temperature, operating pressure, permeation rate, flow velocity and the presence of ions (Antony et al., 2011). For example, crossflow rates that are not uniformly maintained across the membrane can cause higher concentration factors in some parts of the membrane which cause localized scaling issues. Importantly, concentration polarization plays a vital role in scale formation in high pressure membrane systems, as it leads to elevated salt concentrations near the surface of the membrane where particles may deposit.

There are a number of widely applied methods for estimating the scale forming potential of feed solution (Antony et al., 2011). The Langelier Saturation Index (LSI) and the Stiff & Davis Saturation Index (S&DSI) predict scaling by calcium carbonate

as a function of pH. The supersaturation index (S) expresses the level of saturation of a solution with respect to the various mineral salts.

Prediction of scale formation and scale prevention measures (i.e. appropriate pre-treatment of feeds) are two essential management protocols for the successful operation of NF and RO systems. Based on the ion analyses, the pH and the temperature of the feed water, projections can be made for any potential precipitation and the most appropriate pre-treatment, if any, can be determined.

Three basic methods are used to control scale:

- Optimisation of operating parameters and system design:
  - recovery reduction to avoid exceeding solubility limits of scale-forming salts as measured in retentate;
  - feed flow reversal to reduce the elapsed nucleation time by periodically switching the feed entrance and retentate exit positions at times less than the induction time for the scale formation. Supersaturated retentate at the exit port is replaced with unsaturated feed and vice versa.

- Removal of the ions responsible for scale formation by appropriate pre-treatment including:
  - coagulation to remove particulate and colloidal matters;
  - softening by ion exchange or sodium carbonate to remove calcium and magnesium;
  - acidification to increase the solubility of alkaline species such as calcium carbonate.

- Use of specially formulated chemicals, i.e. antiscalants, to prevent precipitation of scale forming compounds. One of the major advantages of antiscalants is the low dosage levels required, which have minimal impact on the feed solution quality. Antiscalants do not eliminate the scaling species or its tendency. Scale inhibition occurs by disrupting one or more aspects of the crystallization process and delaying the onset of crystallization or retarding the growth of mineral salt crystals. They are often regarded as kinetic inhibitors.

If scaling occurs due to equipment failure (for example failure of the antiscalant dosing system, or emergency stopping of the plant without time for a controlled shutdown), it is important to detect the scaling early. Calcium sulfate scaling is almost impossible to remove and it often requires the membrane element replacement. Other types of scaling can benefit from properly designed cleaning strategies, for example, water wash, alkaline or acidic cleaning, acidic or basic detergents and other proprietary formulations.

3.1.2. Metal oxide fouling

Soluble species in the feed water can be oxidized ahead of the membrane, or within the membrane element itself, to form insoluble species which can then deposit on the membrane.

Both manganese and iron can cause fouling by this mechanism, but iron fouling is most prevalent. Iron fouling can occur rapidly and is caused by the oxidation of ferrous iron into ferric iron ions and the subsequent precipitation of ferric hydroxide onto the membrane surface. Iron fouling may be avoided by one of these two methods:

- Removal of the iron from the feed;
- Prevention of oxidation of ferrous ions.

From the analyses of total iron, total dissolved oxygen and pH, the magnitude of potential iron fouling can be determined beforehand and the appropriate pre-treatment system can be used. As a general guideline, iron concentrations as high as 4 mg L^{-1} can be tolerated if the solution contains essentially no dissolved oxygen (less than 0.1 mg L^{-1}). If oxygen is present (> 5 mg L^{-1}) the iron concentration should be maintained below 0.1 mg L^{-1}.

In the context of membrane applications in hydrometallurgical operations, iron removal has been demonstrated to be beneficial for copper recovery by electrowinning (EW). Guezennec et al. (2014) tested two pre-treatments for iron removal on a copper-rich bioleaching solution (Table 2):

- Hydrolytic Fe(III) removal using calcium carbonate: bioleaching solution was heated up to the temperature of 90–95°C and 115 g of CaCO3 was proportioned to the solution. 96% of Fe (III) was removed from PLS solution by hydrolysis. There was, however, significant loss of copper in the residue which most probably results from difficulties in the filtration of the precipitated iron residue.

- Fe(III) removal by jarosite precipitation: bioleaching solution was brought to pH 1.7, and then maintained in the state of boiling for 20 hours. To accelerate precipitation of iron in a form of jarosite, crystal nuclei were added to the solution. After cooling the solution the precipitated residue was filtered. Jarosite precipitation removed only 70% of the iron from the solution but the precipitate was much easier to filter than the precipitate obtained with the hydrolysis method. The loss of copper in the residue was much lower.

Iron fouling can often be removed by acidic washes. Manganese however is a very permanent scale if Mn(II) is oxidized to Mn(IV) within the membrane housing. Manganese is often removed prior to the membrane housing by the following process:

- Oxidation to Mn(IV) using hypochlorite. This produces MnO$_2$ solids.

- Removal of MnO_2 using MF or UF
- Removal of residual chlorine in the feed stream by passing the feed through activated carbon or by dosing of a strong reductant, such as sodium metabisulphite.

Table 2: Summary of treatments for iron removal as tested by Guezennec et al., 2014.

	Initial solution (mg L^{-1})		Mass of precipitated residue (g)	pH	Final solution (mg L^{-1})		Removal to residue (%)	
	Cu	Fe			Cu	Fe	Cu	Fe
Hydrolytic Fe(III) removal using calcium carbonate	45	6	162	3.0	43	0.2	4	96
Fe(III) removal by jarosite precipitation	45	6	52	1.2	44	1.7	3	71

3.1.3. Membrane plugging

Plugging is caused by mechanical filtration in which particles too large to pass through the feed brine passage are trapped by the membrane. Plugging is prevented by suitable pre-filtration (often by the use of MF or UF membranes) followed by 5-micron cartridge filtration.

3.1.4. Colloidal fouling

Colloidal fouling is caused by the coagulation and entrapment of colloids on the membrane surface.

Colloids found in the feed solutions belong to the aluminosilicate class of colloids (clays) and are usually in the 0.03 to 1 micron size range.

The two main parameters which control the rate of coagulation, and thus the rate of colloidal fouling, are:

- Concentration of the colloids;
- Stability of the colloids.

To determine the concentration of colloids in water, turbidity measurements are used. Generally, if the feed water turbidity is kept below 1 NTU, then NF and RO

operations are not overly affected by colloids. Colloids can also be removed by MF or UF pre-filtration.

3.1.5. Biological fouling

Biological fouling is caused by the growth of microorganisms on the membrane surface. If high concentrations of microorganisms exist in the feed solution, a biocide should be used to prevent biofouling. Biofoulants can also be removed by MF or UF prefiltration. If the cell populations are high, other techniques such as coagulation/flocculation/settling, dissolved air flotation (DAF) or disc filtration are required upstream of the MF/UF filters.

3.2. Management of fouling

Management of fouling involves two processes (Al-Amoudi and Lovitt, 2007):

- Minimization of fouling using adequate system design, feed pre-treatments, membrane treatments and membrane modification;
- Membrane remediation by chemical cleaning which is carried out to restore membrane fluxes and rejection characteristics.

The rate of fouling can be reduced with the proper use of cleaning strategies, antiscalants, pretreatments, and where sensible, the adjustment of operational conditions (such as pH and temperature).

3.2.1. Design of membrane systems

A well-designed membrane system can minimize the impact of fouling. The flux rate and concentration polarization are considered as key factors in determining fouling issues (Al-Amoudi and Lovitt, 2007). In order to overcome the deterioration of flux rate and the onset of concentration polarization, the concept of membrane array has been introduced in the design of membrane systems. Typically, membrane systems use multiple parallel modules so that the plant performance in terms of the product quality and recovery remain identical for each module. In the tapered systems (Figure 3), the feed stream is passed through the first module (or parallel set of modules, Figure 3b and c) and is divided into two streams. These streams are the permeate and the retentate. The retentate stream from the first module (or parallel set of modules) is passed through as feed to the second module (or set of modules). The flow velocities within the second module are boosted by decreasing the number of modules in parallel. This system allows a high recovery while minimising the effects of fouling and concentration polarization. The design of a tapered membrane system has to consider the following constraints:

- The flow rate should not exceed the maximum flow rate per membrane element to avoid large pressure drops which could cause membrane element damage;

- The flow rate should be higher than a minimum flow rate per membrane element to aid control of concentration polarization and fouling;

- The recovery for each stage should not exceed the maximum recovery per membrane element to minimize fouling.
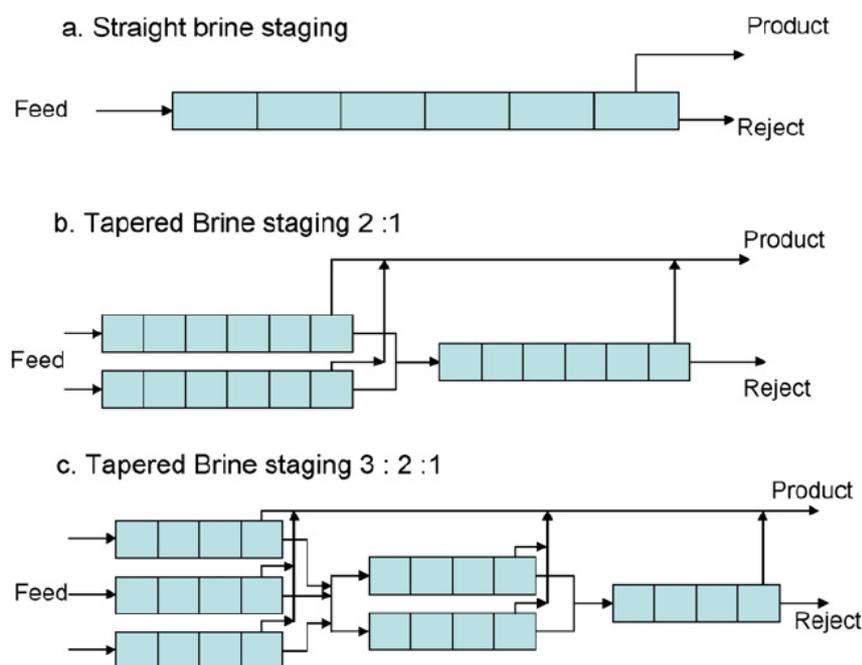
Figure 3: Example of tapered array of membrane systems. (After Al-Amoudi and Lovitt, 2007)

3.2.2. Pre-treatment of feed waters

Pre-treatment, if implemented correctly and effectively, can be used to minimise fouling, scaling and degradation of the membranes. As a result, membrane life can be maximised and efficiency of the membrane system can be maintained. The degree of pretreatment is dependent on the raw water quality, particularly the content of organic and inorganic suspended matter.

Conventional coagulation filtration pre-treatment was designed to remove the majority of the potential foulant materials from feed waters. Coagulation and flocculation using lime, as well as softening by ion exchange and sodium carbonate, have been successfully applied to remove potential scaling species such as calcium and magnesium ions (Al-Amoudi and Lovitt, 2007). The application of MF and UF as NF and RO pre-filters has emerged in the last decade as an efficient method to eliminate colloids and suspended particles as well as microbes (Al-Amoudi and Lovitt, 2007).

Whenever the physical removal of the fouling species is not possible, the addition of scale inhibitors (i.e. antiscalants) helps to control the onset of fouling by modifying the precipitation kinetic of the scaling salts.

3.2.3. Membrane cleaning

Despite the best operations of the membrane system and effective pre-treatments, fouling is expected to occur to some degree. It is therefore required that the membranes undergo recurring cleaning to remove foulants which will build up over time. A cleaning-in-place (CIP) strategy is therefore required as a means of fouling removal.

In general, fouling removal by CIP must be done when some of the following situations are reached (Arnal et al., 2011):

- 10-15% of permeate flux decline;
- 10-15% of permeate solute concentration increase;
- 15-20% of pressure drop increase in a pressure vessel.

The frequency and nature of membrane cleaning depends on the type of foulant to be treated by the cleaning process. Membrane cleaning methods can be divided into physical, chemical, and physio-chemical approaches. In practice, physical cleaning methods followed by chemical cleaning methods are widely used in membrane applications (Arnal et al., 2011).

Physical cleaning methods use mechanical forces to dislodge and remove foulants from the membrane surface. Physical methods include the following (Arnal et al., 2011):

- *Sponge ball cleaning* involves sponge balls made of polyurethane or other materials to be inserted into the membrane modules for a few seconds for scrubbing the foulant from membrane surface. It is normally used for cleaning large diameter tubular membranes when treating heavily polluted solutions such as wastewater and industrial process water.

- *Forward flushing* consists of pumping permeate water at high crossflow velocity through the feed side to remove foulants from the membrane surface. The more rapid flow and the resulting turbulence causes the particles absorbed to the membrane to be released and discharged. This technique is useful to remove colloidal matter.

- *Reverse flushing* involves pumping permeate water in alternate directions, i.e. in the forward (feed to brine) and in the reverse direction (brine to feed). Reverse flush techniques are used to remove colloidal matter.

- *Backwashing* is a reverse filtration process in which permeate is flushed through the membrane to the retentate side. The pressure on the permeate side of the membrane is higher than the pressure within the membranes. In reverse osmosis membranes, backwash is based on flow induced by osmotic

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pressure as direct osmotic cleaning. This cleaning process is based on negative driving pressure between the operating pressure and the osmotic pressure of the water solution on the feed side. This can be done either by reducing operation pressure below the osmotic pressure of the feed solution or by increasing the permeate pressure. Backflow from the permeate to the feed side of the membrane expands the thickness of the fouling layer and fluidizes it. After this, a forward flush is usually used to wash out the detached layer or dilute the fouling layer.

- *Air flushing* or *air sparging* generates a two-phase flow to remove external fouling reducing the cake layer deposited on the membrane surface. It has been shown that a mixture of water and carbon dioxide performs better cleaning results in comparison to water/nitrogen mixture. Air sparging can be applied either during the course of filtration to reduce fouling deposition, or periodically to remove already formed deposits. Air sparging is typically applied in MF and UF applications.

While reversible fouling can be eliminated by physical cleaning methods, chemical cleaning techniques are necessary to remove more refractory foulings. Every RO and NF operation needs to undergo a chemical cleaning regime where chemical agents are used to dissolve most of the deposited material on the membrane surface. Most chemical cleaning agents are mixtures of compounds, and many of them are recommended by membrane manufacturers according to the type of foulant (Al-Amoudi and Lovitt, 2007; Arnal et al., 2011). Typical chemical cleaning agents are summarized by Al-Amoudi and Lovitt (2007) and reported in Appendix A.

Alkaline cleaning is essential for the removal of organic foulants or inorganic colloids such as silica. Acid cleaning is used to remove inorganic colloids such as iron and scale since precipitated salts are generally more soluble at low pH. Alkaline cleaning uses sodium hydroxide and sodium carbonate to raise the pH, while acid cleaning uses acids including nitric acid, citric acid, sulfamic acid, phosphonic acid, ammonium bifluoride to lower the pH. These cleaners can be incorporated into detergents where the surface tension is also reduced. Both alkaline and acid cleaning strategies require a pH often above or below the window of chemical resistance of the membrane, thus causing damage to the membrane material which impacts the membrane lifetime.

The physio-chemical cleaning methods use physical cleaning methods with the addition of chemical agents to enhance cleaning effectiveness. The applications usually consist of forward flushing with permeate between cleanings when more than one chemical cleaning is used. Arnal et al. (2009b) studied the cleaning of UF membranes by the application of air in combination with different chemical solutions, e.g. sodium hypochlorite, hydrogen peroxide, sodium hydroxide and deionized water. The experimental results were compared to those obtained with chemical solutions without air bubbles (Arnal et al., 2009a) and showed a significant improvement in the cleaning effectiveness when using air bubbles with chemical solutions.

The effectiveness of the cleaning process is checked by measuring the water flux after cleaning at defined operating conditions. A low water flux after cleaning might indicate that the cleaning was not effective. Another important parameter to monitor is the operational flux. Many plant operators have noted that even when the permeate flux is fully restored, it cannot be maintained for as long as when membranes were initially used (Arnal et al., 2011). It should be noted that, despite the use of CIP, there is often an incremental build-up of residual refractory foulants that leads to the required application of continually higher pressures and eventually membrane replacement. This is the main reason why membranes have a discrete life in service.

4. Application of membrane separation in hydrometallurgy

Membrane separation technologies have been applied to a wide range of mineral processing plants. Recent advances in membrane separation technology have broadened the range of potential applications (Soldenhoff et al., 2005; Cameron and Edwards, 2012).

Existing operations of membrane separation technologies in the hydrometallurgical sector include treatment of acid mine drainage (AMD), pre-concentration of pregnant leach solutions (PLS) in heap leaching operations, separation of acids and metals from waste and process streams, as well as gold and cyanide recovery from heap leaching operations (Cameron and Edwards, 2012). A review of such applications is given below.

4.1. Nanofiltration for the treatment of AMD

Acid mine drainage (AMD) is a typical by-product of the mining industry which occurs when rock containing reduced sulfur is exposed to air and water. Metals and sulfate are released from a variety of rock types and a broad range of metal concentrations and pH can result. Treatment of AMD is often seen as an end-of-pipe process aimed at producing a discharge stream that meets specified limits of acidity and concentrations of metals and sulfate. Extensive reviews have been published on treatment options for AMD (Johnson and Hallberg, 2005; Fu and Wang, 2011) and lime neutralization and biological treatments are recognized as the traditional approach (Al-Zoubi et al., 2010b). Lime is added to precipitate some of the sulfate as gypsum and some metals as hydroxides. In biological treatments, anaerobic conditions are used to reduce sulfates to sulphides leading to the precipitation of metal sulphides.

Membrane treatment by RO and NF has been proposed as a treatment technology capable of achieving strict discharge criteria while providing high efficiency, easy operation and a low environmental foot print. Recent studies investigated the use of membrane separation to treat acid mine drainage for either final discharge and/or metal recovery (Zhong et al., 2007; Rieger et al., 2009; Al-Zoubi et al., 2010a; Al-Zoubi et al., 2010b; Mullett et al., 2014). The authors explored membrane performance under different experimental conditions with particular attention to the effects of solution temperature, operating pressure, feed flow and feed concentration on solute rejection and permeate flux. RO and NF are known to provide similar rejection performance for polluting metals (Zhong, et al., 2007; Carvalho et al., 2011). NF has been suggested as the preferable treatment because it has higher fluxes at lower pressure leading to lower capital investment and lower cost of operation and maintenance (Al Zoubi et al., 2010a; Carvalho et al., 2011).

Bayer (2004) reported the results of a NF-RO operation to treat acid mine drainage from a copper mine in US. The full-scale plant operated on a feed solution characterized by a pH of 3 and total dissolved solids concentration of 92 g.L^{-1}. High

quality water was generated for discharge. The severe potential of fouling by gypsum precipitation was successfully managed by the addition of an antiscalant.

Eriksson et al. (1996) used NF to pre-concentrate heavy metals in a solution prior to lime precipitation. The objective was to reduce the volume sent to chemical precipitation and to minimize the production of sludge. The NF system operated at 75% recovery. Pre-concentration of heavy metals positively impacted on the efficiency of lime precipitation, and one single step precipitation was enough to produce an effluent within the discharge regulations.

González-Muñoz et al. (2006) explored the use of NF as a second step in an integrated process with sulphide precipitation, to treat an acidic with a high metal concentration solution. A water stream that was able to be directly reused in the production process was obtained.

4.2. Nanofiltration for selective separation of sulfate and chloride

NF offers the potential to selectively separate sulfate from chloride. To date this application of NF has been largely overlooked, although it has potential in wastewater treatment prior to discharge as well as in optimization of hydrometallurgical operations for resource recovery.

Macintosh et al. (2003) investigated the ability of NF to selectively separate chloride from sulfate to recover ammonium sulfate (amsul) for reuse as a fertilizer additive. It was found that a rejection of sulfate as high as 99% occurred in conjunction with negative rejection of chloride. This led to a very efficient removal of chloride from the ammonium sulfate solution. Ammonium sulfate was concentrated in the retentate, while chloride was concentrated in the permeate stream. It was found that the extent of the sulfate-chloride separation was a function of the molar ratio of sulfate and chloride (Macintosh et al., 2003): the higher the molar ratio, the more chloride permeates through the membrane and concentrates in the permeate.

The sulfate-chloride separation is attributed to the unique ability of NF to exploit the Donnan effect. The Donnan effect stems from membrane charge and the need of charge balance either side of the membrane (Artug, 2007). Figure 4 shows that in a sodium sulfate and sodium chloride solution, the transport of chloride through the membrane is augmented under the influence of Donnan equilibrium. A higher concentration of chloride results in the permeate, while the feed is chloride-depleted.
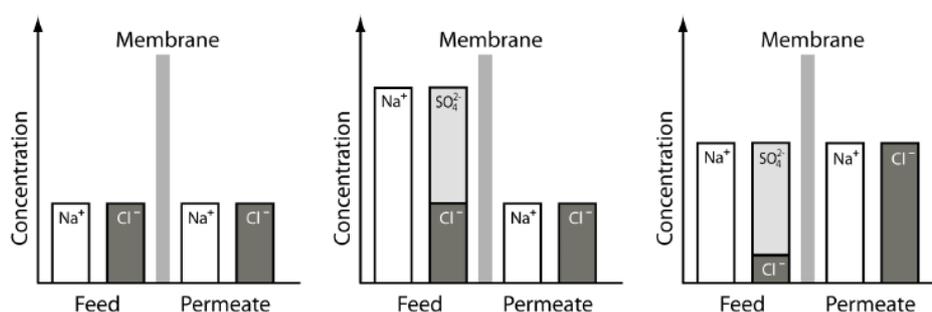
Figure 4: Representation of the Donnan equilibrium.

4.3. Nanofiltration in the copper industry

The copper extraction industry deployed NF membrane separation with the double objective of upgrading the PLS prior to copper extraction, and recovering sulfuric acid for reuse in the leaching process.

Van der Merwe (1998) used a combined RO – NF system at a copper mine in South Africa to treat an acidic copper-containing rinse solution from a pickling bath. A two-pass RO followed by NF was used to i) concentrate the copper from an initial concentration of 1 g L^{-1} to 29 g L^{-1}, ii) produce clean water for discharge, and iii) recycle sulfuric acid by means of NF to be reused in the process. This process is a full-scale example of recovery of metal and acid that would otherwise be lost. The alternative would have been to neutralize the acid and precipitate the copper as a voluminous sludge (Cameron and Edwards, 2012).

The unique properties of NF to aid acid separation and recovery were described by Eriksson et al. (1996). Sulfuric acid was recovered for re-use in a copper smelting plant. The feed solution contained heavy metals and acid concentrations above 30 wt%. Technical grade acid was successfully recovered by a multi-pass NF system.

NF was used to remove water from a PLS generated during copper heap leaching and concomitantly upgrade the diluted PLS prior to copper extraction (Eriksson et al., 1996). The NF pilot plant ran at 50% recovery, the feed pressure was 22 bar and gypsum precipitation was observed at recoveries approaching 50%. The NF retentate was twice as high in copper than the PLS and fed the copper extraction plant. The addition of antiscalant and sulfuric acid for pH adjustment was needed to manage gypsum scaling.

The applicability of NF to upgrade PLS prior to electrowinning was also investigated and implemented on a full-scale plant by Lien (2009). After membrane filtration, the concentration of copper entering electrowinning was double the concentration in the PLS. Concomitantly, sulfuric acid was recycled in the permeate and re-used in the leaching process.

For the typical composition of BIOMOre PLS a two-pass RO followed by NF is recommended to i) concentrate the copper from an initial low concentration of up to a few g L^{-1} to at least 15 to 30 g L^{-1} (making it eminently suitable for downstream recovery), ii) produce clean water for reuse, and iii) recover and recycle sulfuric acid in the leaching process.

4.4. Nanofiltration in the uranium industry

Under low pH conditions, uranium is generally present as a uranyl sulfate complex such as $UO_2(SO_4)_2^{2-}$ and $UO_2(SO_4)_3^{4-}$. These are large, high molecular weight, multivalent ions that are often strongly rejected by NF membranes. As such, there is potential application for NF treatment of uranium containing acidic streams for uranium concentration and acid recycling. These opportunities have been previously recognized in Edwards (2010), Goode and Brown (2010), Manis et al. (2011), and Soldenhoff et al. (2005).

NF was piloted to upgrade a weak uranium-containing resin-in-pulp eluate solution as well as to recover sulfuric acid (Goode and Brown, 2010). The feed solution had 135 g L^{-1} sulfuric acid and 4 g L^{-1} of uranium. A 75% recovery membrane system produced a permeate with very low uranium concentrations, an acid content similar to the feed, and a retentate with an increased uranium to sulfuric acid ratio.

The reduced volume uranium-rich stream produced in the NF process required proportionally less neutralization reagent to remove impurities, and less hydrogen peroxide for uranium precipitation. In addition to these significant reagent savings, the value of the acid returned to the plant contributed to the savings.

4.5. Nanofiltration in the gold industry

NF has found its applicability in the gold processing industry. In alkaline cyanide solutions, gold is present mainly as an aurocyanide complex (i.e. $Au(CN)_2^{1-}$). It is generally recovered from weak cyanide solutions by either the Merrill-Crowe process or by adsorption on activated carbon followed by elution and electrowinning. Because of the detrimental impact of copper-cyanide complexes on the gold extraction process, the use of NF for separating $Au(CN)_2^{1-}$ from $Cu(CN)_3^{2-}$ has been investigated.

Soldenhoff et al. (2005) reviewed several patented NF processes for gold processing designed to separate $Au(CN)_2^{1-}$ from $Cu(CN)_3^{2-}$ in copper-rich cyanide solutions. This separation can be achieved by treating either the PLS from cyanide leaching operations or the loaded eluate from activated carbon extraction. It is however not known whether this separation has been successfully implemented on a large scale.

4.6. Nanofiltration for metal pre-concentration and acid recovery

The ability of NF to split a metal-containing acidic stream into a more concentrated metal stream and a relatively metal-free enriched acid stream has been reviewed in the previous sections. A simplified flow sheet for this purpose, which is generally applicable to hydrometallurgical circuits, has been proposed by Soldenhoff et al. (2005) and Cameron and Edwards (2012) and is shown in Figure 5.

The feed first goes through RO, from which the permeate is discharged to the environment or recycled back to the plant as process water, and the retentate flows to the NF unit operation. The retentate from the NF is sent to a conventional treatment system (e.g. high-density sludge plant if it needs disposal), while the enriched acidic stream (i.e. recovered acid) may be recycled to the process. The flow sheet could easily be altered to add a unit operation for metal recovery if the NF retentate stream contains a valuable metal (such as copper).

The benefits of such an operation include recovered acid, potential for water recycling, decreased reagent costs (e.g. acid and lime), possible metal recovery, smaller effluent treatment system to treat the retentate from the NF and enhanced environmental stewardship. For example, a mineral processing operation that has a requirement for sulfuric acid (such as a BIOMOre project on commercial scale, or a heap leaching operation) may benefit from such an operation because of the acid recovered for recycling to the process.
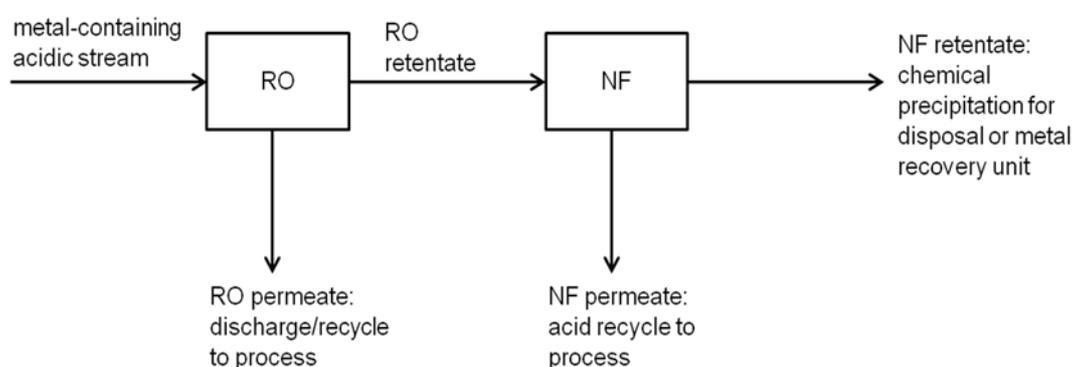

Figure 5: Simplified flow sheet of a NF-RO membrane process for acid and metal recovery.

5. Knowledge gaps and research questions on membrane separation

5.1. Fouling management

Fouling is one of the main problems in any membrane separation; it leads to the need for pretreatments and membrane cleaning and is the primary cause of limited recoveries, feed solution loss, and short lifetime of membranes. A total control of fouling is essential to reduce the need for cleaning and enhance the permeate yield and quality.

When applied to the mining and mineral processing industry, inorganic fouling related to scaling (i.e. precipitation of salts) is the predominant form of fouling on the membrane surface (Van der Bruggen et al., 2008). Scaling is a thermodynamic and kinetic process and is observed when the ion concentration in the feed exceeds the solubility limit at a certain point in the filtration module. The most common constituents of scale are calcium carbonate, gypsum, barium/strontium sulfate and silica, although other less common scalants exist that can have very significant impacts on operations, particularly when considering the unique feed waters associated with industrial and mining applications. Classical solutions to fouling are the optimization of pretreatment methods and cleaning of membranes.

Suggested pretreatment methods often make use of other pressure driven membrane separations such as UF and MF. Other options include oxidation (e.g. ozonation), adsorption and flocculation. Membrane modification is potentially the most sustainable solution to obtain fouling-resistant membranes. The idea is to insert hydrophilic groups into a polymeric structure, so that the overall material becomes more hydrophilic and less prone to organic and colloidal fouling. Most of the surface modification studies as reported in the literature refer to MF and UF membranes (Kim et al., 2002; Du et al., 2009). Van der Bruggen (2009) and Khulbe et al. (2010) review the art of membrane modification as applied to RO and NF membranes. The authors identify increasing hydrophilicity, increasing negative membrane charge, and decreasing roughness as the key aspects to achieve fouling reduction. Membrane modification continues to grow as an area of research for fouling prevention and minimization.

Cleaning of NF membranes has become a standalone research area. Physical cleaning is a significant part of the cleaning protocol and includes flushing (backflush, forward flush, reverse flush), scrubbing, air sparging, vibrations and sonication. Chemical cleaning involves chemical reactions such as hydrolysis, saponification, solubilisation, dispersion, chelation, and peptisation. Membrane manufacturers often develop specific cleaning strategies and products suitable for their own membranes. However, the cleaning protocol should also depend on the characteristics of the feed solution. This leads to a wide variety of cleaning mixtures and protocols in the literature.

It has been shown that chemicals used in CIP have sometimes damaged the membrane materials, thus reducing the membrane lifetime and efficiency of the separation process (Arnal et al., 2011). Chemical cleaning has proven to be inefficient for some kinds of fouling and also creates environmental issues related to the waste chemical disposal. Arnal et al. (2011) report that, in general, 5-20% of the operating costs of a large plant are associated to cleaning procedures. In this context, intense research work is being undertaken to develop new cleaning methods, called nonconventional or emerging techniques that are more efficient and environmentally safer. Some of these techniques are being applied to RO membranes and others recently started for MF and UF membranes, however more research is required to test and implement these techniques on a large scale and in NF applications. Arnal et al. (2011) provide a thorough description of nonconventional cleaning techniques and a short summary is provided below;

5.1.1. Osmotic backwashing with hypersaline solution

Osmotic backwash is an online cleaning technique which is induced when the feed-side osmotic pressure exceeds the applied hydraulic pressure across the membrane. Hypersaline solution is added to the feed side to increase the osmotic pressure. The technique is recently developed and is considered an innovative, effective and potentially chemical-free cleaning technique. It is performed by injecting into the feed channel a pulse of high concentration solution, i.e. hypersaline solution (HS), that can supply more than 100 bar of the cleaning force and which is used to remove the foulants from the membrane surface, especially colloidal matter and biofilm material. HS injection promotes direct osmosis across the RO membrane and the flow of the water from the permeate side to the feed. The reversible flow helps to dislodge any foulants and scaling on the membrane surface and promotes lifting, sweeping and removal of the concentration polarization layer.

As for operating conditions, it is recommended that the concentration of the HS solution injection be 5-10% NaCl and the flow rate close to the normal RO operation as a starting point. The most critical parameter is the pulse duration. Pulse duration should be longer than the residence time for a maximum achievable cycle-averaged permeation rate. A shorter pulse is ineffective in inducing osmotic permeation particularly towards the end of the channel. In fact, short pulse is significantly diluted on the membrane surface to the point where its concentration may drop below that required for inducing osmotic flow.

5.1.2. Ultrasonic fields

Application of ultrasound for fouling control and cleaning has been studied in MF and UF applications, and applied to minimize fouling due to particulate and organic matter. The basic physical phenomenon behind the effect of ultrasound is cavitation that is promoted by the pass of the ultrasound waves through the liquid medium in series of alternate compression and expansion cycles. Cavitation mainly promotes formation, growth and implosive collapse of bubbles in the liquid that has significant mechanical and chemical effects reducing fouling on the membrane surface.

Variables needed to be investigated include the intensity of the ultrasound field, the solute concentration and the irradiation time.

Arnal et al. (2011) review some studies applying cavitation for fouling management in RO systems. In particular, Feng et al. (2006) reports that on-line ultrasonic defouling of RO membranes resulted in a significant increase in the permeate flux as well effective removal of organic and inorganic foulants such as $CaSO_4*2H_2O$ and $Fe(OH)_3$.

There are however no ultrasound technologies that are used in large-scale membrane plants, possibly due to the cost of energy required by an ultrasound cleaner to produce cavitation.

5.1.3. Electric fields

Electric field is based on a phenomenon referred to as electrokinetic, which describes the application of an electric field on the membrane surface to attract the particles from the membrane surface, lifting them and carrying them over. The electric field imposes an electrophoretic effect on the charged molecules dragging them away from the membrane surface, reducing the concentration of the polarization layer and increasing the flux.

The applied electric field strength depends on the conductivity of the feed, electrode placement and material, as well as the electrochemical properties of the membrane surface and the dispersed solutes. Finally, zeta potential and charge of the species present in the feed should also be considered.

Similar to the hypersaline backwashing and ultrasonic cleaning, this technique can be applied in the work cycle without interruption. The main disadvantage is the uneconomic power levels required and the cost of the electrodes. The main research effort on the use of this technique for membrane cleaning is related to UF membrane with only a few studies on RO membrane applications.

5.1.4. Magnetic fields

Magnetic water treatment has been used to control and clean membrane surfaces following scaling by calcium carbonate. It has been suggested that a magnetic field decreases the hardness of water and can reduce and remove existing scale or produce a softer and less tenacious scale.

Magnetic fields are applied normally in the feed flow or in the storage tank, and possibly in full recirculation mode in such a way that feed water is exposed to magnetic fields several times. Although a promising technology, results in the literature are contradictory and more research is needed in the mechanism that the magnetic field has over formation and growing of precipitates onto NF and RO membrane surfaces.

Research on membrane cleaning must continue in order to enhance a process that represents a minimal percentage of the operating costs. Within physical cleaning methods, the non-conventional cleaning techniques as summarized above seem to be very promising in membrane cleaning. With regard to chemical cleaning, research should focus on the combination with physical methods, such as air flushing, since greater efficiencies can be achieved.

Another research gap is the lack of a modelling tool that allows researchers and operators to predict the onset of fouling in real time. Several researchers have attempted to improve the knowledge on scaling potential and precipitation in membrane systems by using mathematical models. Radu et al. (2014) propose a micro-scale numerical model for studying mineral precipitation in RO/NF feed channels. A novel method is proposed, which combines physical and chemical processes in a numerical framework and aims at describing small-scale effects in relation to the overall process performance. This study highlights the need for rigorous mechanistic modelling approaches that allow the detailed description of multiple factors governing scaling in a complex process like membrane filtration.

Finally, Antony et al. (2011) identify some knowledge gaps in the management of scaling by antiscalant addition:

- Despite the availability of prediction tools, pre-treatment options and antiscalants, scale formation and subsequent performance decline still remain a major challenge for membrane operations.

- Studies on antiscalant suitability and efficiency are generally performed with commercially available antiscalants and antiscalant formulations are proprietary in nature, thus making it hard to assess and understand the antiscaling efficiency for modelling and prediction of outcomes. A greater transparency in terms of constituents will help molecular level understanding of different categories of chemical additives to various scale types.

- Research on antiscalant assessment should be performed on complex feed solutions, characterized by the possibility of co-precipitation of more than one component of unknown proportions. Research should also focus on the impact of the combination of antiscalants in various feed compositions on scale formation.

5.2. Membrane resistance

Membrane lifetime and chemical resistance of NF membranes are related to the occurrence of fouling, and therefore, the need for cleaning. Applications where fouling requires frequent cleaning often face a fast membrane deterioration, because cleaning agents damage the membrane to some extent and the membranes are in contact with very acidic and/or very alkaline cleaning solutions (Van der Bruggen et al., 2008).

Membrane resistance to highly acidic and/or alkaline streams, which are typical of hydrometallurgical operations, has hindered the applicability of membrane technology in such applications. Feed solutions with pH lower than 1 and greater than 10 are not uncommon in metal extraction processes.

Tanninen et al. (2004) tested the separation efficiency and acid resistance of commercial and experimental NF membranes in long-term filtration experiments. They used a solution containing 25 g L^{-1} CuSO4 and 8 wt% sulfuric acid. Commercial NF membranes showed good selectivity, retaining most of the copper sulfate and letting most of the sulfuric acid pass into the permeate. However, only the membranes designed to be acid resistant maintained their separation efficiency during the two-month experiment.

Membrane modification has been shown to improve membrane resistance and performance when treating acidic streams. Navarro et al. (2008) studied the effects of pre-treating NF membranes by immersing them, for different periods of time, in hydrofluoric and phosphoric acid solutions. These acidic treatments impacted on the chemical and charge properties of the NF membrane, as well as on permeate flux and ion rejection. In general, such treatments enabled both improved flux and rejection properties of the membrane, as well as reduced fouling. Changes in the performance of the membrane were partially explained as a consequence of changes in membrane charge, hydrophilicity and pore size.

Other membrane modifications can include larger brine spacers and brine spacers with alternative mesh structures to improve the turbulence above the membrane surface.

The development of ceramic NF membranes for applications in organic solvents may solve the problems of changes in performance and limited lifetime, due to their superior chemical resistance. Ceramic membranes are substantially more expensive, but this may be compensated by higher fluxes (especially at high temperatures) and the prolonged lifetime. However, only few ceramic NF membranes are commercially available today, in spite of the good performance of these membranes. Attempts have been made to make these ceramic membranes hydrophobic, so that filtration of non-polar solvents would be feasible. However, this work is in progress and needs to be further developed.

5.3. Nanofiltration modelling and simulation of complex solution matrixes

Modelling the performance of a NF membrane comprises two aspects (Van der Bruggen et al., 2008): flux prediction and rejection prediction. These two factors allow full understanding of a lab-scale membrane module. Scaling up to larger installations requires that changes along the filtration module are taken into account, i.e. the influence of the permeate yield. This can be done by taking concentration increases into account. Other important aspects to be modelled are the influence of membrane fouling on flux and the prediction of fluxes and rejections for acidic and alkaline feed solutions.

Different models have already been proposed for the description of NF membrane separation. The mass transport models most used in the literature are classified in three groups: empirical, semi-empirical and mechanistic (Artug, 2007).

Empirical models are based on regression analyses of experimental data and give no, or very limited, information on the physical mechanisms regulating the separation process. For this reason, empirical models are not suitable to gain an in-depth understanding of the physical process; however, they provide fast and reliable predictions of membrane performance within the measurement range. Major drawbacks of empirical models relate to their dependence to a large number of experimental data and their limited extrapolation capability on conditions that are previously "unseen" by the model.

Semi-empirical models couple the strength of empirical models, i.e. reliable prediction based on experimental data, with some physical understanding of the separation process. They are therefore more complicated to build and implement, but are more reliable when applied to "unseen" process conditions and more informative of the separation process itself. Similarly, to the empirical approach, these models consider the membrane as a black box; therefore they do not characterize the membrane by its charge and structural properties. However physical separation mechanisms such as convection and diffusion are taken into account in the model description. Examples of semi-empirical models include the Solution-Diffusion Model (SDM, Artug, 2007) and the Spiegler-Kedem model (Artug, 2007).

Mechanistic models are the most sophisticated and complicated as they aim at modelling all the physical processes involved in membrane separation. A thorough understanding of the physical process can be inferred by using those models, however their predictive ability is often less accurate than the empirical approach due to the inherent complexity of the model itself and its dependence to a large number of parameters that require a complex calibration process. The accuracy of these models has been demonstrated in simple binary and ternary ion systems and their application to complex feed solutions is rather limited. Mechanistic models rely on parameters such as the structural parameters of membranes, physicochemical properties of the solution, and interactions of the solution components with each other and with the membrane itself. The most common mechanistic model is based on Nernst-Plank and Navier-Stokes equations (Hilal et al., 2004; Artug, 2007). The complexity of this modelling approach relates to the physical complexity of the simulated processes as well as to the numerical complexity. Simplifications are needed to allow the implementation and commercial use of these models.

A series of empirical, semi-empirical and mechanistic models have been published (Lefebvre et al., 2003; Palmeri et al., 2006; Artug, 2007; Van der Bruggen et al., 2008; Palmeri et al., 2009;). Although successful to various degrees, none of these models have been commercialized on a large scale or used in NF applications by the industry. Membrane modelling is often restricted to RO seawater applications with feed solutions limited to binary, ternary and quaternary ion systems.

The use of modelling tools to deepen the understanding of membrane separation is often restricted to academic research and largely overlooked by industry. This contributes to a poor understanding of NF separation principles by the industry, hence expensive, and not always efficient, experimental and pilot trials to validate process solutions. The reference to NF as a "loose" RO membrane, as given by many membrane practitioners, is the most evident example of misunderstanding of NF principles and shows how the strength of NF as an in-process solution technology has yet to be fully appreciated.

A synergetic and holistic integration of the needs and knowledge of industry and academia should trigger the research into the development of a user-friendly, readily available and versatile model of membrane separation. Such a model should provide reliable predictions as well as improved understanding of the separation process, membrane characterization and process optimization (Hilal et al., 2004). The ability to successfully develop such modelling techniques will result in a smaller number of experiments subsequently saving time and money in the development stage of a process. A comprehensive NF model should integrate chemical speciation models (e.g. OLI software) and design membrane models (e.g. Dow ROSA software) with a proper empirical, semi-empirical and/or mechanistic modelling approach.

5.4. Impact of solution pH and membrane surface characterization

The pH windows of operation for typical hydrometallurgical processes tend to be between 0 and 2 in the low pH range, or around pH 12 to14 for alkaline systems such as the Bayer process. The following section focuses on the low pH range, as applicable to BIOMOre.

An aspect of NF modelling that is particularly relevant to the mining and mineral processing industry is the impact of extremely low feed pH on membrane performance. The effect of solution pH on membrane performance is relatively unexplored, although its impact on solute rejections has been reported (Zhong et al., 2007; Al-Zoubi et al., 2010a; Mullett et al., 2014). To understand the impact of pH on membrane performance, the importance of electromigration in determining ion rejection needs to be considered.

Electromigration is controlled by the membrane charge density and charge polarity, which are both characterized by the zeta potential (ZP) of the membrane surface. This parameter is usually evaluated from streaming potential analyses (Tay et al., 2002; Carvalho et al., 2011). The solution pH has a significant effect on ZP, because it impacts the charge on the functional groups of the membrane material and of the molecules in solution (Artug, 2007; Carvalho et al., 2011). The pH of the system may also affect the "openness", i.e. pore size, of the membrane (Childress and Elimelech, 2000), thus impacting on size exclusion rejection mechanism. The solution pH at which the net membrane charge is zero is the iso-electric point (IEP). The membrane surface is negatively charged when the solution pH is higher than the membrane IEP and positively charged otherwise. Previous work has been carried out to determine the ZP and IEPs across a range of commercially available NF membranes (Mullett et

al., 2014, and references therein). These studies were conducted for a range of single and binary salt solutions, and the IEPs of most commercially available NF membranes range from pH 2.5 to 4. The experimental work of Childress and Elimelech (2000) demonstrated that membrane charge and position of the IEP change as a function of feed pH and chemistry, highlighting the importance of membrane characterisation every time a new feed is to be treated by membrane filtration.

Thorough understanding of the membrane performance (i.e., permeate flux and ion rejection) as a function of feed pH is mandatory because pH affects several of the system characteristics (Childress and Elimelech, 2000). Many studies focusing on the relationship between feed pH, membrane charge, and ion rejection, agree on the significant effect of feed pH, with abrupt changes and minimum rejections being expected at the IEP (Hagmeyer and Gimbel, 1999; Qin et al., 2004; Artug, 2007). Minimum rejections at the IEP are explained as a consequence of the fact that size exclusion is the only active separation mechanism (Ferreira-Esmi et al., 2013). In the case of a NaCl solution, Childress and Elimelech (2000) found that water flux was maximal and salt rejection minimal at the membrane IEP, primarily due to decreased electrostatic repulsion and increased pore size. Zhong et al. (2007) also found minimum rejections at feed pH very close to the IEP. Al-Rashdi et al. (2012) found minimum rejections at the IEP for some, but not all, metals. All the reviewed papers explained the observed trends as a function of feed pH and membrane charge polarity relative to the IEP; however, no detailed explanation was given regarding the occurrence of minimum rejections either at or above the IEP. These studies demonstrate the complexity of NF separation mechanisms and the need for further research.

The position of the membrane IEP relative to the solution pH is particularly relevant in more complex, multi component feeds such as hydrometallurgical streams. Since the IEP of commercially available NF membranes ranges between pH 2.5 and 4 bracketing the pH range of many hydrometallurgical process streams and waste streams, understanding the rejection behaviour for a particular membrane - hydrometallurgical feed (such as AMD) is critical for evaluation of a specific NF treatment strategy. Of most pertinence is understanding the parameters that define membrane selection.

Furthermore, at near neutral pH, the rejection characteristics of most commercially available NF membranes are very similar and are defined by the rejection of magnesium sulfate under standardised salt rejection test conditions. Those practised in the art of NF applications to hydrometallurgical streams will have observed that two membranes with identical magnesium sulfate rejections at neutral pH, will display vastly different rejection characteristics as the solution tend towards more acidic or basic conditions.

Because the membrane IEP, ZP and general rejection characteristics change with solution pH and solution chemistry, experimental campaigns and further research should focus on:

- Characterising commercially available NF membranes in terms of membrane charge, shape of zeta potential curve and position of the IEP as a function of solution chemistry and pH;

- Assessing the performance of the characterised membranes in complex matrix solutions typical of hydrometallurgical operations;

- Determining the commercial implications associated with optimal NF membrane selection in the application of membrane technology to the mining and mineral processing industry.

6. Study on PLS pre-concentration, product recovery and effluent treatment

NF offers the ability to selectively separate different ions in solution, to a large extent dependant on ion charge and size. The simple-to-understand analogy would be like mechanical screening by particle size. It can be used to separate copper sulfate from sulfuric acid (separation of copper ions from hydrogen ions, essentially pre-concentration), or separate water from sulfuric acid (separation of hydroxide ions from sulfate ions, i.e. essentially recovering acid for re-use, or recovering water from effluent, depending on the point-of-view).

The prediction of NF performance in terms of ion rejection and system recovery is assessed by modelling NF operations on a typical PLS solution. The objective of this exercise is to determine the ability of NF to upgrade the typical BIOMOre PLS by concentrating valuable metals, e.g. copper ions.

Note that the influence of fouling and scaling on NF performance is excluded from the analysis. However, scaling by calcium sulfate precipitation is expected to considerably impact membrane performance. The results of NF as given below are subjected to appropriate fouling mitigation treatments.

6.1. Composition of pregnant leach solution

The composition of the PLS generated by bioleaching of copper in the BIOMOre project will be known when real leaching tests are done, after the conclusion of this report. An estimate of the PLS composition has been based on known case studies, and on initial leaching tests by consortium partner IMN, and on mass balance modelling by consortium partner CLC. The available data are summarized in Table 3. In particular, the PLS composition as given by Rotuska and Chmielewski (2007) and Guezennec et al. (2014) originated from bioleaching of a black shale deposit investigated in the BioShale project (D'Hugues et al., 2008). For reference, the composition of PLS solutions generated from heap leaching processes from different copper mines located in the United States are also reported (Table 3) below.

Table 3: PLS composition from previous Hatch projects and literature sources. Ion concentration is expressed in mg L^{-1}.

	PLS estimate		Guezennec et al., 2014 – BioShale	Rotuska and Chmielewski, 2007 - BioShale	Hatch confidential client PLS 1	Hatch confidential client PLS 2	Eriksson et al., 1996 – US copper mine
	Low	High					
Cu	1,000	4,000	44,910	4,324	816	340	700 - 800
Fe	400	10,000	5,770	2,061	36	2,500	200 - 300
Al					306	3,950	1,500 – 2,000
As	5.3	53		13.5			
Zn	4.6	46		115	3.2	930	150 -200
V	1.1	11					
Co	1.4	14		8.65	3.1		
Ni	0.9	9		4.74	4.2		15 - 20
Mo	0.6	6					
Rh	0.01	0.1					
Ca	500	2,000			578	500	400 - 500
Na					1,179		200 - 300
Mg					1,265	2,890	3,800 – 4,200
Mn					64	1,620	400 - 700
SO$_4$	10,000	40,000			21,188		15,000 – 30,000
Cl	500	10,000	460		497		
NO$_3$					96		
pH	0.6	2.0	1.78	2	1.75	2.3	2.7

The PLS compositions as reported in Table 3 show the high degree of variability of the PLS and its dependence on various factors, including ore deposit mineralogy, type of extraction process, and location.

For the sake of the desktop study as proposed in this section, an anticipated PLS composition was chosen. A sensitivity analysis on the PLS composition was carried out by varying each ion concentration by ±50% and ±80% to account for the uncertainty in the PLS composition. Table 4 shows the composition of the PLS as used in the following desktop study.

Table 4: PLS composition used in the prediction of NF performance. Ion concentration is expressed in mg L^{-1}.

	PLS	Reference	PLS -50%	PLS +50%	PLS -80%	PLS 80%
Cu	4,000	Table 3 PLS estimate	2,000	6,000	800	7,200
Fe	2,000	Rotuska and Chmielewski, 2007	1,000	3,000	400	3,600
As	29	Average between low and high of Table 3 PLS estimate	15	44	6	52
Zn	25	Average between low and high of Table 3 PLS estimate	13	38	5	46
V	6	Average between low and high of Table 3 PLS estimate	3	9	1	11
Co	8	Average between low and high of Table 3 PLS estimate	4	12	2	14
Ni	5	Average between low and high of Table 3 PLS estimate	2	7	1	9
Mo	3	Average between low and high of Table 3 PLS estimate	2	5	1	6
Ca	578	Average between low and high of Table 3 PLS estimate	289	867	116	1,040
Na	1,179	Average between low and high of Table 3 PLS estimate	590	1,769	236	2,122
Mg	1,265	Average between low and high of Table 3 PLS estimate	633	1,898	253	2,277
Mn	64	Average between low and high of Table 3 PLS estimate	32	97	13	116
SO$_4$	18,500	Calculated assuming all metals are in sulfate form	9,250	27,750	3,700	33,300
Cl	1,820	Calculated assuming all sodium forms sodium chloride	910	2,730	364	3,276
pH	2	Estimate	2	2	2	2

6.2. NF performance

The results of the study on NF performance are summarized in Table 5. The chemical speciation software OLI was used to determine the osmotic pressure, chemical speciation and scaling tendencies of the feed solutions. Based on the

estimate feed osmotic pressure as given by OLI, the operating pressure and maximum volumetric recovery were predicted.

The maximum volumetric recovery is a function of the feed osmotic pressure. For PLS's characterized by an osmotic pressure ranging from 1 to 10 bar, the volumetric recovery ranges between 70 and 90%. The higher the volumetric recovery, the higher the concentration factor (CF) of rejected ions in the NF retentate and the greater the PLS upgrade.

Table 5: Prediction of operating pressure, scaling tendencies and maximum recovery.

Parameter	unit	PLS	PLS -50%	PLS +50%	PLS -80%	PLS +80%
Osmotic pressure	bar	6	3.5	8.7	1	10.5
Scaling tendencies	n/a			Calcium sulfate dihydrate		Calcium sulfate dihydrate
Operating pressure at 0% recovery	bar	11	8.5	13.7	6	15.5
Estimated maximum recovery	%	80	90	75	90	70

A conservative approach was taken to estimate the maximum recovery based on hydraulic parameters. This approach used the estimation of true osmotic pressure of the feed as reported in Table 5. The apparent osmotic pressure is a better indicator of the potential recoveries when NF membranes are involved because it takes into account the reduced influence of the mono-valent ions (e.g., sodium and chloride) which readily transmit. As such, the apparent osmotic pressure will be lower than the true osmotic pressure. This results in a higher possible volumetric recovery, therefore higher CFs for metal ions in the NF retentate.

Scaling caused by the precipitation of calcium sulfate will most certainly affect membrane operations, thus limiting the maximum achievable recovery. As a result, the achievable recovery may be less than that estimated based on hydraulic considerations. Based on the results shown in Table 5, it is expected that the factor limiting the recovery of NF operations for the PLS upgrade is the onset of fouling due to precipitation of calcium sulfate. A pre-treatment strategy and cleaning regime to manage gypsum scaling at low pH values (feed pH around 2) are essential for the successful implementation of a membrane plant. A detailed review on gypsum mitigation and management strategies is given in Section 6.4.

6.3. Prediction of pre-concentrated PLS composition

Table 6 shows the composition of the NF retentate at maximum recovery based on hydraulic parameters. The NF retentate composition was estimated by an empirical deportment model developed by Hatch and based on previous project data.

The rejection of multi-valent ions by the NF membrane has been set to 98%. This value is typical of NF operations and well documented in the literature.

The rejection of mono-valent ions was set to 0%, although its value is strongly dependant on the charge balance that will form on the feed and permeate sides of the membrane. A negative rejection of mono-valent ions may occur but its magnitude will depend on the molar ratio between sulfate and chloride (Macintosh et al., 2003) and the rejection of free sulfate ions not associated with the protons (sulfuric acid). Negative rejections will translate into augmented mass transport and a higher concentration of mono-valent anions in the permeate.

Table 6: Predicted composition of upgraded PLS at estimated maximum NF recovery. Ion concentration is expressed in mg L^{-1}.

	PLS	PLS -50%	PLS +50%	PLS -80%	PLS +80%
Estimated maximum recovery (%)	80	90	75	90	70
Cu	19,600	19,600	23,520	7,840	23,520
Fe	9,800	9,800	11,760	3,920	11,760
As	143	143	171	57	171
Zn	124	124	149	50	149
V	30	30	36	12	36
Co	38	38	45	15	45
Ni	24	24	29	10	29
Mo	16	16	19	6	19
Ca	2,832	2,832	3,399	1,133	3,399
Na	1,179	590	1,769	236	2,122
Mg	6,199	6,199	7,438	2,479	7,438
Mn	316	316	379	126	379
SO$_4$	90,650	90,650	108,780	36,260	108,780
Cl	1,820	910	2,730	364	3,276

6.4. Gypsum management

Scaling caused by gypsum precipitation represents the major limiting factor of the NF operations for the PLS pre-concentration. Gypsum scaling will most certainly occur as a consequence of approaching the solubility limit of calcium sulfate at increasing recovery. The occurrence of gypsum scaling is a function of the concentration of calcium and sulfate in the feed solution relative to the concentration factor dictated by the recovery.

The most effective form of gypsum control is to maintain a calcium concentration factor that ensures that the gypsum concentration is below supersaturation levels. If the volume recovery required to achieve this is low, then the membrane process may not be cost effective. Other gypsum control and management strategies are proposed in the following sections.

6.4.1. Pre-treatment of feed waters by removal of scaling species

The most effective strategy to prevent gypsum scaling is the removal of the scaling forming species, in particular calcium ions. Pre-treatment of feed solutions by ion-exchange softening for calcium removal is common practice in membrane applications. It consists of the removal of calcium ions from the feed solution by a strong acid cation exchange resin that operates in the sodium form and is regenerated with sodium chloride.

In the context of the PLS's generated from copper mining operations, IX softening is not applicable for two reasons:

Most of the resins used for calcium removal will also take up copper ions due to their low selectivity: the copper concentration is high enough to compete with calcium for adsorptions sites on the resin, thus reducing the efficiency of the process;

The adsorption capacity of cation exchangers decreases at acidic pH, thus a pH adjustment would be required. This is impractical because of the typical PLS volumes.

6.4.2. Pre-treatment of feed waters by additives and antiscalants

The addition of scale inhibitors (i.e. antiscalants) has been used to control the onset of fouling by modifying the precipitation kinetics of scaling salts. The proper selection of an antiscalant additive depends upon the water chemistry and the system design. Antiscalants are polymeric additives, and mainly polyelectrolytes, polyphosphates and phosphonates. Antiscalants are effective in retarding the kinetics of gypsum crystal nucleation and growth, and their action depends on pH and polymer concentration (Prisciandaro et al., 2013). The solubility of gypsum is typically limited to 230% with the use of an effective antiscalant.

Shih et al. (2005) assessed and ranked the performance of commercial antiscalants designed to inhibit gypsum scale formation on RO membrane surfaces. The study focused on the ability of antiscalants to retard the observed onset (i.e., induction time) of gypsum crystallization from supersaturated solutions. Significant differences were found among commercial antiscalants with respect to achievable levels of induction time retardation. Antiscalant effectiveness with respect to dosage also varied significantly among available antiscalant types and formulations.

Prisciandaro et al. (2013) compared the efficiency of two antiscalants as well as inorganic additives to hinder or delay gypsum scale formation. The experimental work as presented in this study compares the effectiveness of chloride salts (NaCl), antiscalants (NTMP, $C_3H_{12}NO_9P_3$, and PBTC, $C_7H_{11}O_9P$), and citric acid to influence gypsum nucleation by retarding nucleation kinetics. It was found that, when an additive is added to the solution, induction time increases, and gypsum nucleation is retarded. A chloride excess is the least effective in delaying the nucleation, PBTC is quite effective, citric acid is a rather strong retardant, and NTMP is the strongest retardant among the studied additives.

The experimental work conducted by Shih et al. (2005) and Prisciandaro et al. (2013) used pH neutral solutions. It is widely accepted that the effectiveness of antiscalants decreases with decreasing pH, and that the efficacy of antiscalants at pH lower than 5 has yet to be been demonstrated on a large.

Due to the acidic pH of PLS solutions, the addition of antiscalants to control gypsum precipitation will require a pH adjustment to pH values of higher than 5. However, due to the large typical PLS volumes the adjustment of the PLS pH to pH ~ 5 needs to be carefully evaluated as it might have considerable impacts on operating costs, solute stability (e.g. iron and aluminium stability) and process efficiency in downstream units such as electrowinning.

It is worth noting that the sole use of antiscalants to manage gypsum scaling is not recommended in full scale plant operations. Although scaling can be managed effectively by antiscalants under optimal conditions (e.g., consistent feed composition, correct dosage of antiscalant), additional scaling mitigation techniques are advisable prior to the feed entering the membrane plant. Iron removal, pH adjustments, calcium and/or sulfate reduction measures need to be considered and integrated with antiscalant addition as part of a broad approach to gypsum scale minimisation and management.

6.4.3. Gypsum cleaning strategies

Gypsum scaling is known for its resistance to traditional cleaning strategies as it is only slightly soluble in dilute mineral acid solutions such as hydrochloric, sulfuric and phosphoric acids.

Alkaline solutions have been used to remove gypsum scale (Wasco and Alquist, 1946; Prisciandaro et al., 2013). Calcium sulfate was shown to react with 30-50%

sodium hydroxide and/or sodium carbonate solutions to form sodium sulfate, which readily dissolves, and calcium hydroxide and/or calcium carbonate. Calcium hydroxide and calcium carbonate are then treated with mineral acid cleaning.

Bakhteeva et al. (1987) demonstrated that superior surface cleaning was obtained when using sodium carbonate followed by acetic acid. The idea is that sodium ions can displace calcium ions and convert them into the salts of weak acids. Calcium carbonate treated with the acid forms carbon dioxide which facilitates mechanical destruction and separation of gypsum mass from the membrane surface.

Using physically generated micro-bubbles to assist with the cleaning of RO membranes has been investigated by Wilson et al. (2013) and Fazel et al. (2013). It has been shown that microbubbles used in combination with cleaning chemicals helps to agitate and facilitates the removal of deposits on the membrane surface. The principle is based on the increasing velocity of water which creates a more turbulent cleaning system and a good distribution of bubbles. Wilson et al. (2013) and Fazel et al. (2013) identified the bubble size and optimum flow speed as the main parameters to control in microbubble cleaning operations. Application of air to facilitate the cleaning of membranes has been recognised as an effective and efficient method for removing foulants and calcium carbonate scale deposits; however, there are very few reported studies of this technology being applied to the cleaning of gypsum scaled NF and RO membranes. Further research is needed to identify the ability of microbubbles to clean gypsum scaled membranes and to verify that the introduction of air doesn't impact the membrane integrity.

The management of gypsum scaling in applications characterised by acidic feed waters has largely been overlooked although precipitation of gypsum has been shown to impact the vast majority of membrane operations in hydrometallurgical applications. Testing the effectiveness of antiscalants and cleaning strategies presented in the previous sections is critical in assessing membrane performance for PLS pre-concentration. This is the single most important parameter that will ultimately determine the viability of the membrane process as a pre-concentration technology.

6.4.4. Design of NF operations

If none of the suggested pre-treatment options and cleaning strategies proves to manage the gypsum problem efficiently and effectively, then minimising the recovery relative to the solubility limit of calcium sulfate might be the safest mode of operation. In this context, gypsum forced precipitation in a seeded reactor might be the most effective solution. This process involves a series of low recovery NF filtration steps and temperature controlled gypsum precipitation in a seeded reactor. The principle is to exploit the relationship between gypsum solubility and temperature, and is based on the following steps:

Filtration of PLS through NF membranes at a temperature at which the gypsum solubility is high (for example 40 °C, Azimi et al., 2007) until gypsum supersaturation is reached, e.g. 10 to 50% recovery;

Treatment of the NF retentate in a gypsum seeded reactor where temperature is either cooled or heated to encourage gypsum precipitation at a low solubility point;

- Returning the supernatant from the seeded reactor to its initial temperature;
- Filtration of the supernatant in a second NF filtration step;
- The cycle is repeated until the desired recovery is reached.

Minimising the design recovery to account for gypsum solubility might limit the overall efficiency of NF operations and could lead to membrane separation being a suboptimal technology for PLS pre-concentration. It is worthwhile noting that the above analysis is based on an estimated composition of the PLS which may, or may not, be representative of the actual PLS recovered during the BIOMOre study.

The most appropriate management option to limit and control gypsum scaling and successfully upgrade the PLS will ultimately be determined by the real composition of the PLS developed during the BIOMOre project: the PLS pH and the concentration of copper, iron, metallic impurities, calcium and sulfate will determine the choice of the optimal technology for PLS pre-concentration.

6.5. Product recovery from waste streams

In the case of the BIOMOre project, the leaching system is sulfuric acid based, i.e. the liquors contain sulfuric acid and metals in the form of sulfates, such as copper sulfate. The ore at Rudna mine also contains chlorides, mainly sodium chloride. During leaching of the ore, the chlorides are mobilised and the liquors therefore contain a mixture of chlorides and sulfates. As chlorides hinder the performance of the microorganisms during the bio-regeneration phase, it is preferable to reduce the concentration of chlorides from the liquors, i.e. separate chlorides from sulfates, alternatively, to recover sulfates (sulfuric acid and/or copper sulfate) from waste streams.

NF offers the ability to selectively separate sulfate from chloride.

Sulfate-chloride separation has been tested by Hatch to recycle a sodium sulfate solution, and to produce a sodium chloride and water stream for reuse. Bench-scale studies have revealed that a sulfate to chloride molar ratio of about 160 led to a chloride transmission of 220%, which translated in a chloride concentration in the permeate of more than double its concentration in the initial feed. On the contrary, a sulfate to chloride molar ratio of 3.5 led to a lower chloride transmission and lower concentration of chloride in the permeate. In this case, the chloride concentration in the permeate was similar to the concentration in the feed.

6.6. Capital and operating costs for a commercial-size implementation

For a commercial-scale implementation of BIOMOre, an engineered design of an ultrafiltration (UF) and nanofiltration (NF) combination was developed. The objectives of the combined treatment unit are to i) pre-concentrate the PLS to achieve a higher copper concentration, and ii) to recover water for re-use in the process and to minimise any effluent volumes.

The basis for the sizing of the treatment unit is to treat a 20% side stream of the PLS stream that goes to the metal recovery plant, with the composition given in Table 4 above. The process flowsheets for the UF and NF units are given in Figure 6 and Figure 7.
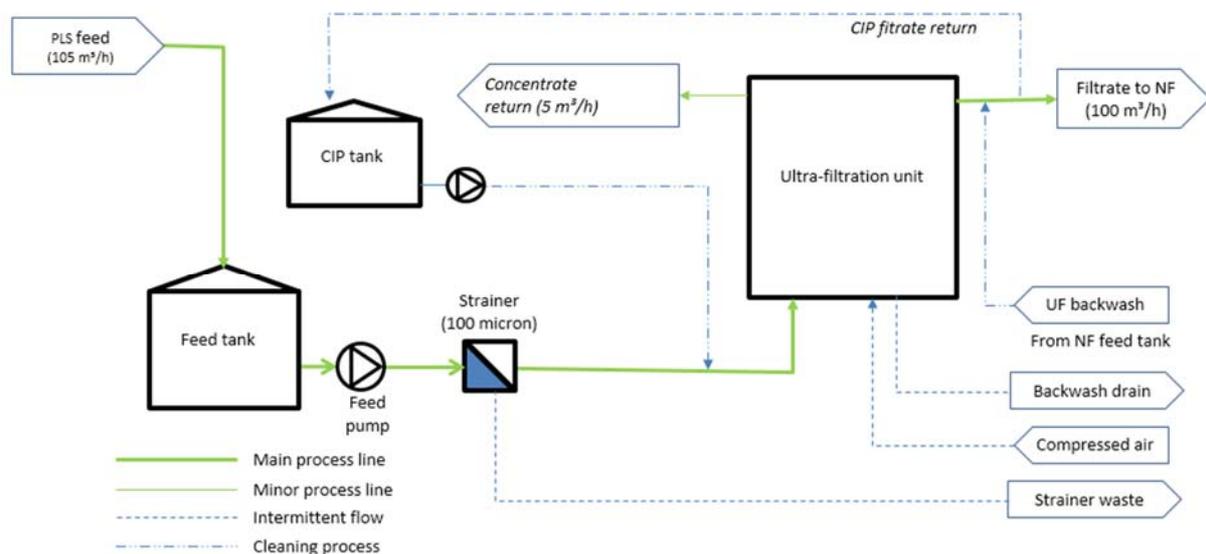

Figure 6: Process flowsheet of the UF unit on potential commercial scale to produce a feed to the NF unit shown below.
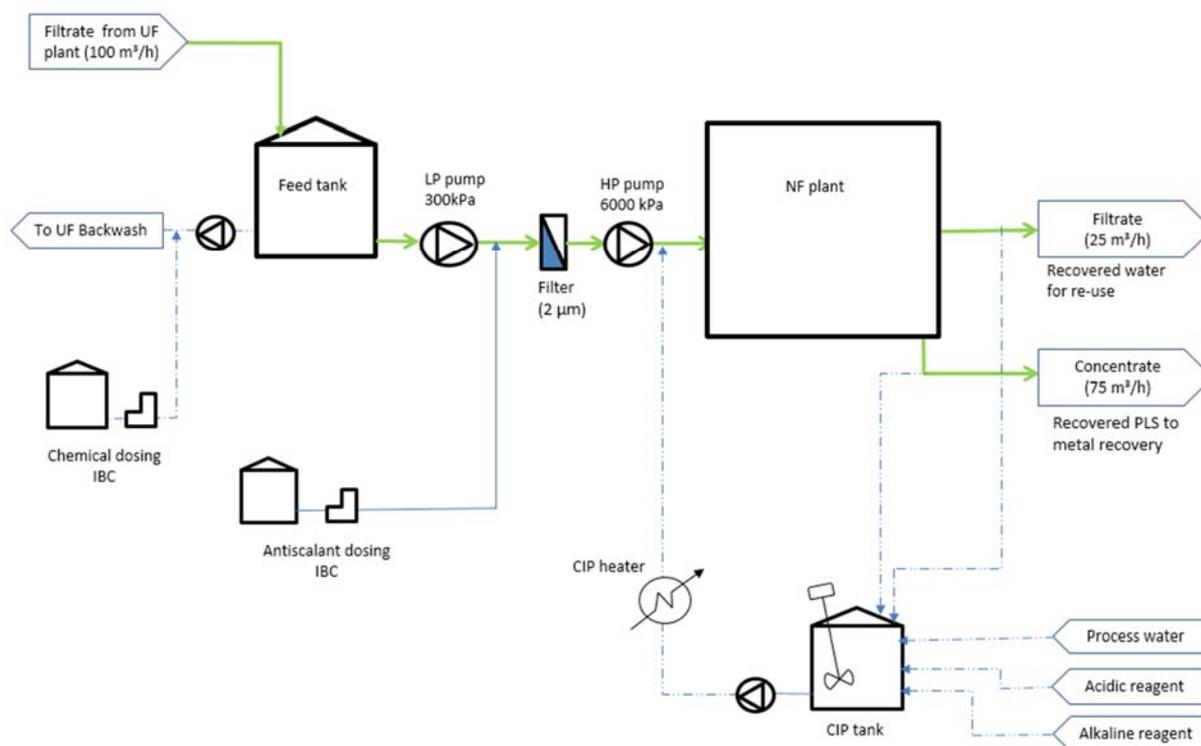
Figure 7: Process flowsheet of the NF unit on potential commercial scale to pre-concentrate PLS

The pertinent results of the fully installed capital cost and operating cost estimates are given in Table 7.

A sensitivity analysis was also performed. Whereas the base case treated 20% of the PLS flow at a membrane plant recovery of 25%, it is generally recognised that such a low recovery hardly results in the optimum cost efficiency. It is generally more economical to design and operate a membrane plant for higher recoveries. The cost effectiveness arises from using a smaller plant at a higher recovery. Xxx below gives the expected capital cost and operating cost for a larger plant to treat the full PLS flow, albeit at low recovery, and smaller plants that operate at higher recoveries.

Table 7: Pertinent operating parameters and results from the capital cost and operating cost sensitivity analysis

Stream flow rate (m³/h)	500	200	100	50	35
Membrane plant recovery (%)	25	25	25	50	70
Capital cost of UF + RO (supply and installation) (M€)	16.1	8.1	4.1	2.1	1.4
Annual power consumption (MWh)	1 736	695	347	256	269
Operating cost (membrane + labour + power) (€1000/a)	853	341	171	115	118
Comment	Full PLS flow	40% of PLS flow	20% of PLS flow	10% of PLS flow	3.5% of PLS flow
Risks	Fe and organic fouling	Fe and organic fouling	Fe and organic fouling	Gypsum and organic fouling	Gypsum and organic fouling
Risk mitigation	Testing to confirm assumptions determine scaling prevention techniques and cleaning regimes				

From these results it is seen that it is more cost effective to design and operate a smaller PLS pre-concentration plant at high recovery, rather than a larger plant at lower recovery. From an operability point of view, and from a risk point of view, a plant that operates at a higher recovery is more susceptible to maintenance and fouling.

7. Alternative technologies for PLS upgrade and product recovery

A short review of alternative technologies for PLS pre-concentration is given below. The reviewed technologies might offer advantages comparing to NF and RO relative to gypsum scaling as well as overall fouling implications.

7.1. Membrane distillation

Membrane Distillation (MD) is an emerging membrane-based technology mostly used for water desalination. Different to pressure-driven membrane systems, the MD driving force is the difference in temperature either side of a membrane that creates a vapor pressure gradient (Dow et al., 2014).

In MD processes (Figure 7), a micro-porous hydrophobic membrane is used to separate two aqueous solutions at different temperatures. This process takes place at atmospheric pressure and a temperature below the boiling point, requiring low-grade thermal energy or solar heat sources. The hydrophobicity of the membrane prevents the transport of liquid across the membrane while water vapor is readily transported from the warm side to the cold side where it condenses.

Volatile acids such as hydrochloric and hydrofluoric acid can permeate the membrane as a gas allowing the recovery of a very clean acid. Tomaszewska and Mientka (2009) found that both water vapor and hydrogen chloride were transported through the pores of a hydrophobic membrane, while sulfuric acid is concentrated on the feed side. A similar result was found by Kesieme et al. (2013).

Although MD has never been used in large scale operations, it is a very promising technology in the context of PLS pre-concentration as it offers many advantages, such as low energy consumption, high recovery of volatile acids and fresh water, as well as concentration of metals and non-volatile acids on the feed side. In particular, as salt concentration in the feed has a relatively small effect on mass flux of MD processes (Cath et al., 2004); MD is less affected by fouling and scaling, thus requiring less intensive pre-treatments when compared to pressure-driven membrane technologies. A cartridge filter is considered sufficient to guarantee low fouling and scaling rates (Kesieme et al., 2013).

Due to the low maturity of MD processes and the novelty of MD applications in the hydrometallurgical sector, a thorough experimental campaign on the suitability of MD for PLS pre-concentration is required. This may involve the gradual concentration followed by gypsum seeded reactor regime similar to that described for the NF process.
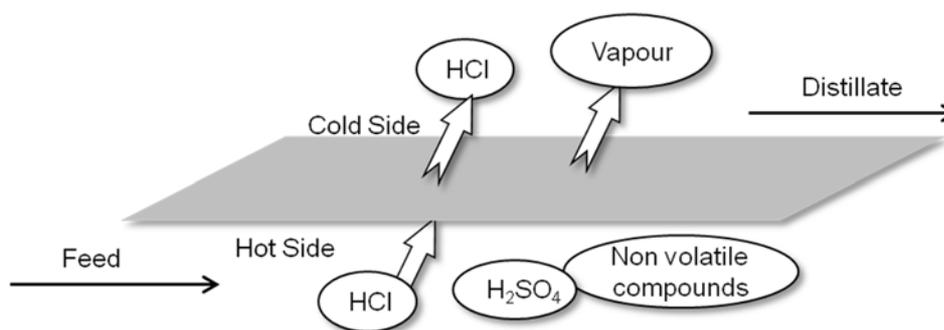
Figure 8: Schematic representation of separation by membrane distillation.

7.2. Ion exchange resins

Ion exchange (IX) technology is a widespread technology, largely applied in hydrometallurgy for the primary recovery of metals such as gold, uranium, nickel, copper, and other valuable metals (Alexandratos, 2009; Fu and Wang, 2011; Van Deventer, 2011).

Savov et al. (2012) describe a combined process with IX and SX, the so-called IX/SX by IONTECH Engineering (Figure 8). The combined process overcomes the limitation of SX by pre-concentrating and purifying the PLS prior to EW. This is a two-step process:

- The PLS from leaching operations goes through IX columns, where valuable metal is adsorbed on the resin. The column is then regenerated with sulfuric acid solution and a purified copper-loaded regenerate is obtained, suitable for further treatment through an SX or EW process.

- An organic extractant that binds valuable metal but not impurity metals is dissolved in an organic solvent (diluent) and is mixed with the regenerate. The loaded organic solution is separated from the aqueous solution in a settler tank. The barren aqueous solution, called raffinate, is sent back to the leaching-ion exchange process. Sulfuric acid solution, mostly spent electrolyte returned from the EW process is then added to the loaded organic mixture, which strips the copper into an electrolytic solution ready for electrowinning.
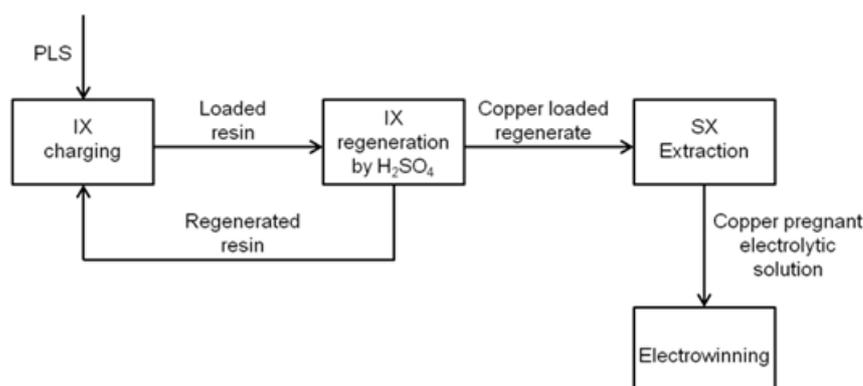
Figure 9: Schematic representation of an IX/SX/EW flowsheet as proposed by IONTECH Engineering.

The first commercial operation utilizing combined IX/SX/EW was operated in 2004, at the Tsar Assen Copper project (Tsekov et al., 2005). Savov et al. (2012) review a leaching-IX-SX-EW copper project at the Buchim mine site in Macedonia. Feed solution pH ranges from 1.8 to 2.2, with designed feed flow rate of 650 m^3 h^{-1}. Copper concentration in the PLS is between 0.5 - 1 g L^{-1} and iron concentration is about 0.3 g L^{-1}. Elution of each column with a sulfuric acid solution (160 - 200 g L^{-1} H_2SO_4) produces an upgraded loaded solution of 15 - 18 g L^{-1} copper to feed the SX/EW circuit.

Amongst the findings of the IX/SX process of major relevance is that the system can operate with very low-grade copper PLS and the integration of the IX process in SX/EW scheme is also used for control of metal/acid ratio as well as Cu/Fe ratio, which are very important for SX efficiency.

For future ores using BIOMOre technology, a trade off study comparing IX/SX to NF in terms of efficacy of PLS treatment, product recovery, technical risks and capital investment may be required to better inform decision makers in their technology choice.

8. Conclusions and recommendations

Pressure-driven membrane separation technologies and their application in hydrometallurgical operations for pre-concentration of pregnant leach solutions (PLS), product recovery, acid extraction, and effluent treatment are reviewed in this report, especially for the PLS of BIOMOre project.

An overview of membrane separation principles and operating conditions are given for membrane technologies, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). In the context of this report, membrane separation is investigated as the lead technology to pre-concentrate BIOMOre PLS to upgrade the concentration of copper, improving the efficiency of the copper extraction process. To this end, NF has been shown to be the most suitable amongst pressure-driven membrane technologies, due to its technical maturity, process flexibility and cost advantages over RO. MF and UF are regarded as necessary pre-treatments to remove suspended solids prior NF and RO operations.

A thorough review of membrane fouling is given in the report, with particular attention to gypsum scaling prevention, minimisation and management strategies. Gypsum scaling is expected to be the major factor limiting the efficiency of NF for PLS pre-concentration and product recovery. Supersaturation of calcium sulfate is expected to be found in the PLS feed and during other NF operations. Due to the low pH of the PLS and its complex chemistry, minimisation and management of gypsum via traditional means (e.g. feed softening, addition of antiscalants) are not effective. Novel cleaning strategies and gypsum minimisation techniques (e.g. microbubbles and magnetic fields) as well as original flow sheet options (e.g. incremental recoveries by NF coupled with forced precipitation in seeded reactors) have been suggested as potential solutions to manage gypsum scaling. For future project phases, not currently part of the BIOMOre project, a substantial research effort is recommended as well as thorough experimental testing of the proposed solutions.

A review of NF operations in hydrometallurgical applications is also presented. Particular focus is given to the ability of NF for PLS pre-concentration, product recovery and effluent treatment by: i) selectively separation of sulfates from chlorides, ii) recovering clean undiluted acid from metals extraction operations (e.g. copper, or uranium), iii) pre-concentration of metal containing streams, recover acid as well as clean water production for reuse when coupled with RO.

Although NF has a great potential in hydrometallurgical operations, its development has been hindered by the popularity of RO. Traditionally NF has been regarded as a sub-case of RO rather than an alternative technology in its own rights. Such a misconception has led to limited research of NF comparing to RO. A proper NF modelling tool is of primary importance to assist with the application of NF in the mining and mineral extraction industry.

Finally, the BIOMOre copper concentration factor resulting from NF filtration ranges from 3 to 10 depending on the PLS composition and volumetric recovery. The management of gypsum scaling in this application is of major importance.

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Annex A

Chemical cleaning agents as recommended by manufacturers and summarised by Al-Amoudi and Lovitt (2007).

Type of foulant	Type of membranes					
	DuPont B-10'	FilmTec FT-30	Fluid System	Nitto Denko	Toyobo	Toray
CaCO$_3$	HCl at pH 4, citric acid (2%w) pH 4 (NH$_4$OH), Nutek-NT 600 (5%w), citric acid (2%w) + Na$_2$EDTA (2%w), pH 4 (NH$_4$OH)	HCl (0.2%w), phosphoric acid, H$_3$PO$_4$ (0.5%w), citric acid (2%w), pH 4, sulfamic acid, NH$_2$SO$_3$H (0.2%w)	Citric acid (1%w), pH 2.5	Citric acid (2%w) pH 4 (NaOH)		Citric acid (1–2%), pH 2.5-4 (NH$_4$ or NaOH), ultrasil 70 0.5% pH 2-2.5, peracetic acid 100–200 ppm
CaSO$_4$/BaSO$_4$ /SrSO$_4$/CaF$_2$	Citric acid (2%w) pH 8 (NH$_4$OH), EDTA (1.5%w), pH 7–8 (NaOH/HCl), sodium hydrosulfite, Na$_2$S$_2$O$_4$ (1%w)	HCl (0.2%w), phosphoric acid, H$_3$PO$_4$ (0.5%w), Citric acid (2%w), pH 4, sulfamic acid, NH$_2$SO$_3$H (0.2%w)		Sodium tripolyphosphate,STP (2%w) + Na$_4$EDTA (0.85%w), pH 10 (H$_2$SO$_4$		
SiO$_2$	NaOH, pH 11, Biz (0.5%w), pH 11 (NaOH)	NaOH (0.1%w) + Na$_2$EDTA (0.1%w), pH 12, max 30 °C	–	-	Citric acid (2%w) pH 4 (NH$_4$OH)	
Metal oxides	Citric acid (2%w) pH 4 (NH$_4$OH), sodium hydrosulfite, Na$_2$S$_2$O$_4$ (1%w), citric acid (2%w) + EDTA (2%w) pH 4 (NH$_4$OH), v	Phosphoric acid, H$_3$PO$_4$ (0.5%w), sodium hydrosulfite, Na$_2$S$_2$O$_4$ (1%w), sulfamic acid, NH$_2$SO$_3$H (0.2%w)	Citric acid (1%w), pH 2.5	Citric acid (2%w) pH 4 (NaOH)	Citric acid (2%w) pH 4 (NH$_4$OH)	-
Inorganic colloids	HCl at pH 4, citric acid (2%w) pH 4 (NH$_4$OH), NaOH, pH 11, Biz (0.5%w), pH 11 (NaOH), Drewperse 738 (1%w), SHMP (1%w)	NaOH (0.1%w) + sodium dodecylsulfate Na-DSS (0.05%w), pH 12, max 30 °C	-	Sodium tripolyphosphate,STP (2%w) + Na$_4$EDTA (0.85%w), pH 10 (H$_2$SO$_4$	Citric acid (2%w) pH 4 (NH$_4$OH)	-
Biological matter	Formalin (0.25–2%w) followed by Biz (0.25%w)	NaOH (0.1%w) + Na$_2$EDTA (0.1%w), pH 12, max 30 °C, NaOH (0.1%w) + sodium dodecylsulfate Na-DSS (0.05%w), pH 12, max 30 °C, sodium tripolyphosphate, STP (1%w) + trisodium phosphate, TSP (1%w) + EDTA (1%w)	Sodium tripolyphosphate, STP (1%w) + sodium phosphate, TSP (1%w) + EDTA (1%w) pH 10–11 (HCl)	Sodium Tripolyphosphate, STP (2%w) + Na$_4$EDTA (0.85%w), pH 10 (H$_2$SO$_4$), Sodium Tripolyphosphate, STP (2%w) + sodium dodecyl benzene sulfonate (0.25%w), pH 10 (H$_2$SO$_4$	1–5 ppm chlorine, pH 6.5–7.5, Formalin (0.5–2%w)	Sodium lauryl sulfate 0.2% pH 10-11 by NaOH, ultrasil 10 0.7% pH 10-11
Organics	NaOH, pH 11, Biz (0.5%w), pH 11 (NaOH), SHMP (1%w)	NaOH (0.1%w) + Na$_2$EDTA (0.1%w), pH 12, max 30 °C, NaOH (0.1%w) + sodium dodecylsulfate Na-DSS (0.05%w), pH 12, max 30 °C, Sodium tripolyphosphate, STP (1%w) + trisodium phosphate, TSP (1%w) + EDTA (1%w)	Sodium tripolyphosphate, STP (1%w) + trisodium phosphate, TSP (1%w) + EDTA (1%w) pH 10–11 (HCl)	Sodium tripolyphosphate,STP (2%w) + Na$_4$EDTA (0.85%w), pH 10 (H$_2$SO$_4$), sodium tripolyphosphate,STP (2%w) + sodium dodecyl benzene sulfonate (0.25%w), pH 10 (H$_2$SO$_4$)	1–5 ppm chlorine, pH 6.5–7.5, formalin (0.5–2%w)	-

Flow rate velocity as high as possible, pressure as lowest as possible, temperature does not exceed manufacturer recommendation (<45 °C).