Application of membrane processes in mining and mineral processing

Marinela Panayotova\textsuperscript{1,*} and Vladko Panayotov\textsuperscript{1,2}

\textsuperscript{1}University of Mining and Geology, 1700 Sofia, Bulgaria
\textsuperscript{2}BAS - Technical Sciences, 1000 Sofia, Bulgaria

Abstract. Sustainable mining and mineral processing is of paramount importance for producing metals needed for our society development. Membrane processes are able to contribute to the comprehensive extraction of metals from mined ores, while at the same time decrease the amounts of used water and reagents and ensure discharge to the environment of wastewater meeting the legislation requirements. Membrane-based technologies are still underused in metals obtaining although their development and price have made their application affordable. The paper presents in brief membrane processes and displays examples of their application in various areas of mining and mineral processing, such as using with clean acid mine drainage and mine influenced water, recovery of metals, reagents and water in hydrometallurgy, recovery of lithium from brines, and treatment of wastewater. Emphasis is placed on pressure driven membrane processes, as well as on the very recent studies in the area. Advantages of membrane processes application in mining and mineral processing are pointed out as well as constrains to be overcome.

1 Introduction

The sustainable development of our society and our normal life needs metals - ferrous, nonferrous and minor. For the present, all metals can be ensured in required amounts only by the "chain" mining - extractive metallurgy (mineral processing, hydrometallurgy, pyrometallurgy and electrometallurgy).

Ores extraction by mining and metals extraction by mineral processing and/or hydrometallurgy are related with generation and /or use of different aqueous streams. When sulphide minerals, such as pyrite are disturbed by mining activities and exposed to oxygen and water chemical reactions take place - finally leading to formation of acidic water containing sulphates and ions of various metals in elevated concentrations, i.e. the so called acid mine drainage (AMD) is formed. When it is not treated, the AMD can result in a considerable pollution to both soil and groundwater [1].

Membrane technologies have been and are being studied for removing and concentrating different metals from AMD [2-5].

Generally, flotation is most effectively carried out with clean water. Changes in water quality are unwanted because this could affect the reagent regimes, finally resulting in compromise of the flotation performance. It is known that water quality impacts the flotation results and the following negative effects can be observed: loss of separation efficiency, loss of recovery, loss of concentrate grade, contamination of products [6]. At the same time the minerals industry is being requested to save freshwater by using recycled water and to minimize the discharge of wastewater into the environment. Since the flotation efficiency can be affected by the water quality, different approached have been and are being developed to cope with the problem. Among them membrane technologies are being studied to remove metal ions and improve the quality of water used in flotation [7].

Nowadays the shortage of many metals necessary for the modern economies, in combination with the increasing demand and the need to use low-grade ores, requires more efficient technologies for metals extraction. Hydrometallurgy plays a key role in processing and recovery of metals from challenging raw materials. Traditionally hydrometallurgical flowsheet includes i) ores leaching, ii) purification of the pregnant leach solution (PLS) by solvent extraction followed by stripping or by ion exchange followed by elution, and iii) metal recovery - where in many cases electrowinning is applied. In the latter case use of membrane technologies to pre-concentrate PLS is regarded recently as an way for lowering the energy consumption, enhancing the recovery of valuable metals and ensuring high recovery of reagents and fresh water [8].

Lithium (Li) is a very important metal in the production of rechargeable batteries, ceramics and glass, as well as lubricating greases. It is used in metallurgy (as casting additive, flux and alloying element) and in many other industries. Lithium can be extracted from either hard rock minerals and brines. Salt brines represent the most abundant lithium sources. They comprise approximately 60% of all known lithium deposits [9]. In the recent 10-15 years extensive work has been carried out to improve
Li recovery from brines by applying membrane technologies.

Membrane technologies have been and are being widely studied and applied to recover valuable metals from wastewater from mineral processing and extractive metallurgy while at the same time ensuring high quality of treated water. Even more, they may be applied also to leachates from mining waste.

Figure 1 presents a summary of the possible applications of membrane technologies in metals extraction.

Membrane technologies have been existing for around 50 years, but they are still not widely used in the general mining industry. That is why this paper aims at shedding some light on the opportunities presented by the membrane processes for more profound use of resources and sustainable production of metals, with an emphasis on the recent (3-4) years.

![Fig. 1. Possible applications of membrane technologies in metals extraction](image)

### 2 Membrane technologies in brief

Membranes are semi-permeable structures or films of materials that allow only certain species or substances to pass and prevent passage of others.

Different forces can drive substances to pass through membrane - Table 1 [10].

Although there are some studies devoted to application of emulsion liquid membranes and supported liquid membranes techniques for extraction and recovery of metals from liquids (wastewater, waste liquids) the works on these applications are not so many and they are dealing with specific cases of extraction [13, 14].

Membrane distillation that can operate at low temperatures (60-90°C) enables the use of waste heat and thus seems a promising technology [15].

Forward osmosis is considered also a promising technology since it does not require a pressure application.

### Table 1. Membrane processes classification based to the driving force

| Driving force            | Membrane process                                                                 |
|-------------------------|----------------------------------------------------------------------------------|
| Pressure difference     | Microfiltration - MF, Ultrafiltration - UF, Nanofiltration - NF, Reverse osmosis - RO |
| Electric potential difference | Electro dialysis - ED, membrane electrolysis - ME, (membrane electro-)deionization - EDI, membrane electrophoresis |
| Chemical potential difference | Pervaporation, Per-traction, Dialysis , Vapour permeation, Liquid membranes - LM, Forward osmosis - FO |
| Temperature difference  | Membrane distillation - MD                                                       |

However, both MD and FO are evaluated as emerging membrane-based technologies and still enough studies and data are absent on their application [16].

Electrodialysis has been studied as a method for recovering the reagents and metals from stripping solutions [17], separating and recovering lithium from brines [18-20] and even in the mineral extraction from deep sea water [21]. However these applications are still in the study stage.

The most studied and used membrane techniques, including in mining, mineral processing and extractive metallurgy, are based on a pressure difference between membrane feed and permeate sides - Table 2.

PDMPs performance generally is evaluated according to the following characteristics:

- Trans-membrane flux \( J_v \) [m/s]:
  \[
  J_v = V_p / (S_m \times t_p)
  \]  
  (1)

  where: \( V_p \) - the volume of permeate [m³], \( S_m \) - the surface of the membrane in contact with the flux [m²], \( t_p \) - the time [s]

- Solute passage \( P \)

  \[
  P = C_p / C_f
  \]  
  (2)

  where \( C_f \) is the solute concentration in the feed and \( C_p \) - its concentration in the permeate

- Solute rejection (retention), in %

  \[
  R = (1 - P) \times 100 = (1 - C_p/C_f) \times 100
  \]  
  (3)

- Selectivity coefficient

  \[
  \alpha_{(1:2)} = P_1 / P_2 = [C_p/C_f]_1 / [C_p/C_f]_2
  \]  
  (4)

  When retentate is concentrated to a small volume, the volume concentration factor (VCF) is determined

  \[
  VCF = V_f / V_r
  \]  
  (5)

  where \( V_f \) is the volume of the feed at the start of filtration and \( V_r \) is the retentate (concentrate) volume.

- Recovery
Table 2. Pressure driven membrane processes (PDMPs) [1, 10-12]

| Process | Microfiltration | Ultrafiltration | Nanofiltration | Reverse osmosis |
|---------|----------------|----------------|----------------|----------------|
| Membrane material\(^1\) | CC, PP, PS, PVDF, CA | CC, PS, PVDF, CA, TFC\(^2\) | CA, PVDF, TFC | CA, TFC |
| Membrane structure | porous, symmetric or asymmetric | microporous, asymmetric | tight porous asymmetric, thing film composite | dense, semi-porous, asymmetric |
| Retained diameter, \(\mu\)m | 0,1 - 10 | 0,01 - 0,1 | 0,001 - 0,01 | < 0,001 |
| MWCO, kilo Dalton | 100 - 500 | 20 - 150 | 2 - 20 | 0,2 - 2 |
| Operating pressure, bar | < 2 | < 10 | < 35 | < 75 |
| Separation mechanism | size exclusion | size exclusion | combination of size exclusion and solution diffusion | solution diffusion\(^4\) |
| Permeate flux | high | high | medium | low |
| Usual module configuration\(^3\) | tubular, hollow fiber | tubular, hollow fiber, spiral wound, plate-and-frame | tubular, spiral wound, hollow fiber | tubular, spiral wound, plate-and-frame |
| Examples of rejection | bacteria, microparticles, fat, oil, grease, colloids | macromolecules - proteins, pigments, polysaccharides, detergents, viruses | high molecular weight compounds, polyvalent ions | high and low molecular weight compounds, poly- and monovalent ions |

\(^1\) CC - ceramic, PP - propylene, PS - polysulfonic, PVDF - polyvinylidene fluoride, CA - cellulose acetate, TFC - thin film composite membrane
\(^2\) The RO and NF membrane presently of choice worldwide is the polyamide TFC. TFC membranes, composed of a strong asymmetric support membrane and a thin dense polyamide toplayer, have a higher permeability and can be used at higher temperatures at a broader pH range, compared to the others. Celulose acetate membranes are chlorine resistant while TFC membranes have low resistance to chlorine.
\(^3\) Molecular weight cut off range
\(^4\) Solutes dissolve in the membrane material, then diffuse through it due to the concentration gradient. The separation is based on the differences in the solubilities of the solutes in the membrane and the different diffusion rates.

\[ \text{Recovery, } % = \frac{m_{P,end}}{m_{F,ini}} \]  

where \( m_{P,end} \) - permeate mass at the end of the experiment, \( m_{F,ini} \) - feed mass at the beginning of the experiment.

The permeate flux in membrane separation process, which determines its productivity, depends on the properties of the membrane, properties of the feed solution, trans-membrane-pressure, solute mass transfer coefficient (which influences the concentration polarization), membrane fouling.

The main factors influencing the selectivity and permeability of PDMPs are the pressure applied over the treated water (working pressure), the temperature and acidity of the treated water, the concentration and nature of the salts dissolved in the treated water.

The concentration polarization and the fouling are the main factors affecting membrane performance. Concentration polarization is the observed differential solute concentration between membrane surface and bulk stream. It is reversibly influenced by operation parameters. The fouling is formation of deposits on the membrane surface. It is irreversibly influenced by operation parameters.

3 Membrane technologies for treating AMD and mine influenced water

The high concentrations of sulfate ions and metals in AMD pose a severe risk to the environment. Most often lime is added to AMD to raise its pH and precipitate the dissolved toxic harmful metals. However, the sludge produced by this process has no economic value and has to be disposed of, covering large areas of land. Acid mine drainage can be effectively processed and made satisfactory for discharge using membrane technology.

Studies on membrane processes application for treating AMD commenced at the 90-ties of the previous century with an emphasis mainly on RO.

Probably one of the earliest applications of membrane technologies was at Cananea de Mexicana where a full-scale RO - based plant was installed in 1997 to treat AMD - with copper recovery directly from concentrate - thus the process was paid back within 6 months [22].

NF and RO (single pass units) were applied successfully at the Kennecott Utah Copper's Bingham Canyon Mine Water Treatment Plant, now property of Rio Tinto Group, to treat AMD (pH 2,9 - 3,4, SO\(_4^{2-}\) - 73,8 g/L, Mg - 9,9 g/L, A1 - 5,96 g/L, and Ca, Cu, Fe, Mn, Zn - in the range of 0,150 - 0,599 g/L, TDS - 92 g/L) and contaminated groundwater. The solute retention for all pollutants was higher than 97 %. The main encountered problem was gypsum scaling [23].

Zhong and co-authors tested commercial polyamide ultra-low pressure reverse osmosis (ULPRO) and nanofiltration (NF) membranes for their ability to remove heavy metal ions from AMD. Rejections achieved were 97 % and 95 % respectively pointing at the possibility to recover metals from the concentrate obtained. In addition ULPRO removed also a major part of the dissolved...
monovalent ions thus decreasing the total water conductivity by 96% and rendering the treated water suitable for irrigation purposes [24].

Results from studies and applications of RO, ED, NF and UF for the treatment of AMD and mine influenced water (MIW), carried out till 2008, are comprehensively presented and discussed by Mortazavi [25].

A group of scientists at Freiberg University of Mining and Technology studied (2008 – 2010) the applicability of different RO and NF membranes for treating AMD. Experiments were carried out at two different pressures of 20 and 30 bar and at two different concentration levels in order to resemble the concentration range of actual AMD found in the mining industry. The results showed that NF membranes (NF99, DK, GE) successfully treated AMD, the heavy metals rejection was > 98% at higher fluxes and at lower pressure (consequently energy consumption) compared to RO. The DK membrane performed in the best way since it showed the highest rejection even at low studied pressure (20 bar) and high AMD concentration. The treatment has also been successfully conducted on a large scale in order to check its applicability at a commercial scale [3, 26, 27].

In 2010 the Interstate Technology and Regulatory Council (ITRC) at the Environmental Research Institute of the States announced that any one of the pressure driven membrane processes can be implemented to treat MIW, including surface and ground water [12]. According to ITRC the treatment goal(s) determine the process selection. The application of a given PDMPs generally depends on the: a) water quality requirements for the permeate (i.e., product water), b) location and source of water needing treatment, c) availability of utilities, d) options to dispose concentrates (retentate), e) quality of the water to be treated. Actually RO was successfully used to treat MIW rich in sulfates and TDS to achieve drinking water standards [28].

The EMalahleni water treatment plant (South Africa) was a solution for treating the coal mining industry influenced water in a reclamation project. AMD was collected from 3 mining sites, neutralized by lime addition which removed iron, magnesium and aluminium. After the clarification water was treated with UF and RO to produce potable quality water. The membrane separation step was repeated 3 times to maximize water recovery and minimize the concentrate volume. The feed water contained mainly calcium, magnesium and sulphate, with a small concentration of monovalent ions (sodium, chloride and potassium), and iron, manganese and aluminium [2, 29].

Dow NF 270 polyamide thin film and a TriSep TS 80 polyamide thin film nanofiltration membranes were studied for their ability to remove and concentrate ionic species from MIW in wide range of pH values of the polluted water [30]. The study proved that NF can be successfully used to achieve metal recovery objectives and meet discharge standards.

A study was carried out with the aim to assess the applicability of RO and NF to treat AMD from gold mines, as well as the main operational conditions. The results pointed that the NF had a higher potential to treat the AMD than the RO, since NF ensures higher permeate flux and satisfactory solutes retention efficiency. The best results were obtained with NF270 membrane at feed pH of 5.5 where the maximum water recovery rate was 60%. The estimated capital cost of the UF-NF unit at an effluent volumetric flow rate of 15 m³/h was US$ 131250.00, and the operational cost was 0.263 US$/m³ of effluent [31].

A very recent study has been carried out at a pilot-scale level with real AMD in order to determine and estimate the operating conditions for using a commercial NF membrane (NF270) to recover water and concentrate copper, as well as to find how NF can be coupled with SX for the selective copper recovery [32]. The water was acidic (pH 3.5) with high conductivity (5510 μS/cm) and high concentrations of some pollutants, in g/L: 4.67 SO³⁻, 0.53 Cu, 0.38 Al, 44,70 Zn, 72,0 Mn. The study has proved that the combined NF-SX technology achieved a high recovery of water and copper from AMD. Thus, freshwater consumption can be reduced and wastewater treatment costs can be decreased.

Since UF works on low operating pressure (consequently energy consumption) and at high water recovery, studies have been carried out to use this membrane process to treat AMD and MIW. However, a means had to be found to modify the pollutants so that they could be retained by the larger pores of UF membranes. Here came to aid application of surfactants and polymers and micellar enhanced ultrafiltration (MEUF) and polymer enhanced ultrafiltration (PEUF) were proposed. PEUF is based on use of water-soluble polymer to complex metallic ions. The formed complexes possess a higher molecular weight than the MWCO of the membrane. The complex is retained by the UF membrane. Further, the retentate can be treated to recover metallic ions and polymeric agent for reuse. The polymers used (polyacrylic acid, polyethyleneimine, diethyiaminoethyl cellulose and humic acid) achieved selective separation and high recovery of heavy metals with low energy requirements [33].

The MEUF is based on the use of a surfactant in the feed stream of the UF process. Dissolved ions which are intended to be separated are attracted by oppositely charged surfactant molecules. They attach to the surface of a micelle formed when the concentration of the surfactant exceeds the critical micelle concentration. Thus formed large ion-micelle complexes can be retained by the ultrafiltration membrane. Ions that are not attached to the surface of a micelle can penetrate through the membrane pores because of their small size. A drawback of MEUF is that it can cause secondary pollution to the environment if the used surfactants are leaked to the permeate. That is why, biosurfactants have been developed [15]. MEUF was successfully applied at pilot level to remove Cd and Cu from phosphorous rich real wastewaters [34].

Very recently a combination of FO and RO processes was proposed for treatment of mining wastewater [5]. Results from a pilot scale FO-RO (with a capacity of 1 m³/day) pointed that this process could offer reduction in use of energy, chemicals, and piping infrastructure.
4 Membrane technologies for PLS concentration

Mainly gold and copper mines have invested in membrane systems to concentrate their PLS [4].

In the early 90-ties of the previous century HW Process Technologies, Inc., installed at Freeport McMoran Phelps-Dodge Rod Mill El Paso one NF and two RO systems to treat H₂SO₄-based Cu-bearing PLS from heap leaching in order to increase the feed copper concentration to the SX/EW plant, reuse the permeate from the second RO system as rinse water, while the concentrate from the 1st RO system is passed also through a NF system. The NF concentrate was directed to copper refinery, while NF permeate was sent to Cu dissolving. In this way a Zero-Liquid (waste)-Discharge was achieved [22].

In 1999 the same company obtained an US patent for method for separating gold and/or silver from copper or other contaminant metals in which a NF membrane is used to form a retentate containing most of the multivalent metal cyanide complexes and a permeate, containing most of the precious metal cyanide complexes [35]. In next stages the precious metal(s) can be recovered from the permeate and the other valuable but non-precious metals - from the retentate where they present as multivalent metal cyanide complexes.

Minera Yanacocha is the largest gold producer in South America. Its mining and processing operations are in the Andes Mountains at height in the range 3500 - 4100 meters. The gold is extracted by heap leaching with diluted cyanide solution (30 - 50 mg/L free cyanide). Seven RO modules are installed (initial installation in 2003) at Yanacocha complex (250 m³/h each one) and five excess water treatment plants, two carbon plants for recovering precious metals, and two Merrill Crowe processing plants [4]. During the rainy season, the PLS is being diluted and RO plants are used to dewater the PLS making the Merrill-Crowe gold extraction process more effective. Additional RO plants are installed to remove the cyanide and metals left and to allow the permeate water to be discharged and the concentrate to be returned to the extraction process. At the same time chlorine consumption (for cyanide destruction) is reduced by 75% and overall operating cost is 70% less than that of a conventional precipitation plant [22].

Because of the harmful impact of copper-cyanide complexes on the gold extraction process, the use of NF for separating Au(CN)₃⁻ from Cu(CN)₂⁻ has been studied. Soldenhoff and co-authors reviewed some patented NF processes for gold processing designed to ensure separation of Au(CN)₃⁻ from Cu(CN)₂⁻ in copper-rich cyanide solutions [36]. This separation can be realized by treating either the PLS from cyanide leaching operations or the loaded eluate from activated carbon extraction.

Treatment of copper-gold cyanide PLS from heap leaching where it is fractionated into a small, 1/10⁶, volume copper concentrated stream and a large, 9/10⁶, volume gold-bearing stream has been proposed [37]. The copper stream is processed further by sulfide-acid-re-neutralization-treatment to recover copper and return cyanide back to the process. The gold-(or gold-silver) permeate stream is processed to recover gold and the cyanide (concentrated by a membrane process from the barren solution) can be returned to the leaching. Thus both permeates and concentrates from the applied membrane processes provide added value.

Studies have been conducted also on membrane processes application to PLS from a pressure-oxidation (POX) of refractory gold ores [38, 39]. POX represents a hydrometallurgical oxidation of concentrated ore pulp under high pressure (20 bar) and temperature (135–200 °C). During the pressure oxidation process, the sulfide in the host mineral matrix is oxidized by oxygen, thus producing soluble metal sulfates and sulfuric acid. In this way, the gold originally occluded in the sulfide minerals is completely released, allowing further high gold recovery by cyanide leaching. POX is efficient process for refractory gold ores but it generates a large volume of liquid effluents, characterized by high acidity and substantial metal content, and some of metals (Cu, Co and Ni) are of great economic value. The aim was to concentrate metals, and recover acid and water by applying combination of UF, NF and RO. The UF process is used as a pretreatment to avoid presence of suspended solids in the feed to NF system. NF membrane concentrates Cu, Co and Ni. An average concentration factor of 2 was observed for metals in the NF retentate. This concentration was favorable to subsequent recovery processes of metals (Co, Ni and Cu). The NF permeate (a metals-free solution with a low concentration of acid) is passed to the RO stage. There the acid is concentrated in RO retentate (with 2.5 times higher concentration of the H₂SO₄ and low impurity content - totally 0.58 mg/L) and could be recirculated to control acidity in the POX process. The RO permeate was water with quality for industrial reuse in the company. The best performance at a pilot-scale operation was while operating at recovery rate of 90%, 40–50%, and 50% for UF, NF, and RO, correspondingly. The total estimated cost of the proposed treatment was US$ 1,137/m³ of effluent, including the neutralisation of UF and NF concentrates. A large-term work in a mining company validated suitability of the proposed treatment scheme. The same working group conducted further studies to find the most chemically stable membranes in order to increase the process sustainability [40]. Commercially available NF membranes (NF90, NF270, MPF34, DK, Duracid) and RO membranes (BW30, LP, TFC-HR, XN45, and SG) were assessed in terms of key performance parameters. The DK (as NF) and SG (as RO) membrane showed the highest capability for application in POX effluent treatment.

Application of membrane process has been studied and proposed also for recovering nickel from spent nickel electrolyte after electrowinning of Ni from purified PLS of the base metal refinery in the PGM cycle (Bushveld Complex, South Africa) [41]. Energy costs limit the recovery of nickel in the electrowinning unit to 50% thus making the recycling of the spent nickel electrolyte significant for cost-effective nickel production. In the "classical scheme" four units are necessary for nickel concentration and sending back to the cycle. They are replaced by one NF unit. The retentate stream where
nickel is concentrated is recycled back to the nickel electrowinning cells together with the sodium sulphate to ensure the needed conductivity while the permeate is recycled back to the leaching circuit in order to reduce the overall sulphuric acid consumption of the base metal refinery.

Very recently a study has presented a promising process chain for the separation of Ge and Re from an acidic multicomponent PLS obtained by bioleaching [42]. The proposed treatment chain includes consecutively MF, NF, and RO. For the MF pretreatment rotating ceramic and polymeric (MV020) membrane filters are proposed. Over 99% of the leached sludge particles are retained and can be recycled for bioleaching as leaching bacteria are still present. In the further step the sterile solution is passed to NF system. With NF99HF it is possible to remove all cations (Co^{2+}, Cu^{2+}, Fe^{3+}, Zn^{2+}) at retention ≥ 99% and Mo at retention > 97%. Concentrate is sent to the refining stage while the permeate stream is transferred to the next RO step (with RO90 membrane). There the Ge is concentrated in the retentate while Re passes to permeate. Both high tech elements can be further extracted from the corresponding streams by solvent extraction or adsorption.

5 Membrane technologies in obtaining lithium from brines

According to some estimates, nowadays 2/3 of the worldwide produced lithium is extracted from brines. This technology evaporates normally half a million litres of brine per ton of lithium carbonate. The process is chemicals intensive, extremely slow, and delivers large volumes of waste [43]. Methods have been searched for to speed the extraction and mitigate its environmental impact, including recovering at least some part of the water in brine as pure water.

Brines are highly saline solutions, containing typically large amounts of Na^+, and lower concentrations of Li^+, K^+, Mg^2+, and Ca^2+. The equivalent anions generally are mainly Cl^− with minor amounts of SO_4^{2−}, HCO_3^{−} and borates. Lithium concentration is low (in the range 0.3 - 1.5 %), concentrations of the other metals are high, and the chemical properties of the presenting Na^+ and K^+ are similar to those of Li^+. Consequently efforts to directly precipitate Li^+ salts from brine lead also to precipitation of large amounts of Na^+ and K^+ salts [44]. In addition, presence of Mg in high concentrations is also detrimental, since it possesses greater affinity to lime as compared to lithium, leading to inefficiency in lime precipitation of Li and also hinders the ED separation of Li [9].

Consequently, it is essential to find process for efficient separation and recovery of lithium from brine sources. NF and ME are the membrane processes mainly used in this application.

NF and low pressure reverse osmosis (LPRO) have been studied for their ability to separate lithium from salt lake brines with an emphasis on Mg^2+/Li^+ separation [45]. The results pointed that NF90 membrane was more efficient for Li^+ separation from a diluted brine because of its higher hydraulic permeability, lower critical pressure, its high rejection of Mg^{2+} (approximately 100 %), low rejection of Li (only 15 %), its higher selectivity between monovalent ions (40 %) obtained at lower operating pressure (below 15 bar) and its lower roughness showing decreased predisposition to fouling. However, the further step aimed to separate from the obtained permeate Li^+ and Na^+ by using the NF90 was not successful and dialysis at zero pressure was used to ensure the separation. Other authors also pointed that NF is suitable process for separation of Li^+ and Mg^{2+} from brines [46, 47].

Membrane electrolysis combined with crystallization is proposed as a new technology for lithium carbonate production from lithium-rich brines [44, 48, 49]. In the first stage brine is introduced in a membrane electrolyzer where anodic and cathodic departments are separated by anion exchange membrane. Water reduction increases the pH of the catholyte, and there Mg^{2+} and Ca^{2+}, migrated due to the applied voltage, are removed as Mg(OH)_2 and Ca(OH)_2. In the second stage brine, from which Mg^{2+} and Ca^{2+} are removed, is introduced in the middle compartment of a three-compartment water electrolyzer. Anodic and cathodic compartments are separated from the middle compartment by anion-exchange (AEM) and cation-exchange (CEM) membranes correspondingly. Monovalent cations (left in the brine after the first stage) migrate from the middle compartment through a cation exchange membrane to the cathodic compartment where water electrolysis leads to alkalinisation. It is found that under the experimental conditions applied, the ionic migration rate across the CEM decreased in the order Na^+ > K^+ > Li^+. A side-crystallizer is attached to the cathodic compartment and Na^+ is recovered as NaHCO_3 by introduction of CO_2 in the system. At heating the bicarbonate solution, the bicarbonate is converted to carbonate solid samples. Na_2CO_3 with a purity of 99.5% of was obtained from real brine samples. Thus the solution is depleted in Na^+ ions and it is more suitable for Li_2CO_3 recovery in a successive stage. This solution is introduced (in the 3rd stage) into the middle of another three-compartment water electrolyzer, similar to the one applied in the 2nd stage. Since the water is deprived of Na^+ ions, mainly Li^+ ions pass to the cathodic compartment, where, due to the alkalinization caused by the electrolysis and introduction of CO_2, Li_2CO_3 (with a purity of 93.8 wt. %) is precipitated in a side-crystallizer, attached to the cathodic compartment. The method proposed recovers fresh water as a by-product (around 90 % of the initial volume).

More on the advantages and challenges of the membrane-based technologies applied to the lithium recovery from brines till the middle of 2019 can be found in the work of Li and coauthors [50].

Studies development in that area hinted to the idea that an integrated membrane separation process could be a potent alternative to conventional Li recovery methods. An integrated membrane process combining NF and MD was studied for the enrichment of Li from simulated salt lake brine [9]. NF90 and NF270 NF membranes were used in experiments. It has been found that under optimum operating conditions, the Mg/Li molar ratio changed from 10 to 0,19 when NF90 was used, and from 10 to 2,1 at NF270 use. The achieved concentration of Li
from brine was 77 and 56% for NF90 and NF270 membranes respectively. Following NF treatments, the separated Li could be further concentrated (by up to 80%) by means of direct contact MD system. Park and co-authors [51] also confirmed the ability of the combination NF - MD to recover Li from low concentration lithium brine, as they stressed, at "one-tenth of capital cost, process time, and footprint of the conventional process". The cost can be decreased further by using the waste heat from the industrial plants and solar energy.

Very recently a comprehensive technology for preparation of Li₂CO₃ has been proposed [52]. It includes electrochemical intercalation-deintercalation, nanofiltration, reverse osmosis, evaporation, and precipitation. In the beginning the electrochemical intercalation-deintercalation method is used to ensure maximum separation of magnesium and lithium, i.e. to obtain a low mass ratio Mg/Li. The Mg/Li ratio decreased from 58,5 in the brine to 0,93 in the produced lithium-containing anolyte. Further, multivalent ions (e.g., Mg²⁺, Ca²⁺, and SO₄²⁻) are removed from the obtained anolyte via the NF method. Then NF permeate is concentrated by RO. The next step uses evaporation to increase further the lithium concentration. Finally Li₂CO₃ is precipitated by Na₂CO₃ addition. By the proposed technology a direct recovery of lithium from the high Mg/Li brine to the produced Li₂CO₃ can come to 68,7%. When recycling is ensured for the most of the solutions in the system, the total recovery of lithium will be higher than 85%.

6 Membrane technologies for recovering reagents, metals and water from mining waste streams

Treatment of in-plant process effluents and wastewater streams are presented in this section. Membrane processes have been applied for treating in-plant effluents in order to regenerate reagents and/or to separate valuable materials. An example is application of ED for recovery of HCl, zinc and iron contained in effluents from chloride hydrometallurgy [17]. The waste stream was with high concentration of hydrochloric acid and of metal anionic and cationic chloro-complexes. Initially selective membrane-based solvent extraction step was applied to separate in raffinate cationic iron from the stripping solution that contained the HCl together with anionic species of zinc. The stripping solution was passed to ED system where Zn was concentrated in concentrate and the latter was suitable for Zn electrowinning. HCl was recovered in diluate to be re-used in the leaching process.

Another example is recycling of H₂SO₄ from raffinate, generated during copper ore hydrometallurgical processing, by use of bipolar membrane electrodialysis (BMED) system [53]. The raffinate is highly acidic and contains Fe, Zn, Cu, Ni, Cr, Cd, As in high concentrations. The experiments showed that 85,9% of SO₄²⁻ that present in the raffinate could be recovered by the formation of H₂SO₄. The removal rates of other pollutants were, in %: iron - 99,3, zinc - 99,1, copper - 99,0, nickel 84,9%, chromium - 70,6, cadmium - 95,8%, and arsenic - 94,8.

In order to find a sustainable solution for fresh-water demand in mining sectors, MD was proposed to reclaim POX effluent [54]. Different operational conditions were studies and under the optimum ones (PTFE membrane with spacer, feed temperature - 60 °C, recirculation flow rate - 0,3 L/min), the average distillate flux was 6,82 L/m² h and a permeate recovery rate was 33,91% at retention rates for metals > 95,7% and for the acid > 99,9%. The system was working 240 days without any deterioration of parameters, generating a permeate that can be used directly as recycled water in the plant. Since the temperature of the POX effluent is in the range 50 - 80 °C, the effluent can be introduced directly into MD system thus decreasing the energy demand for the effluent processing.

In general, RO is the major membrane process used by the developed countries to treat wastewater streams from mine sites, especially with the aim to achieve water quality meeting the legislation requirements permitting water discharge in natural water bodies. Most often the technology is applied for water polishing after other treatment processes and before discharge to the environment. For example Oceana Gold - Waihi (New Zealand) applies RO since 2008 to remove pollutants, such as TDS, Se and As left after treating the wastewater by a conventional wastewater treatment plant using chemical precipitation and clarification [22]. The water is purified to a level of purity, far in excess of that required by regulators [55].

Many mines in Australia are using the RO technology as a post-treatment process for removing heavy metals and other toxic compounds from their wastewaters before water discharge to the environment [56-58]. However, membrane fouling appears as one of the biggest problems when RO is used in a harsh environment like as mining operations.

A study evaluated the performance of RO plant as a wastewater post-treatment process in mining operations in Victoria, Australia [56]. The data analysis points that the RO treatment significantly improves the quality of the final water before it is being discharged to surface waters. Considering average rejection efficiency for the entire evaluated period (01.01.2015 - 27.11.2018), the concentrations of ammonium, arsenic, nickel, zinc and iron were reduced by 95 %, 66 %, 82 %, 48 % and 10 %, respectively in the RO permeate compared to the feed water. The turbidity and TDS decreased by 85 % and 96 %. However, the sporadic inefficiency of the pre-treatment system, led up to serious failures in RO plant, resulting in a non-compliance with local discharge licence in some days. The conclusion was that since RO membranes are very sensitive to fouling, availability of a reliable and extensive pre-treatment system is the most critical factor to guarantee good performance and high durability of membranes.

Legislative measures forced not only gold and copper mining companies but also coal-mining enterprises to search for solutions to minimize their saline wastewater. A study was carried out aimed at evaluating the performance of an integrated FO - RO system with three different actual coal mine waters from Australia, containing different concentrations of sulphates and silica.
that are usually related with scaling and fouling of membrane systems [59]. Studies have shown that the integrated system concentrated the mine water, recovering more than 80% of the mine water volume and producing treated water of dischargeable quality. It is found that the combination of FO with RO provided a better results than individual FO or RO. The FO unit performed as an effective pre-treatment system prior to RO and showed a potential to successfully replace conventional pre-treatment processes for RO.

7 Conclusions

Application of membrane-based processes in mining and mineral processing industry offers many potential benefits such as (a) Improved selective separation of valuable metals, (b) Water and reagents recovery for reuse in the production process, (c) Reduction of volumes requiring conventional treatments, such as lime neutralization and precipitation. This in turn leads to decreased usage of reagents and reduced costs for disposal, (d) Release of wastewater aligned with stringent regulatory standards for water discharge to the environment and even production of water usable for industrial, agricultural, and domestic purposes, (e) Efficiently dealing with AMD and MIW.

All mentioned translates into smaller and more efficient plants with lower capital and operating costs, as well as decreased environmental negative impacts.

Flexible application of membrane based technologies, with relatively small footprint, compared to traditional technologies, can be ensured by nowadays developments in the area. While RO is still “classics” in the wastewater treatment, in-process technology NF gains increasing attention, since RO and NF provide similar rejection performances for commodity metals and multi-valent ions and NF shows a higher flux at lower pressure, leading to lower capital investment, lower cost of operation and maintenance. MF and UF are considered as necessary and suitable pre-treatments to remove suspended solids prior NF and RO operations.

Among the barriers hindering the application of membrane-based processes in mining and mineral processing the following can be pointed out: (a) Still relatively high capital and operational costs, (b) Fouling and scaling of membranes, since the waters entering the membrane plant have a large amount of complex suspended and dissolved solids. Need of chemicals and pre-treatment to avoid the mentioned problems and to ensure feed solution with predictable quality, (c) Still some improvements in module design and process optimization are needed.

However, the developments of science an technology in the area of membranes and membrane technologies is going to mitigate these problems.

Hopefully, this paper will be useful in providing some information and basis for widening the application of membrane technologies in mining and mineral processing in order to render metals extraction more environmentally friendly and sustainable.

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