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# REVIEW OF MEMBRANE TECHNOLOGY AS A PROCESS TOOL

By

**Darryl Butcher**
Director
BDB Process Pty Ltd, Australia

darryl.butcher@bdbprocess.com.au

**Contributors**

Paul Boshoff, Director and Principal, BDB Process Pty Ltd, Australia
Simon Donegan, Director and Principal, BDB Process Pty Ltd, Australia

## ABSTRACT

The Application of membranes to hydrometallurgical processes as a new mode of separation has now been established at commercial scale. Membranes offer a significant advance in that they represent a mode of discrimination between different ionic aqueous species quite unlike that offered by other techniques such as Resin Ion Exchange, Solvent Ion Exchange, Selective Crystallisation, or Cementation.

Nemaska Lithium Inc. is currently installing membrane electrolysis cells for the recovery of high purity lithium hydroxide. This installation involves a very different membrane application and functionality to that employed by the installations of Paladin Energy Limited.

Paladin Energy Limited installed two membrane plants in their operating facilities: one in Malawi at the Kayelekera Project which is an ambient temperature atmospheric acid leach/RIP circuit; and the second in Namibia at the Langer Heinrich Project which is an elevated temperature, atmospheric alkali leach with CCD washing and NIMCIX resin circuit. Both of these applications were the result of a clear focus by the Company on both optimisation and innovation.

Publicly available data from these two operations demonstrates the significant potential of membranes to simplify circuits, improve selectivity and reduce operating costs compared to the established alternatives.

Neither of these applications operated the chosen membranes within the recommended operating windows published by the manufacturers, but both were technically and commercially very successful and both exceeded the forecast performance used to justify the project capital expenditure. The author and contributors were all involved in both installations and comprised the technical and project management core of the design and development teams in both cases. That experience, and subsequent operating exposure has provided a window into the potential for further, more general, application of membranes in hydrometallurgical processes. It appears likely that membranes will be applied in a broad range of applications to improve process outcomes.

*Keywords: Uranium, Hydrometallurgy, Ion Selectivity, Process Optimisation, Innovation*

## INTRODUCTION

Prior to the mid 1970's, membrane separation techniques were not generally considered important in hydrometallurgy particularly or industry generally. Intriguing in a sense when one considers that membranes are a key element in the function of almost all living things. Humans being no exception. The function of our gut, kidneys, liver, respiratory system, cardiovascular system and many more are all dependent on membrane processes at a cellular or tissue scale.

In contemporary industrial practice, membrane technology now has many and varied applications in the landscape generally. Membranes have been used commercially since the middle of the last century and in the chlor-alkali process at significant scale. In 1987 alone, 35 million tonnes of Chlorine, plus associated sodium hydroxide, were prepared using membrane chlor-alkali processing[(1)]. In the mining process sector however, membrane application has been limited largely to water treatment and a few emerging specialised applications. We generally accept the use of membranes for the Reverse Osmosis (RO) treatment of polluted, brackish and saline waters for ultimate use as high quality process water or domestic consumption. In Australia, this technology emerged in the 1980's and has risen in prominence to what is now reasonably described as general usage or technology of choice. RO is also used at the Ranger Uranium Mine to treat process water to produce water of quality suitable for release into the receiving environment[(2)]. RO membranes are not the whole story, however.

Membrane separation processes differ based on their separation mechanisms and the size of the separated particles. The widely used membrane processes that may have applicability in hydrometallurgy include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), RO, electrolysis, dialysis, electro-dialysis, gas separation and membrane contactors. All processes except (electro)dialysis are pressure driven. MF and UF are widely used in food and beverage processing (concentration and purification of fruit juices, enzymes, fermented liquors, and vegetable oils)[(3)], biotechnological applications and pharmaceutical industry (antibiotic production, protein purification), water purification and wastewater treatment, the microelectronics industry, and others. NF and RO membranes are mainly used for water purification purposes. Dense membranes are utilized for gas separations (removal of $CO_2$ from natural gas, separating $N_2$ from air, organic vapor removal from air or a nitrogen stream). Figure 1 provides an outline of the applicability of some of the separation techniques applicable to the minerals processing sector.

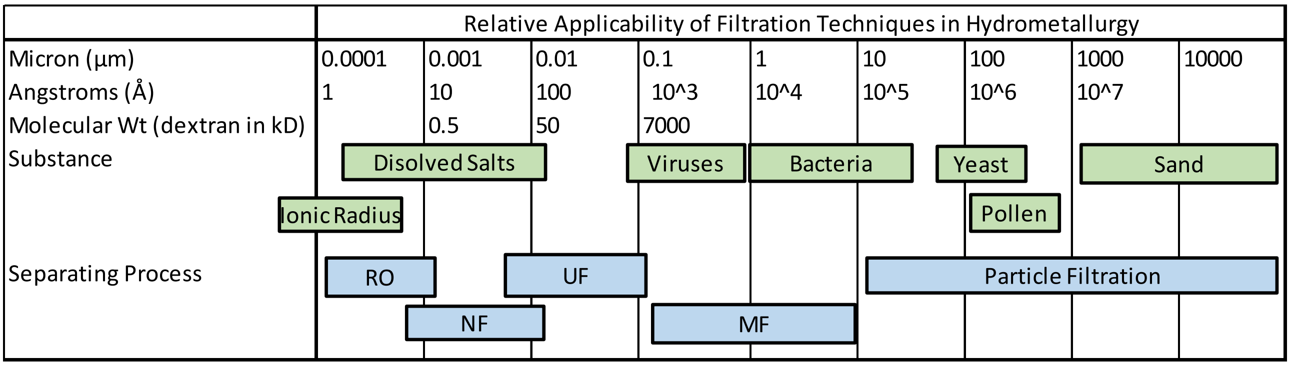


**Figure 1 - Relative applicability of various filtration techniques**

Despite the broad range of applications described above, this paper is focussed on the apparent near-term potential applications of membranes to mineral processing generally and hydrometallurgical processes particularly.

## RECENT APPLICATIONS

Recently, a few mineral processing applications have incorporated membranes to enhance existing operations or in greenfield applications. In 2013, Nemaska Lithium Inc (Nemaska) indicated its intent to use an electro-dialysis step (patented) to convert lithium sulphate ($Li_2SO_4$) to lithium hydroxide (LiOH)[(4)]. In its latest disclosure document, Nemaska confirm, what they now refer to as an electromembrane process will be used[(5)] The Nemaska application, as described, provides a pathway to high purity LiOH that displays significant operational benefits over previous flowsheets. In the period 2013 to 2015, Paladin Energy Limited (Paladin) applied membrane technology to two existing uranium extraction plants[(6)].

The two Paladin Energy Limited applications were both very successful and provide an insight into the potential for membrane applications more generally. In these applications, NF was used to separate different ionic species in aqueous solution on the basis of their valence. By applying NF membranes and pressure to achieve discrimination based on valence gives the hydrometallurgical industry a new and exciting process option.

There is now the potential to readily separate monovalent species from species of higher valence at relatively low cost. There will be limits to the applicability of course, but this is a new and emerging tool. If it follows the path of other innovations in the sector, its applicability will broaden, costs will decline and functionality improve rapidly over the next decade or so. It will also likely alter current perceptions concerning technology of choice for some processes.

Already, the functionality of NF has increased materially in the last decade. When Paladin designed its NF applications, between 2013 and 2015, NF membrane pressures were limited to 40bar and the range of membranes available for initial applicability testing was limited. In the following years, pressure limits have been increased to 60 and 70 bar, allowing higher retentate concentrations where solubility is not limiting. Additionally, new membranes are being developed continuously and the range now available provides greater scope for beneficial and tailored outcomes.

## THE PALADIN EXPERIENCE - NF

The Paladin experience is perhaps instructive in terms of potentially changed perceptions. The technology of choice for uranium extraction is generally considered to be based around a sulphuric acid leach. Alkali processing has generally only been used when acid was not economic, but alkali leaching offers potential benefits in terms of impurity control, in particular, as most of the impurity elements defined by converters are insoluble in alkali conditions. The Langer Heinrich Uranium (LHU) mine (Namibia, Paladin) is a case in point. This mine is based on a resource that is carbonate hosted and the economic mineral is carnotite ($K_2(UO_2)_2(VO_4)_2 \cdot 3H_2O$). There are many such uranium resources known globally (Yeellirrie, Lake Way and Lake Maitland in Australia for example and many deposits in the Colorado Plateau).

The perception has also been that acid-based extraction and processing is inherently lower cost than alkali-based extraction and processing. Until the successful process innovation by Paladin at LHU, this perception was generally true, but with the changes introduced and commercially proven at LHU, it is no longer necessarily so. The application of alkali processing, particularly where the leach reagent is sodium carbonate ($Na_2CO_3$), sodium bicarbonate ($NaHCO_3$), or more typically a combination of the two, in conjunction with NF provides some interesting potential applications. The LHU experience clearly demonstrated a reduction in total process operating costs of 50% - a reduction that cannot be ignored.

Furthermore, alkali processing is not limited to carnotite based or similar resources. It is also able to be applied to primary mineralogies such as uraninite. The author understands that the Kintyre deposit, a uraninite deposit, was tested for its amenability to alkali leaching and that the performance under alkali conditions was as good or better than for acid conditions. The author is aware of other hard rock and primary deposits involving uraninite also being successfully leached under alkali conditions. NF may potentially play an important role in materially reducing the process operating cost of this style of resource under alkali conditions to match or improve upon the more established acid leach routes.

NF allows the separation of $NaHCO_3$ from $Na_2CO_3$, as demonstrated by the membrane application at LHU. In that circuit, $NaHCO_3$ was separated until a concentration limit was reached on the retentate side of the membrane (approximately 1 to 1.2M $Na_2CO_3$). This apparent barrier to further recovery could be overcome (and was) through dilution with fresh water on the permeate side down the “Christmas tree”, or down the series / parallel connected membrane elements that constitute an NF membrane array where the number of parallel connected membranes reduces progressively down the series array – like a Christmas tree shape. It can also be overcome by conversion of some $Na_2CO_3$ to $NaHCO_3$ and this can easily and quickly be achieved by carbonation. Carbonation involves the injection of $CO_2$ gas into the solution. $Na_2CO_3$ is rapidly converted to $NaHCO_3$ as described below:

$$Na_2CO_3 + CO_2 + H_2O \leftrightharpoons 2NaHCO_3$$

In this manner, $Na_2CO_3$ is reduced and the volume of retentate required for the terminal $Na_2CO_3$ concentration achievable is also reduced. This is just one of many potential applications of NF, and enhancements thereof, as a hydrometallurgical processing tool.

At the Kayelekera Uranium Mine (KUM) (Malawi, Paladin) a similar process was introduced but for different reasons[7]. The KUM resource is a sandstone and mudstone hosted uraninite deposit. Rather than the alkali process route, acid processing was selected for this site with continuous RIP for uranium recovery. Resin elution was achieved with 1M $H_2SO_4$ and acid supply was production limiting. NF was introduced here primarily to reduce acid consumption by recycling acid in the CE back to the process (leach). This application, like LHU, was very successful with significant direct and indirect benefits that in combination, reduced total process operating casts at this site by over 15%.

Intuitively, the application of NF, which provides separation based on valence, may not be an obvious choice for a $H_2SO_4$ circuit. The sulphate ion is after all bivalent. In the operating range of CE, at 1M $H_2SO_4$, the acid is only partially dissociated and most is present as hydrogen ion ($H^+$) and bisulphate ion ($HSO_4^-$). NF is consequently able to provide a separation between the $HSO_4^-$ and the uranyl sulphate in ionic form ($UO_2^{2+}$ + $SO_4^{2-}$).

Importantly, NF has been demonstrated, in commercial operation, to provide a discrimination and/or concentrating technique based on valence that, until now, was not available to the industry.

## ELECTRO-DIALYSIS

The electro-dialysis process patented by Nemaska also provides a hitherto unused tool to hydrometallurgy. This is an application to generate a target product. In this case LiOH. Nemaska use a combination of 2 and 3-compartment electrolysis units[(8)], that they refer to as membrane electrolysis cells, in a patented process. In the 2-compartment unit, purified $Li_2SO_4$ solution is converted to LiOH. Fresh $Li_2SO_4$ is added to the anolyte and lithium ion passes through the cationic membrane (that separates the anolyte and catholyte) into the catholyte where it combines with hydroxide ion produced at the cathode. The hydrogen gas produced is collected and utilised. The anolyte becomes an aqueous mixture of $Li_2SO_4$ and $H_2SO_4$. A bleed of this liquor is treated in a crystalliser to separate the $H_2SO_4$ and $Li_2SO_4$. The acid stream is reused in the leach circuit, and the $Li_2SO_4$ is further treated in a 3-compartment membrane electrolysis unit. The 3-compartment unit has a feed compartment for the $Li_2SO_4$ which is separated by an anionic membrane from the anolyte compartment and a cationic membrane from the catholyte compartment. Lithium ion passes through the cationic membrane to enter the catholyte and sulphate ions pass through the anionic membrane to enter the anolyte. Water molecules are split at both the anode and cathode to provide hydrogen ions in the anolyte for $H_2SO_4$ formation and hydroxide ions in the catholyte for LiOH formation. Whereas NF separates on the basis of valence, electro-dialysis achieves separation on the basis of charge polarity. Figure 2 provides a simplified schematic of the flowsheet.

Nemaska report that they have operated a commercial pilot of the membrane electrolysis units for some years, so while not yet proven as a commercially successful technique, such proof may be with us soon.

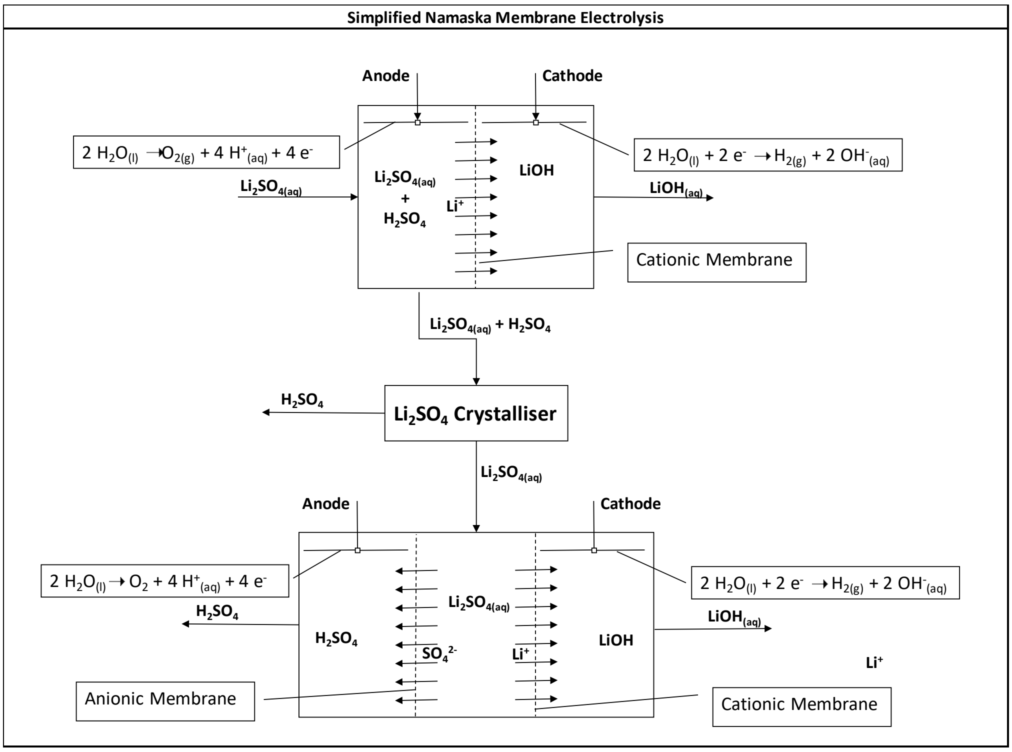


**Figure 2 - Simplified Nemaska membrane electrolysis.**

But the technique perhaps has broader applicability in suitable circumstances. It can potentially be used to recycle reagents and reduce waste streams. This is a target paradigm often quoted, but not so often seriously contemplated in the mining sector. The paper pulp industry takes this approach very seriously and a good example is the Kraft process, where sodium hydroxide (NaOH) is recovered from “green liquor” by the reaction of lime (CaO) with $Na_2CO_3$ via the following reaction:

$Na_2CO_3 + Ca(OH)_2 \leftrightarrows 2NaOH + CaCO_3$

In areas where reagent costs are high, or waste disposal standards are stringent, there are many potential hydrometallurgical applications when one considers the potential of electro-dialysis. By way of example, a common waste or biproduct stream in hydrometallurgy is sodium sulphate ($Na_2SO_4$). This can build as a circuit poison and require a specific bleed: usually to waste, but on some occasions to a crystalliser for sale as a biproduct. Just as electro-dialysis is able to convert $Li_2SO_4$ to LiOH and $H_2SO_4$ as Nemaska has shown, there is potential to convert $Na_2SO_4$ to NaOH and $H_2SO_4$.

## FEED PREPARATION – UF

NF applications require a very clean feed to maximise membrane life, both between cleaning cycles and terminal life (replacement). Here too, membranes find application. The use of UF after clarification of the feed to an NF process is, in the author's experience, a critical element of the process. This brings with it some consequential benefits. Most notably, product streams with very low (<10ppm, particularly for the permeate) Total Suspended Solids (TSS).

This situation lends itself to the production of extremely high purity products and specialist end markets. One of the stated benefits of the Nemaska process to produce LiOH from $Li_2SO_4$ via electro-dialysis is the purity of the product and its subsequent extreme suitability for lithium battery manufacture.

A large portion of the capital and operating cost of a NF process is, in the author's experience, centred in the UF section of the plant and consequently, further membrane treatment of the permeate and retentate streams is likely to be less capital intensive at least. Where the permeate is of relatively low Total Dissolved Salts (TSS), the application of either NF or RO to provide a reagent recycle stream of much higher concentration and a high quality (low TDS) process water may be useful.

## OUTLOOK

Membrane use in general industry, particularly food processing, is widespread. Historically, membrane use within the mining sector has been limited to water treatment applications for environmental or water quality purposes. Recent developments in the use of membranes more generally in the hydrometallurgical sector indicate the emergence of new tools for the hydro-metallurgist.

The application of membrane electrolysis by Nemaska is a significant step in establishing this unit process as a commercially proven reality which may ultimately have far more potential applications. Its analogues in the chemicals industry, such as chlor-alkali, are already established at very large commercial scale and have been operational for many decades, so it has a "head start" as it were. The Nemaska operation will doubtless be closely watched by the hydrometallurgical industry and it will play an important role in the success or otherwise of the technology. This process provides separation on the basis of ionic charge.

In the case of Paladin and its application of NF for reagent recovery and recycling in two quite different circuits. This application may now be considered a commercial reality and the magnitude of the benefits delivered, which included a 50% reduction in total process operating costs in one case[(9)] are such that it cannot be overlooked.

NF provides a mechanism to discriminate ionic species on the basis of their valence. In that sense, it is an entirely new discrimination or selection tool. Many of the ionic species hydrometallurgy deals with are polyvalent and may be manipulated into a valence that will allow them to be concentrated in either the retentate (bivalent and higher) or permeate (monovalent) of an NF system. A situation that is true for both cationic and anionic species. This has, in the author's opinion, great potential to change the way we look at many existing processes, as well as lead to the creation of new, more efficient processes.

NF membranes are already manufactured at commercial scale, but none have yet been manufactured for the specific needs of the hydrometallurgical industry. At the moment we are adapting existing membranes to fulfil identified needs. In the two applications referred to above, the design operating conditions were well outside the published manufacturer's performance data for the membranes used.

It is reasonable to believe that membranes will be developed for specific hydrometallurgical needs in the future. The author is aware, by example, of graphene-based membranes being developed for specific purposes with specific selectivity. It is also reasonable to believe that the operating pressure of membranes will continue to rise, thereby increasing retentate concentration endpoints and functionality.

As membranes are applied to more applications and consequently our collective knowledge of their functionality and applicability grows, the more likely it becomes that they will be further applied in new and innovative applications.

It is also reasonable to expect that operating pressures will continue to increase and that efficiencies in terms of cost and metallurgical outcome will improve as our knowledge and experience grows.

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