Potential Applications of Nanofiltration Membranes in Copper–Cobalt Processing

L. A. Thompson* and **A. J. Linington**

Aveng Extractive Technologies, Johannesburg, South Africa

* Corresponding author: les-lee.thompson@avenggroup.com

Copper–cobalt extraction is a reagent-intensive process resulting in acid consumption greatly contributing towards production costs, which in the current market conditions curtail profitability. Nanofiltration (NF) membranes have become an attractive approach in the mining and minerals industry for product concentration and reagent recovery based on the ability of the membrane to separate monovalent ions from divalent ions. NF membranes can selectively separate acids from metals and salts allowing acid to be recycled as well as the concentration and purification of product streams. Membrane technology in the field of copper–cobalt processing focusses on the concentration of Cu^{2+} and Co^{2+} in the pregnant leach solution, recovery of acid from waste streams to neutralization, recovery of valuable metals from waste ponds and process water recovery. This paper aims to provide insight into the potential applications of NF membranes in copper–cobalt processing circuits as well as a brief overview of the effects of process conditions on membrane performance and process development.

INTRODUCTION

The copper–cobalt industry commonly uses inorganic acids, such as sulfuric acid, in large quantities for primary leaching of copper–cobalt oxide ores and releaching during product purification (Stuurman et al., 2014). This results in numerous acidic intermediate streams containing high metal concentrations and acidic waste streams with low metal concentrations. Acid consumption typically accounts for 10–15% of the operating costs of mines in the Democratic Republic of Congo (DRC) and Zambia (Acid Plant Database, 2015). Due to remote mine locations, poorly maintained roads and cross-border conflict, the cost of sulphuric acid can range between USD 300 and 400 per ton. The pivotal role of acid in the copper–cobalt extraction process has driven many mines to build sulphuric acid plants on site to ensure a reliable acid supply, however elemental sulphur still needs to be imported which faces similar logistical challenges and contributes towards operating costs.

Filter presses and vacuum belt filters have been used for solid–liquid separation on slurry waste streams, such as the counter-current decantation (CCD) underflow, in order to recycle the liquid component, which contains high concentration of acid, back to the process. Nanofiltration (NF) aims to selectively recover acid from the liquid in order to prevent recycling impurities back to the process whilst also reducing the amount of acid in the bleed stream.

The application of NF membranes in the copper–cobalt industry has been slow to emerge due to the high level of technical competence and research and development required to design systems that suit the extreme process conditions of the metals industry (Bessarabov & Twardowski, 2002). The separation of monovalent acids from metals and contaminants allow for a number of unique separation processes with economic and environmental benefits (Mullett et al., 2014). The current market conditions call for a focus on reducing operating costs and increasing plant efficiency in order

Copper Cobalt Africa, incorporating the 8th Southern African Base Metals Conference
Livingstone, Zambia, 6–8 July 2015
Southern African Institute of Mining and Metallurgy   353

to remain profitable and competitive. Nanofiltration membranes especially add value in the recovery of valuable metals from waste streams and tailings ponds. The introduction of a NF system has the potential to reduce water consumption, recover reagents, reduce neutralization precipitation costs and increase production throughput. Membrane systems can also be used in conjunction with ion exchange to optimize recoveries of valuable metals.

Feasibility studies are in progress at various mines in the DRC Copperbelt region and this paper aims to provide insight into the evaluation of potentially viable streams for the implementation of nanofiltration membranes in the copper–cobalt processing circuit. Membrane system projections are presented based on various Cu^{2+} and Co^{2+} example applications and stream conditions. The process development of an industrial membrane system is described, from membrane screening bench tests to pilot and demonstration studies, based on previous work conducted by the authors for sulphuric acid recovery from a barren uranium stream containing 24 g/L H_2SO_4 with a total dissolved solids (TDS) of 48 600 mg/L at pH 1.2.

NANOFILTRATION SYSTEMS AND EQUATIONS

NF membranes can separate metals in acidic solutions by high pressure filtration through a membrane with a charged active surface. The principle of nanofiltration is known as diafiltration: the passage of monovalent molecules through the membrane, referred to as permeate, and the rejection of divalent and multivalent molecules, referred to as concentrate. The ideal separation of ions in a typical copper-cobalt process stream is shown in Figure 1.
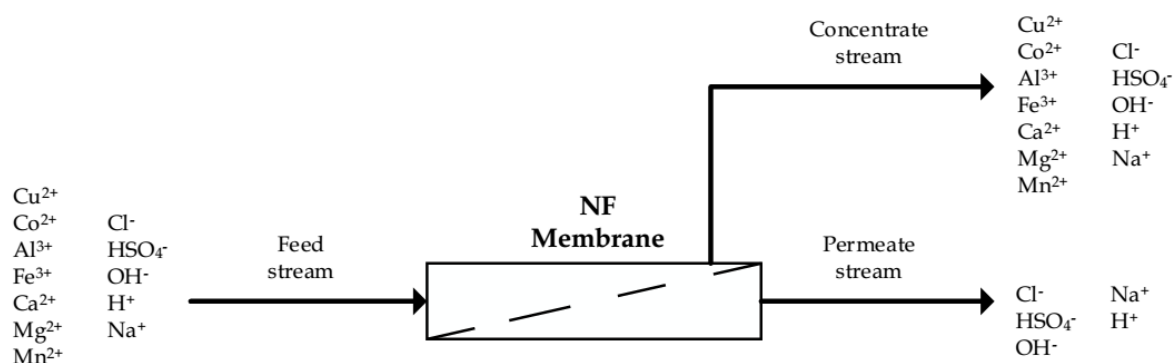

Figure 1. Ideal separation of ions across an NF membrane into Permeate and Concentrate streams.

The extent of divalent rejection is mostly determined by the membrane surface charge and pore sizes. Monovalent passage is not hindered by the membrane but is mostly affected by concentration polarization and surface charge. Monovalent ions pass freely into either the permeate or the concentrate stream, resulting in ion concentrations on both sides of the membrane being essentially the same (Schafer et al., 2005). It is this free passage of certain ions through the membrane that decreases the differential osmotic pressure, allowing NF membrane systems to operate at lower pressures compared to reverse osmosis (RO) systems used in water purification where both monovalent and divalent molecules are rejected (Dow Water & Process, 2014a).

Nanofiltration systems consist of pretreatment to remove suspended solids from the feed stream, NF membranes for separation and a clean-in-place (CIP) system to restore membrane flux when fouling occurs. Serious attention needs to be paid to pretreatment in the copper–cobalt processing circuit due to the nature of the solution. The high level of total suspended solids (TSS) needs to be reduced to avoid fouling and abrasion of the membrane material. Automatic self-cleaning filters followed by ultrafiltration have proved to be an effective prefiltration approach on clarified streams. Membrane flux (J) is the rate of diffusion of certain molecules in the solution through the active layer of the

membrane. Flux is determined by the permeate flow rate and active membrane surface area, as given in Equation 1 and normally expressed in units of LMH (L/m².h):

$$J = \frac{Q_P}{A_m} \qquad [1]$$

where Q_P is the permeate volumetric flow rate in L/h and A_m is the membrane surface area in m².

The observed rejection (Rej) of divalent molecules can be calculated for each component in the system using Equation 2 (Gherasim & Mikulášek, 2014):

$$Rej = 1 - \frac{C_P}{C_F} \times 100 \qquad [2]$$

where C_P is the ion concentration in the permeate and C_F is the ion concentration in the feed. Recovery is the ratio of permeate flow to feed flow given in Equation 3. This is an indication of the volume of the feed stream that can be recovered as permeate:

$$R = \frac{Q_P}{Q_F} \times 100 \qquad [3]$$

Membrane systems can operate at recoveries from 50 to 95 %, depending on feed concentrations. The recovery per membrane is normally fairly low therefore multiple membranes are placed in series inside pressure vessel and placed in parallel to increase the feed capacity. Each component is concentrated to a certain degree when the volume is reduced. The component concentration factor (X) is given by Equation 4:

$$X = \frac{C_C}{C_F} \qquad [4]$$

where C_C is the ion concentration in the concentrate stream.

NANOFILTRATION APPLICATIONS IN THE COPPER–COBALT RECOVERY PROCESS

The following streams have been considered as case examples based on highly favourable stream conditions for the application of NF membranes:
- Pregnant leach solution (PLS);
- Heap wash water;
- Waste pond water.

The membrane projection model was developed in-house and is used to project permeate and concentrate stream concentrations based on feed data. The model takes into account feed conditions, such as composition, TDS, temperature and speciation. Based on assumptions with respect to ion rejection and system recovery, the copper and cobalt concentrations in the respective streams can be projected, as given in Table I.

The PLS stream is characterized by a higher concentration of dissolved salts compared with wash and waste pond water and therefore operates at a lower system recovery to maintain good divalent rejection. Assumptions with respect to parameters for feasibility projections and modelling can be evaluated with bench tests.

Table I. Summary of system parameters used in membrane projection modelling as well as copper and cobalt concentrations obtained for the three case examples.

Description	PLS	Heap wash water	Waste pond water
System			
Feed TDS (mg/L)	100 000	20 000	8000
Temperature (°C)	25	25	25
System recovery (%)	60	80	85
Concentration factor	2.2	4.4	6.1
Components			
Copper			
Rejection (%)	80	85	90
Feed concentration (mg/L)	2100	200	34
Permeate concentration (mg/L)	420	30	3.4
Concentrate concentration (mg/L)	620	880	207
Cobalt			
Rejection (%)	80	85	90
Feed concentration (mg/L)	800	70	8
Permeate concentration (mg/L)	160	11	0.8
Concentrate concentration (mg/L)	1760	308	49

Concentration of the PLS Stream

The CCD overflow from the solid–liquid separation circuit presents as clarified PLS. The PLS forms the feed to solvent extraction (SX). Concentrations in the PLS are typically 1200–2600 mg/L for copper (Mueller et al., 1999) and 100–1800 mg/L for cobalt. The separation of monovalents, water and acid from the PLS concentrates the solution to achieve a higher metals concentration to the SX plant. Figure 2 shows the model projection of a PLS concentration system using NF membranes. Assuming a conservative rejection of 80 % for both copper and cobalt at a system recovery of 60 %, a concentration factor (X) of 2.2 can be achieved.
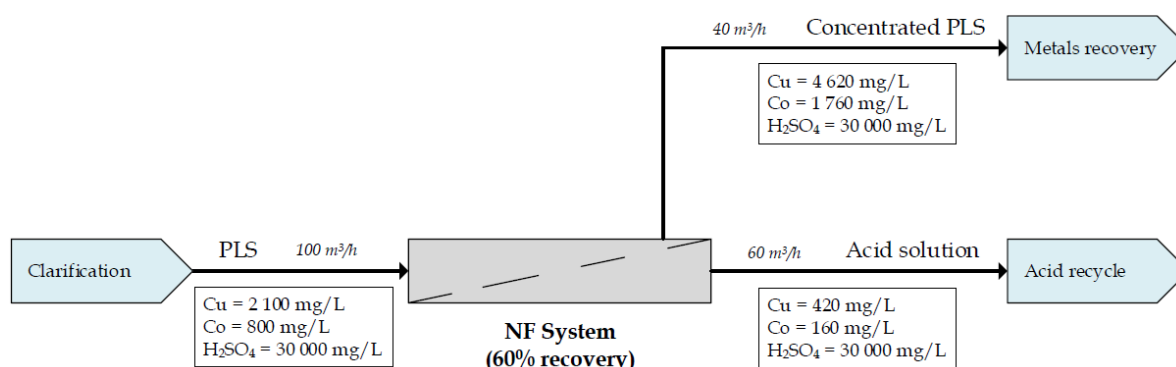

Figure 2. Projection of the concentration of metals from a clarified PLS stream by a nanofiltration membrane system (TDS = 100 000 mg/L, T = 25 °C).

This method can be applied to the PLS from tank and heap leaching. The concentration factor is a function of the membrane system recovery and membrane rejection, which is both limited by TDS in the feed and the saturation limits of scaling components in the solution. The di- and trivalent

contaminants present in the PLS, such as Fe^{3+}, Al^{3+} and Mn^{2+}, will also be concentrated, however due to the reduced volume of free acid, less lime will be require to increase the pH for precipitation. The system subsequently recovers 60% by mass of the free acid present in the feed.

The recovered acid solution which exits the membrane system as permeate can be recycled for use in the following areas:
- Process water in the crushing and grinding circuit;
- Process water in the flotation cells;
- Leach solution make-up;
- Electrolyte make-up;
- Mixed with the clarifier feed.

The acid stream contains low concentrations of metals that pass through the membrane in order to maintain electroneutrality across the membrane surface (Schafer et al., 2005). The benefit lies in the recovery and recycle of acid, reducing impurity precipitation chemical consumption and the reduced volume of the PLS to SX.

Heap Wash Water Recovery
The copper–cobalt extraction process utilizes sulphuric acid for leaching and releaching with most of the front-end process streams containing large amounts of free acid at low pH values. Heap leaching has proven effective for a multitude of complex and low-grade ores (Dhawan et al., 2013). Copper–cobalt ore is stacked and leached with sulphuric acid which percolates through the heap and liberates the metals into solution. The acid is recirculated through the heap in order to concentrate Cu^{2+} and Co^{2+} into the leach solution. Once the leaching cycle is completed, some of the PLS remains entrapped in the heap, resulting in losses of both leach solution and metals recovery. In order to recover some of the retained PLS, the heap goes through a wash cycle. Membranes can be used to recover the diluted metals from wash water, as shown in Figure 3. The diluted metals and acid solution is referred to as loaded wash water. Due to the lower concentration of components in the feed, a higher system recovery can be achieved projected between 60–85 %. The NF membrane also has better rejection of divalent ions at lower feed concentrations due to a lower electropotential difference across the membrane. The projection shown in Figure 3 assumes a rejection of 85 % for both Cu^{2+} and Co^{2+} with a system recovery of 80 %.
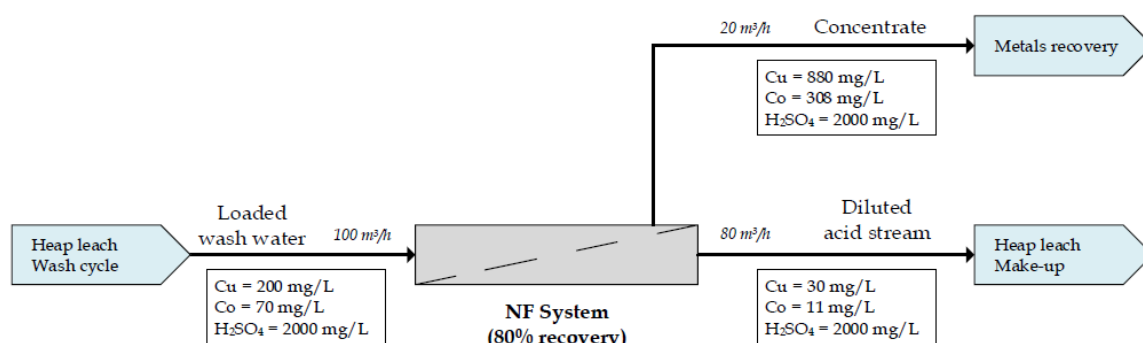

Figure 3. Recovery of low concentrations of copper and cobalt from heap leach wash water (TDS = 20 000 mg/L, T = 25 °C).

The diluted acid stream can be concentrated through the implementation of a RO membrane system which, contrary to NF membranes, rejects a high level of both monovalent and divalent salts. Typical RO membranes achieve rejections of 95–99 % of all components in the feed but operate at lower system recoveries. Depending on the acid concentration required, multiple stages can be placed in series in order to increase the concentration factor. RO systems operate at pressure of up to 80 bar to counteract the osmotic pressure of the feed components.

Figure 4Figure 4 shows the staged RO system treating diluted acid stream recovered through nanofiltration. The acid can be separated from water using RO membranes and reused in heap leach make-up. The limiting factor for acid concentration using RO membranes is the pH range for continuous operation of typically 2 to 11 (Dow Water & Process, 2015; GE Power & Water, 2014).
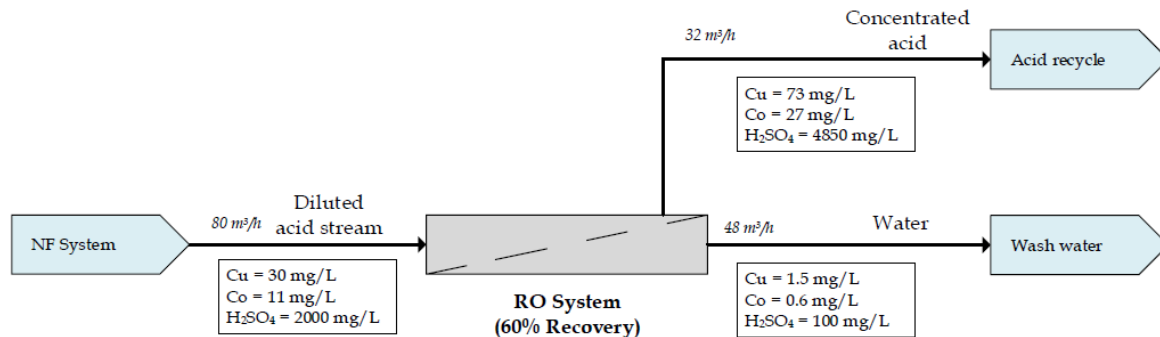

Figure 4. Acid concentration of a diluted stream containing low concentrations of metals (TDS = 12 000 mg/L, T = 25°C).

The recovered water can be reused as wash water and concentrated acid stream used in leach solution make-up. The benefit of this membrane system lies in the increased recovery of Cu^{2+} and Co^{2+} from the heap and the recycle and concentration of heap leach solution.

Metals Recovery from Waste Pond Water
Historic operational inefficiencies and inevitable process fluctuations account for the major contributors towards elevated metals concentrations in sludge and tailings ponds. Reprocessing waste ponds and streams has become an increasingly important focus area due to limited pond capacities and high costs associated with additional tailings dams. Recovery of low concentrations of copper and cobalt, as well as the purification of water for process use, can be achieved with a NF membrane system. Figure 5 shows the projection of a low metals concentration recovery application. The projection is based on a rejection of 90 % for both Cu^{2+} and Co^{2+} at the flow rates and concentrations as indicated in the figure.
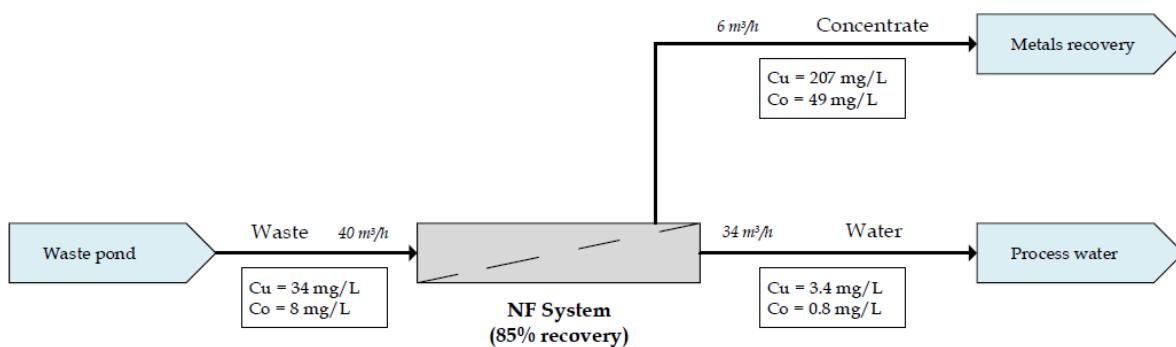

Figure 5. Projection of Cu^{2+} and Co^{2+} recovery at low concentrations from a waste stream (TDS = 8 000 mg/L, T = 25 °C).

A waste stream would be able to operate at higher recoveries (80–90 %) and lower pressures due to a lower level of TDS in the feed and the absence of high concentrations of metals that greatly contribute to the osmotic pressure. The NF system can also be integrated with ion exchange (IX) on the concentrate stream to further upgrade the metals concentrations. The IX system would be substantially smaller, by processing only 15 % of the volume, than if it were implemented on its own. Sulphuric acid is used to elute Cu^{2+} and Co^{2+} from the resin into an acidic solution. The additional IX

step would allow the NF concentrate stream to be upgraded to concentrations that can be integrated into the PLS stream.

EFFECTS OF PROCESS CONDITIONS ON MEMBRANE PERFORMANCE

The key performance parameters of a NF membrane system are permeate flux and divalent rejection. The flux and rejection of a membrane system are mainly influenced by temperature, pressure, system recovery and feed concentration (Dow Water & Process, 2014a). The speciation of feed components also plays a significant role in membrane system design and separation of ions across the membrane surface. The following graphs aim to provide insight into the tendencies and feed condition effects on system performance.

Temperature
Temperature affects not only the viscosity of the feed solution but also the thermal expansion of the membrane material, resulting in a change in pore sizes and ion rejection. Higher operating temperatures lower the viscosity of the feed solution as well as cause swelling of the membrane material, allowing fluid to pass through the membrane more freely and resulting in an increased flux.

The temperature effect is reduced at higher pressures where compression of the membrane causes less pore swelling and shrinkage, therefore less variation in flux. It would be beneficial to operate at a higher pressure on systems where feed temperature variations occur regularly. A qualitative representation of the temperature effect on flux is given in Figure 6.
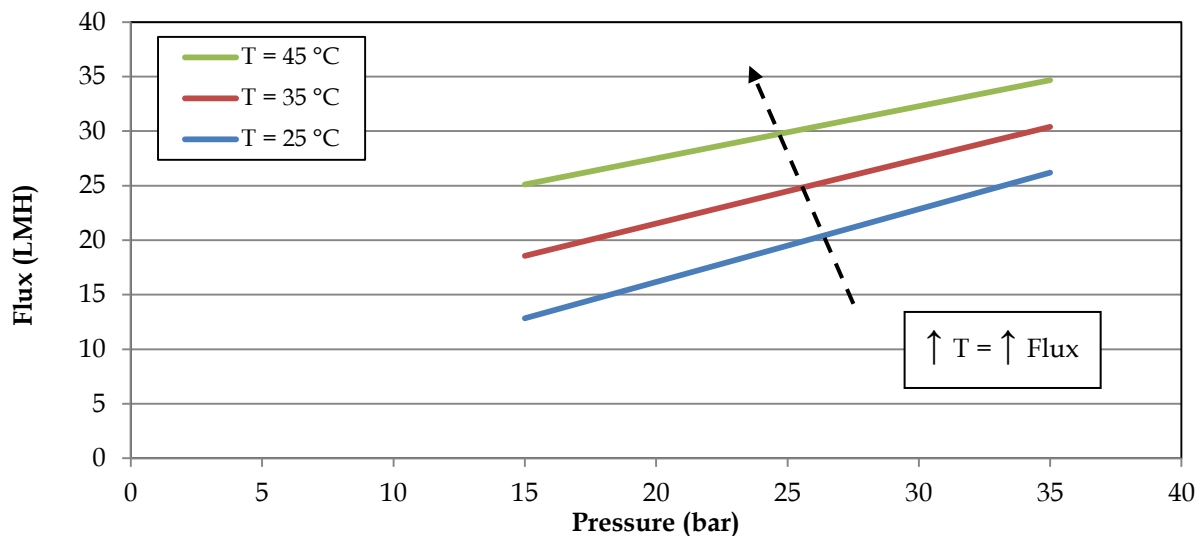

Figure 6. Projection of the temperature effect on flux over the pressure range of 15 to 35 bar (TDS = 50 000 mg/L).

The membrane rejection of ions is only slightly influenced by temperature due to the increased flux through the membrane. Monovalent counter-ions are transported through the membrane at a higher rate creating a charge difference across the membrane. In order to maintain electroneutrality co-ions need to pass through the membrane decreasing the rejection of divalents such as metals and sulphate (Schafer et al., 2005).

System Recovery
Membrane systems are designed with multiple stages in series in order to increase the overall recovery of permeate from the system. The concentrate from the first stage is the feed to the second stage and so forth. The recovery of each additional stage will decrease as feed concentration increases.

A schematic of a three- stage design with a 4:2:1 membrane array to achieve 70 % overall system recovery is shown in Figure 7.
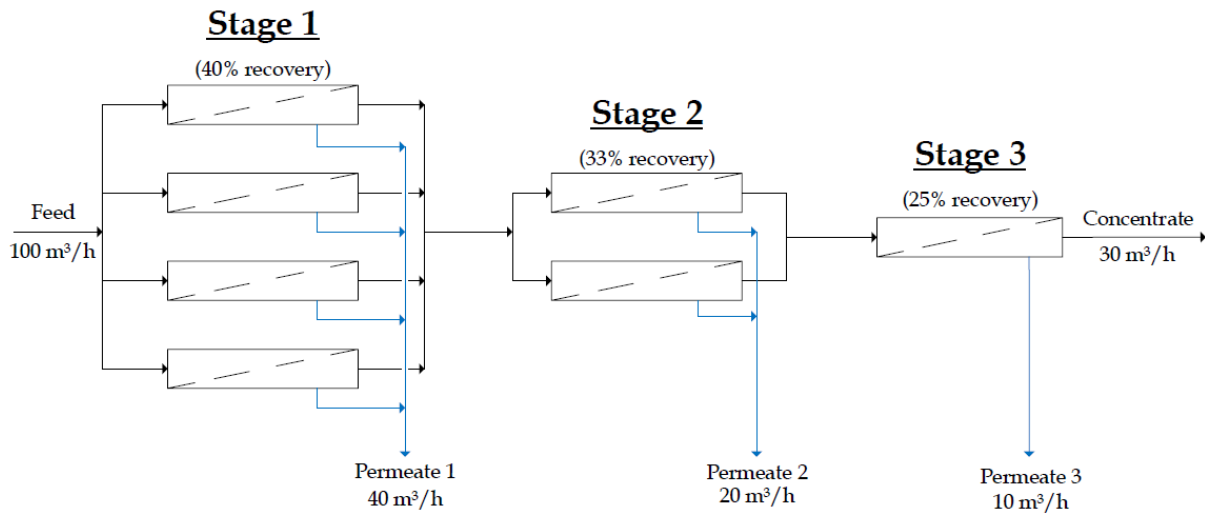.

Figure 7. Three-stage membrane system design for 70 % overall system recovery.

Systems are designed to only concentrate up to the solubility limit of components in the feed in order to prevent precipitation inside the pressure vessels and membrane surface. Feed solubility limits therefore dictate the number of stages and overall recovery that can be achieved. To achieve a high system recovery, multiple stages are employed with lower recoveries per stage. Typically two to three stages are employed for a 60–90 % system recovery (Dow Water & Process, 2014b).

Feed Concentration

High feed concentrations and TDS increase solution osmotic pressure, requiring a larger pressure driving force and faster flow rates to effectively transport monovalent ions through the surface concentration profile and the membrane (Sablani et al., 2001). Permeate flow rate will continue to decrease as feed TDS increases until the NF operating limit of 40 bar is reached and no more permeate flows through the membrane. Figure 8 shows the projection of different feed TDS on NF membrane flux at various pressures.
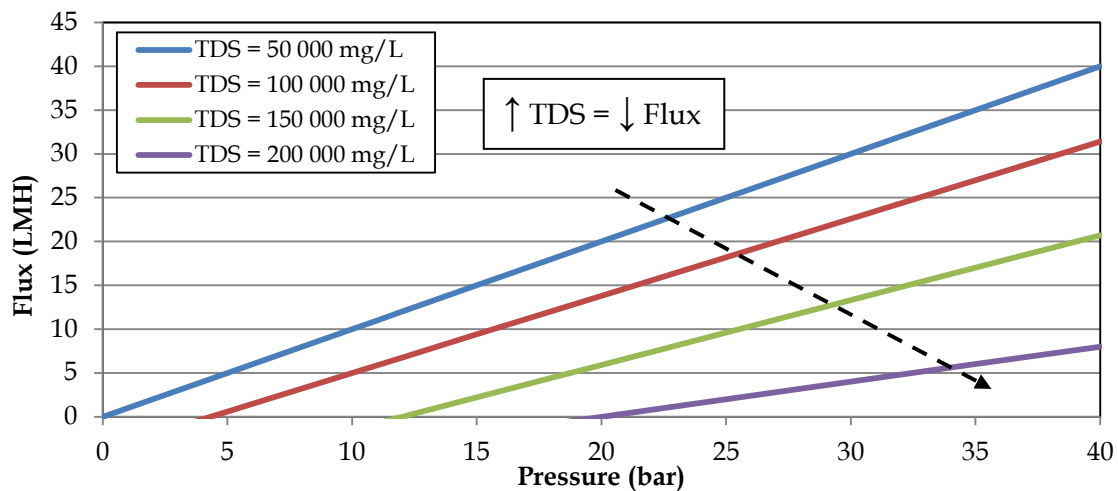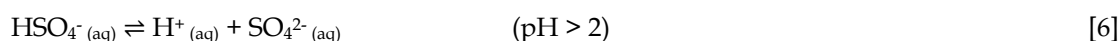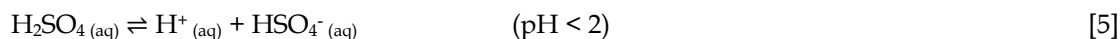

Figure 8. Comparison of flux at different pressures for various feed concentration values (T = 25 °C).

There is a larger decline in flux at high pressures (30 bar < P < 40 bar) compared with low pressures (10 bar < P < 20 bar) as the feed TDS increases. This is due to higher flux at higher pressures which readily forms a concentration barrier at the membrane surface and which hinders the full pressure driving force of ions through the membrane.

pH

The feed solution pH determines the distribution and presence of ionic species. Nanofiltration acid recovery is particularly effective on low pH acid leach solutions. Sulphuric acid dissociation is characterized by the following equilibrium reactions (Van der Merwe, 1998):

$$H_2SO_{4\,(aq)} \rightleftharpoons H^+_{\,(aq)} + HSO_4^-{}_{\,(aq)} \qquad\qquad (pH < 2) \qquad\qquad\qquad [5]$$

$$HSO_4^-{}_{\,(aq)} \rightleftharpoons H^+_{\,(aq)} + SO_4^{2-}{}_{\,(aq)} \qquad\qquad (pH > 2) \qquad\qquad\qquad [6]$$

Below pH 2, the formation of bisulfate (HSO_4^-) predominates, allowing for better recovery of sulphuric acid because the monovalent bisulfate ion will pass through the membrane. Most thin-film composite NF membranes are positively charged between pH 3 and 6 (Schaep & Vandecasteele, 2001). The positive charge readily attracts bisulfate ions (counter-ions) and more effectively rejects co-ions such as Cu^{2+}, Co^{2+}, Ca^{2+}, etc. The combination of both effects allows for higher divalent rejection with fewer co-ion contaminants presenting in the permeate.

PROCESS DEVELOPMENT

Industrial membrane systems are designed to fit the unique process conditions of each site. The complex nature of industrial streams demands sufficient test work in order to produce accurate membrane projection models, taking into account variations in temperature, pH, pressure, concentration and system multi-parameter interactions. A membrane system is developed through screening studies, pilot studies and demonstration plants, where required.

Bench Tests (Membrane Screening Studies)

NF membranes are preselected based on specifications such as acid-, base- or solvent stability and the typical rejection required dictates the molecular weight cut-off ranges (MWCO) ranges. An initial flat-sheet membrane screening study is performed on a batch sample to evaluate the flux, passage and rejection of potentially viable NF membranes. Bench-scale test work is executed on either dead-end or cross-flow filtration units at various temperature and pressure conditions to provide data for feasibility studies. Bench-scale results give a good indication of the minimum flux a membrane would produce over a range of operating conditions. Monovalent passage and divalent rejection provide mostly indicative results due to the large concentration profile that develops at the membrane surface in low flow test work. Bench-scale data are used to select an effective operating range, perform feasibility calculations and produce a more flexible design for a pilot plant processing larger flow rates.

Pilot Studies

Pilot studies are performed on the most suitable NF membranes selected from the membrane screening test work. Pilot testing is performed on spiral-wound 4-inch membranes which are representative of full-scale operation and performance. Typically, flux shows a substantial increase due to the cross-flow operation incorporated into pilot testing. The membrane feed spacer and higher cross flow velocity prevents a thick concentration barrier from building up at the membrane surface. Passage is expected to increase marginally and rejection will decrease due to the higher flow rate through the membrane.

On average, flux is expected to increase between 1.5 and 3 times from bench to pilot results, based on general experience. This is largely dictated by the membrane material, pore size, feed TDS and

temperature. The rejection of larger complex molecules, such as copper and cobalt, decreases slightly from bench to pilot. The bulk rejection of all components in the feed will also decrease slightly. This can be counteracted by using tighter membranes with smaller pore sizes. Pilot plants are sized to operate at a feed flow rate of 3–5 m^3/h. Pilot plants typically contain ultrafiltration (UF) pretreatment, and a simple Clean-in-Place (CIP) system in order to clean membranes and flush the system before and after runs. Membrane stages are determined by simulating multiple elements in series during pilot testing and evaluating the saturation limits of components in the concentrate from each stage.

Demonstration Studies

An additional demonstration study may be initiated to operate for an extended period of time and provide sufficient confidence for investment in a full-scale plant. Demonstration plants can process much larger flow rates and are often installed to tee off the main process line to evaluate the robustness of the membrane system under real feed conditions. The optimum arrangement of membranes in series and stages are often evaluated during the demonstration study. The lifetime of membranes can accurately be projected from long-term, continuous operation. Full-scale membrane system design is based on models developed and bench-marked against pilot and demonstration study data.

CONCLUSION

Nanofiltration membrane systems provide opportunities to concentrate product streams and recover acid in the copper–cobalt processing circuit. There are various process streams containing a high concentration of acid which operate at favourable conditions for NF membrane applications. Of these applications, the PLS, heap wash water and waste pond water are considered the most viable, based on expected feed concentrations and projections. Recycling acid to the process provides benefits not only from an economic point of view but also in terms of environmental factor,s such as discharge stream concentrations and reduced quantities of waste from neutralization. In order to validate the projection parameters used in these models, bench and pilot test work would need to be conducted.

REFERENCES

Acid Plant Database (2015) Sulphuric acid on the Web: Democratic Republic of Congo/Zambia. http://www.sulphuric-acid.com/sulphuric-acid-on-the-web/acid%20plants/Acid_Plant_ Index.html [18 Feb 2015].

Bessarabov, D. and Twardowski, Z. (2002). Industrial application of nanofiltration–new perspectives. *Membrane Technology*, (September), 6–9.

Dhawan, N., Safarzadeh, M.S., Miller J.D., Moats, M.S. and Rajamani, R.K. (2013). Crushed ore agglomeration and its control for heap leach operations. *Minerals Engineering*, 41, 53–70.

Dow Water & Process (2014a). Technical manual excerpt: Basics of RO and NF: Principle of Reverse Osmosis and Nanofiltration. Form 609-02003-1004.

Dow Water & Process (2014b). Technical manual excerpt: System design, Form 609-00071-1009.

Dow Water & Process (2015). Product information: FILMTEC SW30HR-380 High Rejection Seawater RO Element, Form 609-00390-1008.

GE Power & Wate. (2014). Fact Sheet: Industrial RO series. https://www.gewater.com /kcpguest/document-library.do [accessed 12 Feb. 2015].

Gherasim, C. and Mikulášek, P. (2014). Influence of operating variables on the removal of heavy metal ions from aqueous solutions by nanofiltration. *Desalination*, 343, 67–74.

Mueller, J.J., Green, D.H., Bernard, R., Liebezeit, V. and Lawrence, I. (1999). Engineered membrane separation systems for acid hydrometallurgical solution concentration, separation and treatment. *Proceedings of the 5th Annual ALTA Copper Forum*. ALTA Metallurgical Services, Melbourne, Australia.

Mullett, M., Fornarelli, R. and Ralph, D. (2014). Nanofiltration of mine water: impact of feed pH and membrane charge on resource recovery and water discharge. *Membranes*, 4, 163–180.

Sablani, S.S., Goosen, M.F.A., Al-Belushi, R. and Wilf, M. (2001). Concentration polarization in ultrafiltration and reverse osmosis: A critical review. *Desalination*, 141, 269–289.

Schaep, J. and Vandecasteele, C. (2001). Evaluating the charge of nanofiltration membranes. *Journal of Membrane Science*, 188, 129–136.

Schafer, A.I., Fane, A.G. and Waite, T.D. (2005). *Nanofiltration: Principles and Applications*, 1st Edn. Elsevier, Oxford.

Stuurman, S., Ndlovu, S. and Sibanda, V. (2014). Comparing the extent of the dissolution of copper-cobalt ores from the DRC region. *Journal of the Southern African Institute of Mining and Metallurgy*, 114, 343–353.

Van der Merwe, I.W. (1998). Application of nanofiltration in metal recovery. *Journal of South African Mining and Metallurgy*, 98 (Nov/Dec), 339–341.