

Membranes and minewater – waste or revenue stream

Stephen P. Chesters, Phil Morton, Max Fazel

*Genesys International Ltd, UK, 3A Aston Way, Middlewich, Cheshire, CW10 0HS, UK
Carsten.Drebenstedt@tu-freiberg.de*

Abstract

Membrane technologies are capable of treating mine waste waters to produce clean permeate water for reuse and a concentrate stream that can be used for valuable metals recovery. In this paper, the authors have researched and identified 363 mines with potential to use Reverse Osmosis (RO) Nanofiltration (NF) and Ultrafiltration (UF) membrane technology. There are sixty-seven operational membrane plants and fifty-one of these have been commissioned in the last ten years. 69% of these are in gold and copper mines. In precious metal mines, waste water can be concentrated using membrane plant so additional metals can be recovered from barren liquor. Acid mine drainage (AMD) is increasingly treated and then reused or sent off site as a valuable resource for domestic and agricultural use. The membrane plant can suffer from rapid fouling and calcium sulphate (gypsum) scale. The reasons for this are explored and new techniques for preventing sulphate scale and to clean fouled membranes are introduced.

Key words: reverse osmosis membranes; ultra-filtration, waste water; mining, acid mine drainage; metal recovery; membrane cleaning; antiscalants; calcium sulphate, gypsum

1. Introduction

The mining industry is the fourth largest user of water. To extract 1 ounce of gold 33,000 litres (8382 USgalls) of water is required and for 1 kg of copper 18,000 litres (4752 USgalls). GWI 2014 (1) Mining is often carried out in remote locations with scarce water supplies. Mining companies are increasingly conscious of the environmental impact of their activities and are investing significant amounts in water infrastructure and management systems to reuse water, improve metals recovery and treat effluents before discharge. Projections by Frost & Sullivan for 2014 anticipate an estimated US\$13.6 billion of expenditure in mining-related water infrastructure, almost doubling the 2011 global spend. Szyplinska 2014, stated that over 90% of mine water can be reused if treatment technologies such as reverse osmosis and microfiltration are applied. (2) The uptake of this technology has increased over recent years as improvements have been made in the operation and maintenance of membrane plants. The challenging feed waters cause rapid scaling and fouling. In this paper, the authors have identified 363 mines with potential to use RO/NF/UF membrane plants. Sixty-seven operational membrane plants in mines have been identified and referenced Fifty-one of these have been commissioned in the last ten years with 65% of the plants used in gold and copper mines. In precious metal mines, waste water can be concentrated using membrane plant so additional metal can be recovered from barren liquor. Acid mine drainage (AMD) is increasingly treated and then used as a supply to the mine for process and domestic use. The Anglo American Emalahleni project in S. Africa took the AMD water from three coal mines and converted into drinking water for 80,000 people in the surrounding communities. (3)

Membrane plant can suffer from rapid fouling and calcium sulphate (gypsum) scale. The reasons for this are explored and new techniques for preventing sulphate scale and to clean fouled membranes are introduced. Typical mine feed water quality is outside of the parameters of normal RO/NF/UF plant operation. A scaling prediction model has been developed and new sulphate antiscalants formulated that can cope with extremes of pH, soluble metals, and sulphate loading. Details of new methods for cleaning membranes including permeate backflush, use of effervescing reagents and microbubbles are described and explained. Subsequent papers will describe real case studies.

The drivers for recent rapid adoption of membrane plants are both economic and regulatory. The efficient operation of membrane plant can recover precious metal from the waste water and produce

clean water that can be used for the process. Further improvements in keeping membranes clean results in environ-mentally damaging waste waters being reused. The mining companies extract value from this through increased yields, reduced environmental risk and effluent charges, increased good will and water supply to the local communities. The areas where membrane plant can be used in copper and gold mines are described and two examples are used to illustrate the potential.

2. Membrane use in mining

There are many wastewater sources generated by mining which have high concentrations of total dissolved solids (TDS), mainly consisting of sulphate, metals, carbonate and calcium at acid and alkaline pH. Sulphate is produced by the oxidation of pyritic ores simplistically represented by the equation:



Calcium can also be present at elevated levels if lime is added to help neutralise acidic wastewaters. There are a whole host of other possible constituents due to the chemicals dosed in the metal extraction process for flotation, leaching, then cyanide destruction and further pH adjustment. Treating the affected water prior to disposal reduces the environmental toxicity of discharge and stored water. Membranes can remove suspended and dissolved solids producing a low volume concentrate stream typically 25% of the feed volume and a pure stream of water that can be used for process, and even drinking if correctly treated. The concentrate stream can contain enough precious metals to be classed as a pregnant liquor and be diverted to the leaching process for metal extraction. Membrane separation is used extensively around the world in industrial and municipal applications and has a consistent cost effective performance. Only recently has this technology been more commonly adopted in the mining industry.

2.1 Reverse Osmosis (RO), Nano-Filtration (NF), Ultra-Filtration (UF). Micro-Filtration (MF)

Reverse osmosis is a way to get clean water out of dirty water or salt water by forcing water under pressure through a semi-permeable membrane. RO removes all suspended solids and ca. 99% of soluble cations and anions while allowing water to pass through the membrane, as it is one of the smallest molecules with a molecular weight of 18. RO elements have ~100 amu (Dalton) molecular weight cut-off.

Nano-filtration is the same as RO except that the membrane pores are slightly larger so divalent ions are rejected but monovalent ions pass through the membrane. NF has 200-400 amu (Dalton) molecular weight cut-off.

Ultra-filtration (UF) technology uses a membrane barrier to exclude particles as small as 0.001 – 0.1 µm microns, including bacteria, viruses and colloids from fluids.

Micro-Filtration is a physical filtration process where a contaminated fluid is passed through a special pore-sized membrane of 0.1 – 10 µm to separate microorganisms and suspended particles from process liquid.

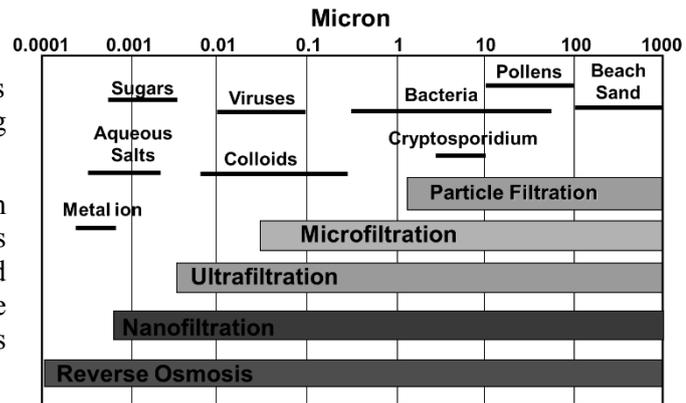


Figure 1 Filtration spectrum of membrane processes. Courtesy of DOW Water Solutions.

2.2 Mines with potential for membrane use

An extensive database of mining companies and their known mine locations was prepared and then researched for the applicability of membrane use. Sites with reference material for actual operational membrane plant were focused on and detailed data compiled. The geographical location of 363 possible or suitable mine sites for membrane plant were identified and positioned on the map as a black dot.

Confirmed membrane plant locations are represented by coloured balloons by geographical cluster areas in figure 2.

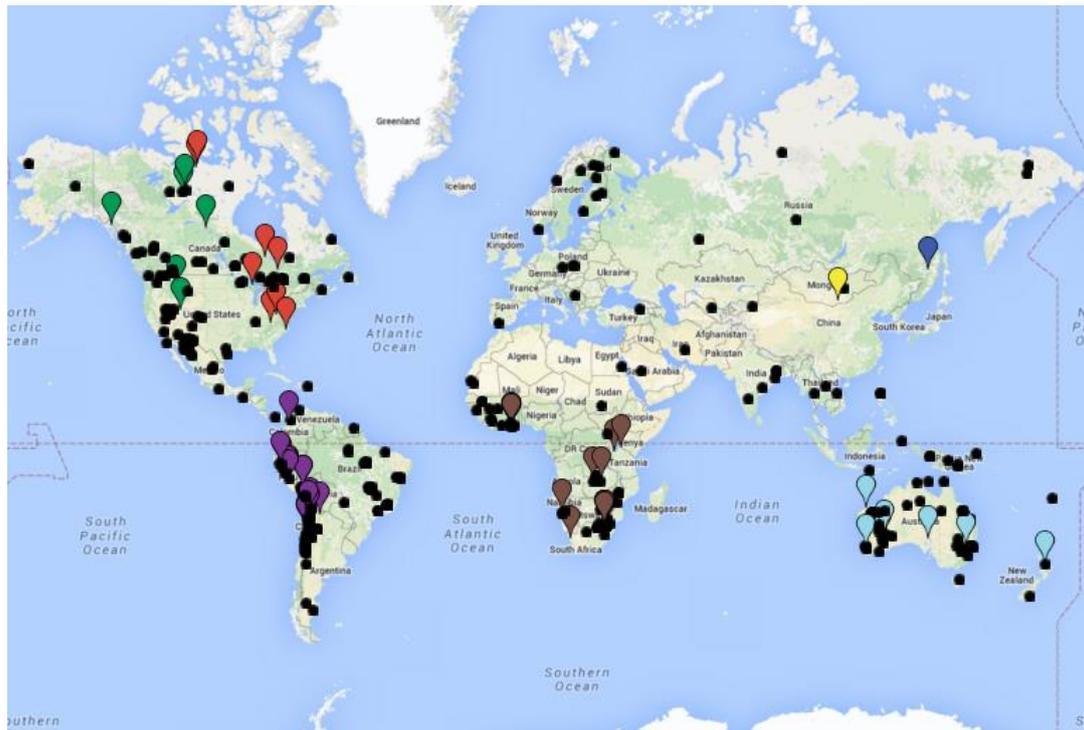


Figure 2 Mine locations and actual membrane plant

2.3 Mines with operational membrane plant

A total of 67 operational membrane plants were identified. Of these, Latin America had the most plants principally in Peru and Chile. The number of plants in Chile was boosted by the presence of 12 sea water RO units. These are required to produce source water that is pumped to the mines due to the lack of local ground water or surface water. Gold and copper account for 69% of the mines that have invested in RO plants. It is thought that many of the plants that are registered as present for acid mine drain (AMD) clean up may also be using the concentrate water for metal recovery. Only 15 plants were registered as being specifically designed for enhanced metal recovery. There is a lack of detailed description of plants design and operation as intellectual property and operating practices are protected.

Table 1. Membrane plants by geography, mine type and water use.

Location	No. of plant	Mines	No. of Plant	Water use	No. of Plant
North America	15	Gold	30	AMD Clean up	22
Latin America	25	Copper	16	SWRO	17
Europe	1	Coal	9	Metal Recovery	15
Australasia	7	Diamonds	3	Drinking	8
Asia	1	Iron	3	Leachate	5
Africa	18	Others	6		

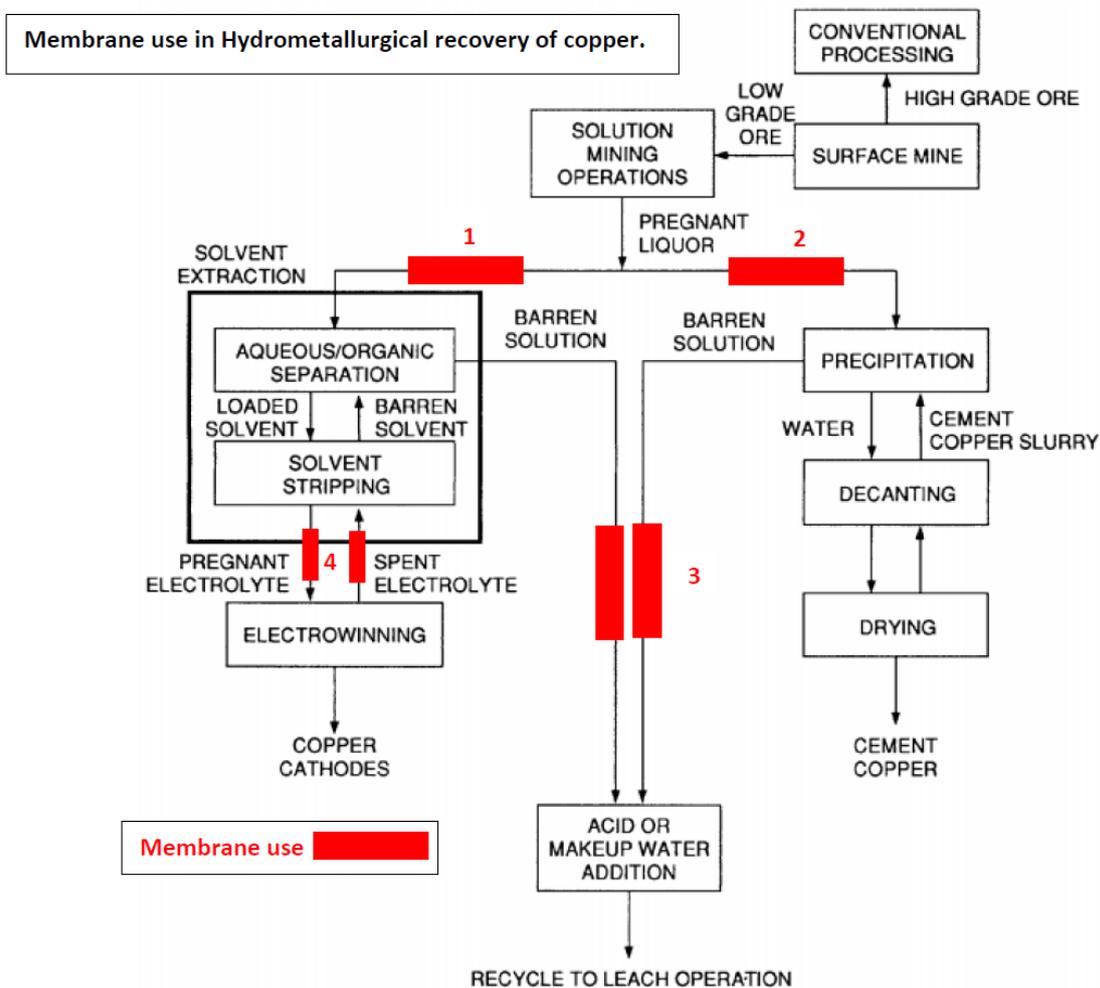
3. Enhanced Metal Recovery

Mining firms are now being forced to treat AMD wastewater in order to get licenses to mine. If the treatment can result in some metal recovery this can help negate the investment costs in treatment and even make a profit. Conventional AMD treatment and metal recovery involved adding lime or limestone to remove the acidity of wastewater, creating a hydroxide sludge and then attempting to extract individual metals. This required a substantial investment in infrastructure and had a high operational energy and chemical cost. The use of membranes allows waste water streams to be treated, fresh process

water to be recovered and reused, and in certain applications precious metals can be recovered. Figures 3 and 4 show areas in the copper processing cycle and the gold heap leaching operation where membranes have been applied. A case study outline of membrane applications in a copper and gold mine is given below.

3.1 Mexicana de Cananea Copper Mine

One of the earliest large scale examples of using reverse osmosis membranes to clean up wastewater and recover metals was the Mexicana de Cananea mine, located in northern Mexico. The mine was facing closure due to insufficient water and a threat of flooding of the operational parts of the mine. 17 Million cubic meters of wastewater had accumulated in the Cananea pit which had been used as a pregnant leach reservoir since the 1980's. After successful pilot plant tests the mine decided to install a full-scale membrane plant in 1997 which was used to: remove water from the pit, recover water from the tailings thickener, increase the copper concentration in the acid leach water feed from the Cananeapitto copper extraction plant, remove excess water from the leach circuits, and produce clean water for mine process water application. Harrison Western 1997 (4)



Adapted from Source: Technical Resource Department: Extraction and Beneficiation of Ores and Minerals, Volume 4 Copper, August 1994 U.S. EPA.

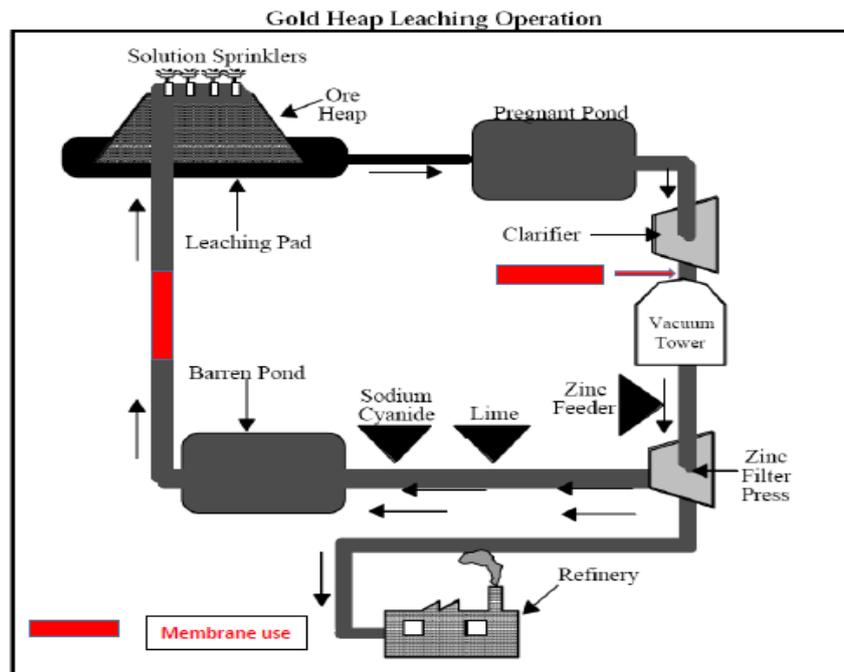
Figure 3. Membrane use in the copper processing cycle

The RO plant was designed to treat a feed water flow of 900m³/hr (4000 US gpm) operating at 50% recovery and producing a 2000 US gpm concentrate stream with 1.6g/L of copper and 2,000 US gpm of clean permeate water for reuse. The objectives were to increase the feed copper concentration to the

SX/EW plant. Solvent extraction and electrowinning (SX/EW) is a two-stage metallurgy process that first extracts and upgrades copper ions from low-grade leach solutions into a solvent containing a chemical that selectively reacts with and solubilizes the copper in the solvent. The copper is extracted from the solvent with strong aqueous acid, which then deposits pure copper onto cathodes using an electrolytic procedure (electrowinning). There was an increase in the cathode copper production by more than 14% creating savings of \$212K in process water cost and \$27K in sulphuric acid costs and reduce the pit water level. The overall water balance of the pit indicated that its level would continue to drop by about 3.5 meters per year, which is equal to approximately 1 billion gallons per year. The typical capital cost for the membrane plant according to Hanison Western (1997) was \$1.5- \$2.5 USD/USgall/day. \$8.5 to 14.5 million. The operating costs included; power consumption, prefiltration and pretreatment operations, antiscalant and cleaning chemicals, membrane cleaning, and membrane replacement. The typical operating costs were \$1.00 - \$2.00 USD/1000 gallons water recovered, giving a payback period of 1-3 years. The cost for a lime precipitation system accounting for the loss of copper would be approximately \$5.00 USD/1,000 US gallons of water recovered.

3.2 Yanacocha Peru Gold Mine

Minera Yanacocha (Yanacocha) is the largest gold producer in South America and its' mining and processing operations are located at elevations ranging from 3,500 to 4,100 meters in the Andes Mountains, 48 kilometers (30 miles) north of the city of Cajamarca. The gold is extracted by blending the ore with lime and placed on the heap leach pad. Dilute cyanide solution (ranging from 30 to 50 mg/L Free cyanide) is applied through drip and spray irrigation to the heap leach surface. There are seven reverse osmosis modules at Yanacocha (250 m³/h each one) and five excess water treatment plants (two in Carachugo and three in Yanacocha), two carbon plant precious metals recovery plants, and two Merrill Crowe processing plants. During the rainy season, there is a production of excess and increasingly dilute pregnant liquor. The reverse osmosis plants are used to dewater the pregnant liquor making the Merrill-Crowe gold extraction process more viable. Additional RO plants also remove excess cyanide and metals allow the permeate water to be discharged and additional gold recovered via a carbon column. Currently, 2,750 m³/hr of barren leach solution is treated and discharged safely into the environment.



Source: U.S. EPA, Office of Enforcement and Compliance Assurance.

Figure 4. Membrane use in Gold leaching operation

4. Membrane Scaling and inhibition

Scaling is the unwanted precipitation of sparingly soluble salts onto equipment surfaces during operation due to the solubility of a salt being exceeded. In an RO or NF plant feed water gets increasingly concentrated as it passes from one membrane to the next and is at its most concentrated just as it leaves the last membrane element in the pressure vessel known as reject or concentrate water. A plant is described as operating at a certain recovery rate. That is the proportion of permeate (product) water to concentrate (reject) Table 2 illustrates the ratio of recovery rate to cycles of concentration water. As recovery rates increase so do the cycles of concentration until solubility of certain salts are exceeded and precipitation is followed by crystal growth.

Table 2. Recovery & cycles

Recovery Rate	Cycles of Concentration
50%	2
75%	4
80%	5
90%	10

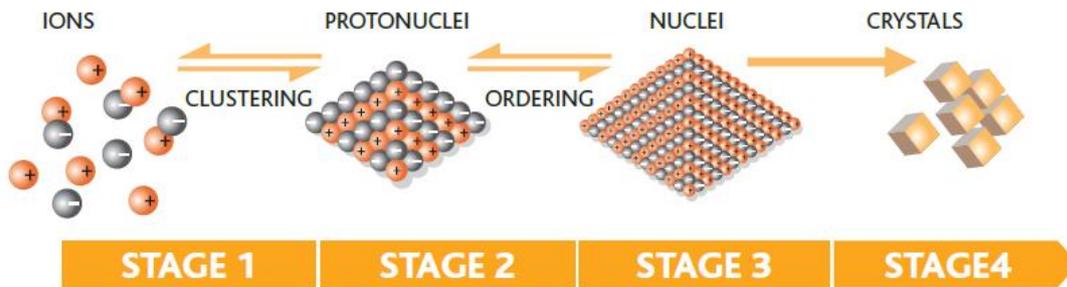


Figure 5. Scale forming process

Figure 5 shows how ions and cations are attracted to each other and start to form shapes when physically closer to each other when concentrated. Eventually these nuclei become more ordered until precipitation from a solution occurs and a solid is formed. Antiscalants inhibit this precipitation reaction by physically blocking the attraction at the nuclei and ordering stage and distortion of crystal growth. Scale formation in membrane systems is a well-known and documented problem. Its presence in the mining industry is particularly severe due to the chemically stressed waters that are used and the presence of soluble metals.

In a report on the NF treatment leach water at the Bingham Canyon mine Bayer (2004) stated that “The primary difficulty was gypsum (calcium sulphate) scaling in the pressure vessels and concentrate lines.” In the Kennecott design report for the Bingham Canyon water treatment plant RO system (KUCC 2002), it is reported that “gypsum saturation in the RO system is exceeded up to 700%, and silica saturation is exceeded as well.” (6) Other studies Harries, 1985 and Jarusutthirak 2007 have warned against fouling due to the precipitation of calcium sulphate and severe reduction in the permeate flux.

One of the earliest studies found which was published in 1970 clearly highlighted the problems of scale formation. The report was written by Donald G. Mason of Rex Chainbelt Inc. on behalf of the Pennsylvania Department of Mines and was titled “Treatment of Acid Mine Drainage by Reverse Osmosis”. Whilst advocating the process of reverse osmosis to clean up the water and produce good quality water fit to drink the report highlighted scaling and fouling issues stating that:

- Iron III in the presence of oxygen at a pH of 3.5 caused serious iron fouling of the membranes, which resulted in a rapid decrease in product water flow.
- Ten percent of modules failed after 813 hours of operation

- Module failures were always associated with chemical cleaning of the membranes using sodium hydrosulfite.

Mining water becomes acidic and laden with sulphate due to the oxidation of pyritic ores simplistically represented by the equation: $4 \text{FeS}_2 + 9 \text{O}_2 + 4 \text{H}_2\text{O} \rightarrow 8 \text{H}^+ + 4 (\text{SO}_4)^{2-} + 2 \text{Fe}(\text{OH})_3$. Calcium sulphate scale is particularly problematic as its formation is complex and it is particularly difficult to take back into solution and therefore clean from a membrane surface.

4.1 Calcium Sulphate Chemistry

There are three major forms of calcium sulphate, hemihydrate – $\text{CaSO}_4(\text{H}_2\text{O})_{0.5}$, dihydrate – $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and anhydrite – CaSO_4 . These have differing solubility isotherms as shown in figure 1. For RO waters the dihydrate form predominates. The solubility of calcium sulphate, in the dihydrate form ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ -gypsum) is similar to calcium carbonate, which decreases with increasing temperature although this is less marked than the other species. However whilst the precipitation of calcium carbonate scale can often be minimized by reducing the pH of the feed water, calcium sulphate solubility is independent of pH until you get to very acidic conditions pH1-2.

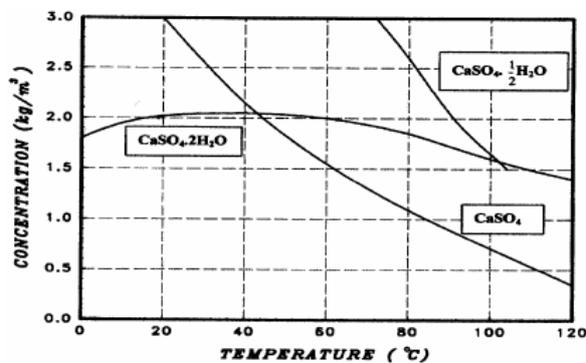


Figure 6: Solubility of forms of calcium sulphate

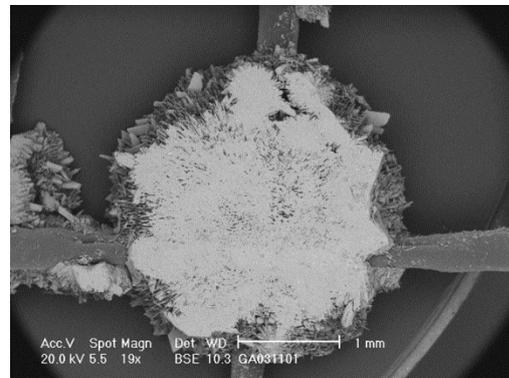


Figure 7: Rosette formation on spacer

It is reported in literature Gouellec et al [1] that gypsum scale forms via lateral growth of crystals directly on the membrane surface as well as the deposition of crystals onto the membrane surface. Studies in the Genesys laboratory in Madrid frequently shows crystal platelets forming in the low flow cross over points of the feed spacer – see fig. 2. This feature is further demonstrated when the spacer is removed from the membrane surface during autopsy and it becomes clear the scale is deposited within the spacer layer rather than at the underlying membrane surface. Studies by Rahardianto et al indicated a variation in scale formation due to varying surface topology of different membranes [2]. Scale formation occurs initially in needle form developing into platelets and rosettes. The scale is frequently damaging to membrane surfaces through particulate abrasion and is difficult to remove with chemicals. The development of calcium sulphate scale in the membrane can be further complicated by the potential for precipitation to occur before water concentration along the membrane surface. In these cases an amalgam of partially formed crystals can form. Ben Ahmed et al investigated the effects of different antiscalting compounds showing that phosphonate compounds inhibited the germination of scale crystals and polyacrylic compounds acted as dispersing and crystal distortion agents.(3)

4.2 Scale inhibition

Controlling scale build up is vital for the efficient operation of a membrane plant. This is done firstly by accurately predicting what scaling species are likely to exceed their saturation points and secondly applying physical or chemical treatments so the predicted saturation points can be extended safely. Reducing the recovery rate can stop the scale formation but means the plant does not operate as efficiently as it could. To determine the scaling potential, you need to compare the ion product I_{p} of the considered salt in the concentrate stream with the solubility product K_{sp} of that salt under conditions in the concentrate stream. (8) This requires an accurate feed water analysis including pH, conductivity and major cations and anions. The operating details of the plant such as flow rates, pressure, temperature and the recovery rate to give cycles of concentration are key to make accurate calculations. Over the last

30 years membrane manufacturers have developed design software that also includes scaling prediction software. The authors have developed their own software and adapted it for use specifically in mining applications.

4.2.1. Scaling Prediction Software

To run the programme data is input about the project, membrane manufacturer and model, water type, plant data and a water analysis for cations and anions. The software then automatically calculates the scaling indices for calcium carbonate, calcium, barium and strontium sulphate, calcium fluoride, calcium phosphate, iron, manganese, aluminium, silica and magnesium hydroxide. Variations in recovery rate, pH and temperature will result in an automatic recalculation of the % saturation point which is expressed graphically. By clicking on the treated button the most appropriate antiscalant and dose rate is chosen and the effect this has on reducing the %saturation of different scale species is expressed graphically. Changes in recovery rate, pH and temperature and water analysis will automatically result in changes in the antiscalant does rate. The untreated and treated situation can be compared. See figure 8

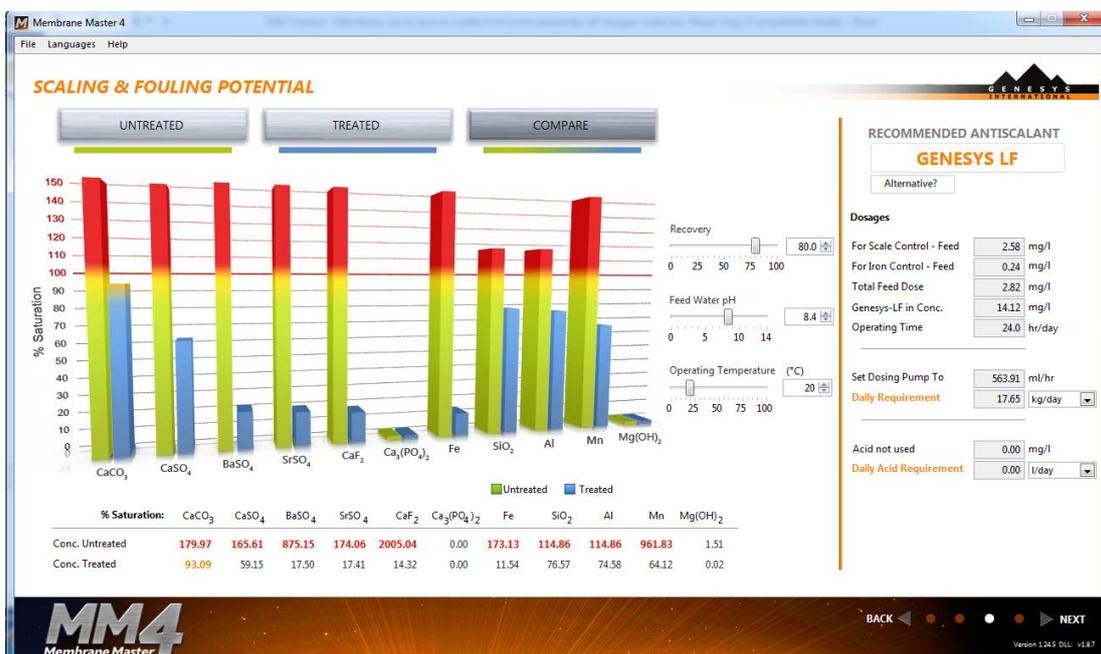


Figure 8. Genesys Membrane Master 4 scaling prediction software

4.2.2. Antiscalants

All antiscalants work at a sub-stoichiometric level by one or more closely inter-related mechanisms of threshold inhibition, crystal distortion and dispersion. Threshold inhibition – prevents the precipitation of salts once the salt has exceeded its solubility product. The chemical inhibitors retard or delay the clustering process of charged ions and protonuclei. The most effective threshold inhibitors are sodium salts of phosphonic acids, which have the added advantage of sequestering iron in a stoichiometric reaction. This is vital in membrane applications, as any soluble iron will cause rapid fouling. Crystal Distortion – chemicals affect the ordering and growth reactions of crystals causing an irregular shape and weak structure. Chemicals with effective crystal distortion properties tend to be polymers of low molecular weight 2,000-10,000. Many of these polymers show some threshold effectivity whilst others have dispersion properties. Importantly they are ineffective at preventing iron deposition and instead tend to react with iron to produce iron acrylate, which irreparably damages the membranes. Crystal Dispersion – occurs when the inhibitor chemisorbs onto the crystal surface and imparts an additional surface charge causing repulsion and ultimately dispersion. The growing crystal needs to be enveloped in a polymer of high Molecular Weight 20,000-40,000 to gain a significant surface charge. Few of the antiscalants on the market utilise polymers of a sufficiently high molecular weight to cause chemisorption on to crystal surfaces.

Formulation – Following an analysis of the chemistry, formation, dynamics and kinetics of the specific scaling species some potentially active ingredients are chosen to be combined into formulations and then tested against known standard performing antiscalants to see if an improved performance can be observed. When developing a calcium sulphate specific antiscalant the key attributes summarized in table 3 were studied.

Table 2. Properties of calcium sulphate scale

Species	Crystal form	Kinetics	Position	Seeding Agents
Calcium sulphate	Monoclinic prisms, needle & platelets	Slow	Last element	Colloidal calcium sulphate

Based on observations above certain assumptions regarding molecules that have differing properties can be made. Calcium sulphate is strongly crystalline developing through weak needle and platelet forms to highly stable rosettes particularly in low flow areas around the membrane feed spacer. Due to these features combinations of phosphonates and crystal distortion and dispersion agents were used to develop a formulation that was more effective than conventional antiscalants. Threshold testing – is conducted by making up standard beaker solutions of specific scaling species. The various formulations are then added at different dose rates and the solution agitated for different contact times at 25°C. The samples are filtered and the filtrate analysed for the presence of the scaling species. The % threshold inhibition can be determined as the percentage of scaling species that remained in solution. The initial results then allow further tests to be conducted with the most promising formulations. Differing operating pH, temperature and incubation times are used. Finally tests on the formulations against all common scaling species are carried out so the final formulation has a broad spectrum of activity whilst being very effective against a specific scalant. The results of threshold testing and product formulation resulted in: Genesys CAS – a calcium sulphate antiscalant blend of three different phosphonic and carboxylic acids.

5. Membrane fouling and cleaning

Fouling is the deposition on the membrane surface and feed spacer of suspended solids in the feed water. It happens in the lead elements of a membrane plant as soon as particles hit the membrane surfaces. The main sources of fouling are bacteria, clay, colloidal silica, organics and metal oxides and hydroxides. Pretreatment chemicals that are used to agglomerate suspended solids for removal by filtration media can also result in fouling of membrane surfaces. They include coagulants such as aluminum sulfate, ferric chloride and organic flocculants. Several methods or indices have been proposed to predict a colloidal fouling potential of feed waters, including turbidity, Silt Density Index (SDI) and Modified Fouling Index (MFI). The SDI is the most commonly used fouling index and acceptable levels are quoted by membrane manufacturers of 2-3. Analysis of the results of autopsies of lead membrane elements by the Genesys Membrane Products laboratory in Madrid showed that 35% had clay (aluminosilicates), 27% organic matter and 22% biofilm. These three foulants made up 84% of the deposits identified. Figure 9.

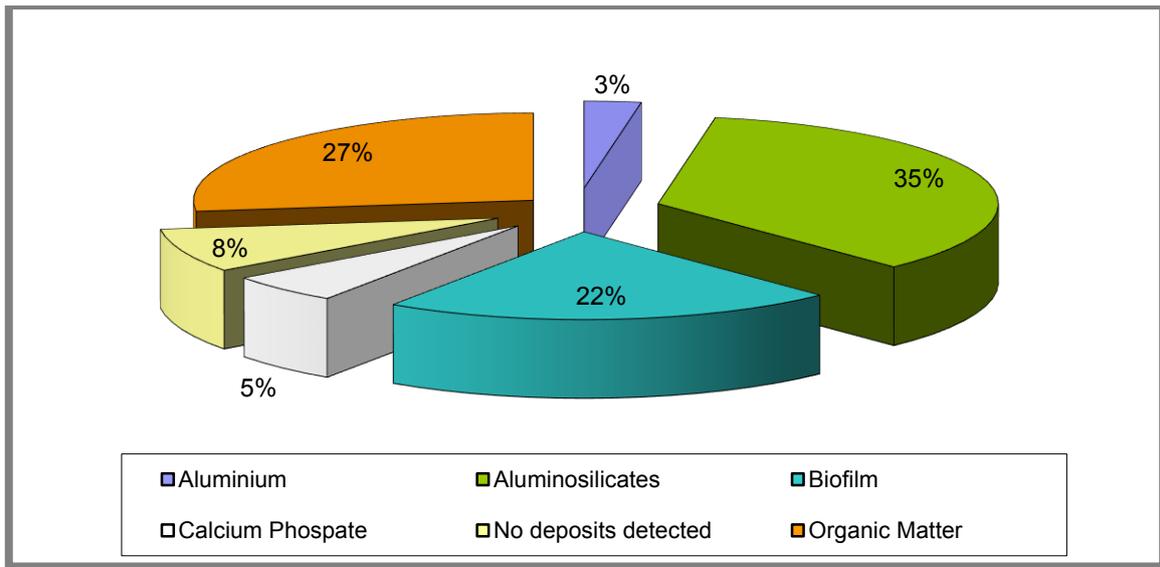


Figure 9. The main types of foulant identified on membrane elements from the first position during autopsy (2001-2014). Source: GMP laboratories statistics

Significantly clay, biofilm and organic fouling are notoriously difficult to remove from a membrane surface because they can become compressed into the membrane surface and pores causing plugging, and are impermeable making them resistant to chemical attack. The types of feed water in mining applications that membrane plants have to deal with contains all of these foulants combined with metals in suspension and solution. Frequently the pre-treatment systems are inadequate and the feed water variable which increases the fouling tendency in mining and is regularly reported in literature. A case study by Nieuwenhuis et al 2000 on a tubular and spiral wound RO plant use to treat AMD and ash water for boiler feed water commented on a successful operation but highlighted “The major issue that was reported with the standard cleaning in place (of the membrane plant) was that it was not completely effective in mitigating biofouling which resulted in the lower reported flux in the spiral wound RO plant” The targeted cleaning frequency was monthly but in reality each train was cleaned 2.5 times per month and the flux was only 20.1 L/m².h compared with a target of 25 L/m².h Cleaning was done with a mixture of commodity chemicals. The propensity for rapid fouling and scaling of membrane plants used in mining has lead the authors to look at more sophisticated methods for effective cleaning outlined below.

5.1. Membrane Autopsy and cleaning tests

An autopsy is a destructive test but gives invaluable information regarding the type of deposit on the membrane surface, the condition of the membrane, and how best to clean it. The excerpts below from membrane manufacturers, confirm that they agree that identification of the deposit on the membrane surface is key to optimum cleaning. “Each cleaning situation is different; therefore specific cleaning recommendations are dependent on the foulant” [2]. “The appropriate solution to use can be determined by chemical analysis of the fouling material. A detailed examination of the results of the analysis will provide additional clues as to the best method of cleaning” [4].

Different chemistries are required to remove different foulants and scalants. The preferred method of analysis is membrane autopsy which uses various scientific methods to accurately identify the individual types and amounts of foulants present. Different cleaning chemicals are tested against the membrane with characterization of flux and salt rejection (SR) used to establish the most efficient cleaning procedure. Autopsy of cartridge filters and SDI filter papers can identify likely deposits present on lead elements. A small sacrificial 2” element could also be installed to simulate operating conditions; an autopsy is performed after a suitable time to establish the fouling nature of the main system. Feed water analyses, scaling prediction software and normalized data can all be used to help give clues to the foulant.

5.2. Cleaning Chemistry

Basic cleaning chemistries are described in table 4 below and are referenced by membrane manufacturers in their cleaning guides. The selection of the appropriate cleaning chemicals has a major effect on the success and, most importantly, frequency of the CIP procedure.

Table 4. Traditional cleaning chemistry

Type	Action	Typical Chemical
Acid	Solubilisation	Hydrochloric, nitric, sulphamic, citric
Non Oxidising Biocide	Biocidal	DBNPA, Isothiazolin
Caustic	Hydrolysis, Solubilisation	NaOH,
Chelant	Chelation	EDTA
Detergent	Emulsifying, dispersion, surface conditioning	STPP
Oxidant	Oxidation, disinfectant	Hypochlorite, ozone, hydrogen peroxide
Surfactant	Emulsifying, dispersion, surface conditioning	SDS

Many different chemical formulations are commercially available. The choice of which to use is often made on cost/kg of the individual product, although in reality, the cost of any effective product in terms of operational costs of a fouled system is extremely low, and pay-back will be quickly achieved. When selecting a suitable chemical it is therefore of greater importance to consider different evaluation criteria; application rates, performance of the individual products against your specific foulants (availability of documented scientific evidence) and onsite technical support. Overall evaluation of the success of a cleaning chemical should be performed over a longer period to give an indication of the change in required cleaning frequency of the RO system. Experience shows that employing a successful cleaning regime can reduce required cleaning frequency by several times per annum. Many researchers have shown that the use of speciality formulated cleaners combining different chemistries incorporating detergents, chelants and surfactants have an enhanced cleaning effect on membranes when compared to the use of commodity acids and alkalis.[1] Commodities also tend to have transition metal impurities which can damage the membranes and leave them prone to subsequent catalysed oxidation reactions.

5.3 Chemical Application

Foulant identification and chemical selection are vital. Since all cleaning situations and RO systems are different, it is not possible to produce a generic cleaning procedure for all membrane plants. All of the factors below must also be considered when designing a suitable cleaning procedure:

- Temperature is vital for removal of organic foulants, generally 35-40°C is acceptable. For removing inorganic scales, temperature of the CIP water may affect solubility and therefore removal. Lower temperatures are generally required.
- Contact time is also vital; in a highly fouled system, cleaning cycle times should be maximized to ensure efficient removal. Speciality chemicals will reduce the time required for cleaning. Sufficient time for optimum cleaning must be allowed, with additional cycles added if necessary, by emptying and refilling with the same chemical.
- pH is important for removal of both MAIN groups – organic based foulants and scales. Monitoring pH changes during the CIP will help to evaluate success.
- RO permeate should be used to prepare CIP solutions and to flush the system between application of different chemicals.
- Pressures and flow rates can be altered in line with membrane manufacturers' guidelines to help remove foulants physically.
- The system should be thoroughly flushed after the CIP procedure to ensure traces of CIP chemicals are removed before returning to service.

5.4 Innovations in membrane cleaning

The use of products formulated with multiple cleaning mechanisms offers enhanced cleaning performance. Conducting an effective clean rather than multiple partial cleans is a gentler and more efficient process to help extend membrane lifespan and reduce operational costs. The authors have completed a 6 year research programme into new cleaners and methods and have published that work. The main innovations are:

5.4.1 High ionic strength osmotic flush

The use of powder high ionic strength cleaners during an off-line clean causes normal osmosis to occur during periods of soaking; permeate water passes through the membrane surface to the feed side breaking up layered deposits. This allows the cleaning chemicals improved penetration to dislodge deposits. These powdered products have proven particularly effective against clay, biofilm and organic removal which make up 85% of the foulants in lead elements.

5.4.2 Effervescing reagents

Incorporating effervescent reagents into the cleaning chemical formulations produces chemical microbubbles that abrade, agitate and dislodge deposits at the membrane surface and in and around the feed spacer, which assists in deposit removal.

5.4.3 Air induced microbubbles

Combining air with the correct cleaning chemical formulation causes a 10 mm air bubble to dissipate into thousands of microbubbles 5-50 microns in size. The microbubbles help physically dislodge deposits without damaging the delicate polyamide salt rejecting layer on the membrane. Smaller plants can easily and cheaply fit a microbubble Genairator™ device to the cleaning circuit which inducts air and creates microbubbles. If a pump forces a fluid flowing into the microbubble generator tube an increase in velocity occurs in the constricted part simultaneously with the decrease in pressure which leads to air being sucked in through the tube. Pressure recovery takes place further downstream and the air bubbles drawn in collapse forming bubbles which then have a tendency to coalesce into larger bubbles around the microbubble generator. In order to optimize cleaning it is preferable to have micro and macro bubbles. This can be achieved using specially formulated cleaning agents which minimize the coalescing of micro, mini and midi bubbles into larger bubbles. The cleaning reagents create a suspension of bubbles and cleaning solution which distribute evenly over the membrane surface in a pulsed fashion. Larger plant can use compressed air which reacts with the cleaning chemistry formulation to create microbubbles.

6. Conclusions

The benefits of using reverse osmosis membranes to clean up waste water streams for discharge have been known about since the 1970's. The first plant to recover metals using reverse osmosis membranes started operating in the 1990's. There has however been a slow adoption of the technology due to capital cost, operational cost, lack of published reference material and a shroud of secrecy. Due to the huge increase in production of membrane elements worldwide the real cost has reduced over the last ten years. Plant designs have become more reliable and 76% of the 67 operational membrane plant have come on line in the last 5 years. Specific mining companies Barrick and Newmont have favoured this technology and repeated successes around the world.

The authors have presented statistics and case study examples of where membranes can be used in mining. The ongoing problems of fouling and scaling still exist as the waters entering the membrane plant have a large amount of complex suspended and dissolved solids. New developments and tools to minimize the problems of scale formation, cleaning and fouling have been presented. These include:

- Scaling prediction software to identify likely scaling species and antiscalants to inhibit the scale
- High performance calcium sulphate, calcium carbonate and silica antiscalants
- Use of membrane autopsy to identify deposits and effective cleaning protocols and products

- Range of pre-formulated cleaning chemistries proven to remove different deposits
- Production of the correct cleaning protocols for individual plant
- High ionic strength cleaners to induce an osmotic flush of permeate water during the soaking stage of cleaning
- Effervescent reagents incorporated in cleaning compounds
- Microbubble generation in the cleaning solution to increase effectiveness of cleaning chemistry

The authors have embarked on a major project to develop mining specific chemical products for the unique challenges that membranes in the mining industry face and will publish subsequent findings in the future.

References

Szyplinska (2012), Thirsty world of mining: Harvesting new water solutions, op. cit.

Harrison Western Process Technologies (1997), Membrane Plant for preconcentration of PLS, Arizona Conference of AIME, Hydrometallurgical Division, Spring 1997, Cananea, Sonora, Mexico May 1997