

**Application of Membrane
Separation Technology to
Mitigation of Mine Effluent and
Acidic Drainage**

MEND Report 3.15.1

**This work was done on behalf of MEND and sponsored by:
The Mining Association of Canada, MEND and
CANMET Mining and Mineral Sciences Laboratories**

October 2008

**Application of Membrane Separation Technology to
Mitigation of Mine Effluent and Acidic Drainage**

By:

Saviz Mortazavi

Work performed for:

Mine Environment Neutral Drainage (MEND) Program



Natural Resources
Canada

Ressources naturelles
Canada

Canada

EXECUTIVE SUMMARY

With increasingly more stringent environmental regulations, growing concern with water quality and management and a greater focus on water recycling and minimization of water use in the mining industry, conventional treatment methods are being challenged to meet lower concentrations of contaminants in the discharge stream. Economics and costs are important factors in technology selection and have a significant weight in the selection of treatment options, unless other factors such as regulatory requirements are the drivers. In the past decade, membrane separation processes have attracted significant attention and are applied in different sectors of the industry especially in water and wastewater treatment

The applicability of different membrane separation processes for the mitigation of acidic drainage has been demonstrated in the literature. Work by various researchers has demonstrated the successful application of Reverse Osmosis (RO), Nanofiltration (NF) and charged Ultrafiltration (UF) membranes for the treatment of acidic drainage and the removal of contaminants and metal species of interest, such as selenium, from neutral drainage streams.

Membrane separation processes, such as reverse osmosis, can generate a highly concentrated retentate. This could create problems with the precipitation of different metal species and could cause scaling and fouling problems; however, these issues can be managed with the proper mode of operation, the use of additives, the implementation of cleaning cycles and module design. The membrane concentrate, in industrial applications, is usually a highly saline stream that requires treatment before disposal. However, this stream could also have a cost benefit by allowing for the economic recovery of metals or other products of interest and improve efficiency of chemical treatment due to increases in the concentration of contaminants. With proper process design and material selection, high water recoveries are possible with the added benefits of waste minimization and volume reduction.

Commercially available hybrid membrane systems that apply combinations of Microfiltration (MF) or Ultrafiltration with Reverse Osmosis or Nanofiltration are reviewed in this report. This report also addresses other membrane options such as the use of charged UF membranes or other

innovative approaches such as the VSEP (Vibratory Shear Enhanced Process) filtration process for acidic drainage (AD) treatment. Although the main focus of the present report was to assess membrane separation technology to AD treatment, the application of membrane separation to other mining applications was also reviewed.

Finally, a number of case studies on the application of membrane separation in mining operations are presented, with an emphasis on the cost impacts and improvements on the environmental performance.

The information in this review shows that membrane separation is an efficient and cost-effective technology for mine water and wastewater treatment and mitigation applications. A comparison with conventional treatment technologies has also shown that membrane separation, if properly designed and operated, can provide superior treatment results and can have lower capital and operating costs. Membranes cannot completely replace conventional treatment technologies and be a stand-alone treatment option. They can be a powerful tool for volume reduction and waste minimization, allowing for the recovery and recycling of water and other potentially valuable by-products such as acid, gypsum (calcium sulphate), heavy metals and sulphur. Because of the volume reduction that membrane separation offers, the footprint and capital costs of the accompanying conventional treatment options such as clarifiers and other chemical treatments could be substantially reduced.

Due to the composition of mining streams and effluents, the most important aspects of membrane separation are membrane fouling and brine disposal. As a result, the main technology development drivers are:

- Membrane fouling – lowering membrane replacement costs, maximizing recoveries;
- Pretreatment as a means of fouling control;
- Maximizing water recoveries; and
- Brine disposal or treatment and the minimization of its associated costs.

SOMMAIRE

Avec des réglementations environnementales de plus en plus strictes, une préoccupation grandissante quant à la qualité et à la gestion de l'eau, une focalisation plus importante sur le recyclage de l'eau et une minimisation de son utilisation dans l'industrie minière, les méthodes de traitement traditionnelles sont remises en question pour arriver à obtenir des concentrations de contaminants plus faibles dans les eaux de déversement. Les facteurs économiques et les coûts sont primordiaux pour sélectionner une technologie et ils pèsent lourdement dans le choix des traitements, sauf si ce choix est déterminé par d'autres facteurs comme des exigences réglementaires. Dans les dix dernières années, des procédés de séparation membranaire ont suscité beaucoup d'intérêts et sont appliqués dans différents secteurs industriels, en particulier dans le traitement de l'eau et des eaux usées

Dans la littérature, on a démontré qu'il était possible d'appliquer différents procédés de séparation membranaire pour atténuer l'acidité des eaux de drainage. Les travaux menés par divers chercheurs ont démontré qu'on peut utiliser avec succès des applications comme l'osmose inverse (OI), la nanofiltration (NF) et les membranes d'ultrafiltration (UF) chargées pour le traitement des eaux de drainage acides ainsi que pour l'élimination de contaminants et d'espèces métalliques intéressantes comme le sélénium dans le drainage neutres.

Les procédés de séparation membranaire, telle que l'osmose inverse, peuvent générer un rétentat très concentré. Le colmatage et l'encrassement sont des problèmes qui pourraient être causés par la précipitation de différentes espèces métalliques. Mais on peut gérer ces problèmes avec un mode de fonctionnement adéquat, l'utilisation d'additifs, l'implémentation de cycles de nettoyage et une conception appropriée du module. Dans les applications industrielles, le concentré est habituellement un fluide extrêmement salin qui doit être traité avant d'être éliminé. On pourrait en retirer certains avantages économiques par la récupération de métaux ou d'autres produits intéressants et on pourrait augmenter la concentration des contaminants en améliorant l'efficacité du traitement. Grâce à une conception adéquate du procédé et un bon choix de matériaux, il est possible de récupérer beaucoup d'eau et d'en retirer certains bénéfiques comme une minimisation des déchets et une réduction du volume.

Dans le présent rapport, on examine les systèmes membranaires hybrides disponibles dans le commerce, soit la microfiltration (MF) ou l'ultrafiltration en combinaison avec l'osmose inverse ou la nanofiltration. Pour le traitement des eaux de drainage acides, le rapport aborde aussi d'autres systèmes membranaires comme l'utilisation de membranes UF chargées ou d'autres plus nouveaux comme le procédé de filtration par l'application d'intenses ondes vibratoires au niveau de la surface membranaire ou système VSEP (Vibratory Shear Enhanced Process). Bien que le thème principal du présent rapport était d'évaluer la technologie de séparation membranaire appliquée au traitement des eaux de drainage acides, on a aussi étudié l'utilisation de cette technologie dans d'autres applications minières.

Enfin, on présente aussi un certain nombre d'études de cas concernant l'application de la séparation membranaire dans des opérations minières, l'accent étant mis sur les incidences financières et les améliorations en matière de rendement environnemental.

Les renseignements contenus dans la présente étude montrent que la séparation membranaire est une technologie efficace et rentable pour le traitement des eaux minières et des eaux usées ainsi que pour des applications d'atténuation. Une comparaison avec des technologies de traitement conventionnelles a aussi montré que si la séparation membranaire est bien conçue et bien exploitée, elle peut fournir de meilleurs résultats à moindre coût en capital et en fonctionnement. Le système membranaire ne peut pas remplacer complètement les technologies de traitement conventionnelles et être un traitement totalement indépendant. Il peut être un outil puissant pour réduire et minimiser la quantité de déchets, en permettant le recyclage de l'eau et la récupération d'autres sous-produits de valeur possibles comme les acides, le gypse (sulfate de calcium), les métaux lourds et le soufre. Grâce à la réduction de volume réalisée avec la séparation membranaire, on peut réduire fortement l'empreinte environnementale et le coût en capital des traitements conventionnels qui l'accompagnent comme les clarificateurs et autres traitements chimiques.

L'encrassement de la membrane et l'élimination de la saumure constituent les deux aspects les plus importants de la technologie de séparation membranaire à cause de la composition des eaux

de procédés et des effluents miniers. En conséquence, les principales priorités de développement de la technologie sont les suivantes :

- L'encrassement de la membrane : diminuer les coûts de remplacement de la membrane, maximiser la récupération;
- Le prétraitement comme moyen de contrôle de l'encrassement;
- La maximisation de la récupération d'eau;
- L'élimination ou le traitement de la saumure et la minimisation des coûts connexes.

ACKNOWLEDGEMENTS

This report has been prepared for the MEND program with partial funding received from The Mining Association of Canada.

Many Thanks are due to the following for their review of this report and their valuable comments:

- David Koren, CANMET-MMSL,
- Gilles Tremblay, MEND Secretariat, CANMET-MMSL,
- Charlene Hogan, MEND Secretariat, CANMET-MMSL,
- Brett Moldovan, Cameco Corporation,
- Chuck Edwards, Cameco Corporation,
- Denis Kemp, Denis Kemp Consulting,
- Wade Stogran, North America Tungsten Corp. Ltd.,
- Charles Bucknam, Newmont Metallurgical Services,
- David Chambers, Centre for Science in Public Participation and
- Ritva Muhlbauer, BHP Billiton, South Africa

DISCLAIMER

CANMET-MMSL makes no representation or warranty respecting the results arising from the Work, either expressly or implied by law or otherwise, including but not limited to implied warranties or conditions of merchantability or fitness for a particular purpose.

CANMET-MMSL shall, due to the nature of this report, not keep confidential and may disclose to third parties the information contained in or regarding this report as well as publish the content of this report in scientific journals or have the content of this report presented at relevant mining conferences.

TABLE OF CONTENTS

EXECUTIVE SUMMARY	I
SOMMAIRE.....	III
ACKNOWLEDGEMENTS.....	VI
DISCLAIMER	VI
TABLE OF CONTENTS.....	VII
LIST OF TABLES	IX
LIST OF FIGURES	XI
LIST OF ABBREVIATIONS	XII
1. INTRODUCTION.....	1
2. ACIDIC AND NEUTRAL DRAINAGE.....	3
3. MEMBRANE BASED WATER AND WASTEWATER TREATMENT TECHNOLOGIES.....	4
3.1. MEMBRANE PROCESSES	4
3.1.1. <i>Pressure driven membrane processes</i>	5
3.1.2. <i>Other membrane separation processes</i>	7
3.1.3. <i>Membrane filtration system selection and design</i>	8
3.1.4. <i>Mass transport and fouling control</i>	17
3.1.5. <i>Methods of fouling control</i>	24
3.1.6. <i>Membrane filtration applications</i>	25
3.1.6.1. Solid-liquid separation.....	25
3.1.6.2. Inorganic contaminants	26
3.1.7. <i>Hybrid membrane processes</i>	26
3.1.8. <i>Process conditions for membrane separation</i>	27
3.1.9. <i>Limitations of membrane processes</i>	29
4. APPLICATION OF MEMBRANE SEPARATION FOR THE TREATMENT OF MINING EFFLUENTS	31
4.1. MEMBRANE SEPARATION AND TREATMENT OF ACIDIC DRAINAGE.....	38
4.2. POST TREATMENT AND BRINE DISPOSAL	50
5. MEMBRANE PROCESS ECONOMICS.....	52
5.1. MEMBRANE SYSTEM CAPITAL COSTS	53
5.2. MEMBRANE SYSTEM OPERATING COSTS.....	54
6. ARSENIC AND SELENIUM REMOVAL TECHNOLOGIES	56
7. BIOLOGICAL TREATMENT OF MINE EFFLUENT AND WATER	58
7.1. MEMBRANE BIOREACTORS.....	58
8. CASE HISTORIES.....	60
8.1. ASARCO INC. GLOBE PLANT IN DENVER COLORADO.....	60
8.2. MEXICANA DE CANANEA MINE IN CANANEA, MEXICO.....	64

8.3. DESALINATION AND REUSE OF ACIDIC DRAINAGE AND ASH WATER.....	67
8.4. CANONSBURG, PENNSYLVANIA URANIUM MILL TAILINGS REMEDIAL ACTION PROGRAM (UMTRA) SITE.....	72
8.5. BLACK HAWK COLORADO PILOT	75
8.6. DEBIENSKO COAL MINES, KATOWICE, POLAND.....	78
8.7. NEWMONT - GOLD LEACHING OPERATION IN PERU	82
9. RESEARCH AND TECHNOLOGY REQUIREMENTS.....	84
10. CONCLUSIONS	87
11. REFERENCES.....	88

LIST OF TABLES

TABLES

3.1. Comparison of the four pressure driven membrane processes.....	5
3.2. List of common membrane materials used in the fabrication of commercial membranes and their applications.....	9
3.3. Main characteristics of common membrane filtration processes.....	16
3.4. Comparison of different membrane configurations.	16
3.5. Direct and indirect methods for controlling membrane fouling	24
4.1a. Rejection data for a PES UF membrane tested with actual AD sample.....	41
4.1b. AD solution feed and permeate compositions obtained from a UF membrane test.....	42
4.2a. Rejection data for a PES NF membrane tested with actual AD sample.....	42
4.2b. AD solution feed and permeate compositions obtained from a NF membrane test.....	43
4.3. Typical stream compositions from the NF treatment of leach water from the Bingham Canyon Mine.....	44
4.4. Typical stream compositions from the RO treatment of the sulphate plume water from the Bingham Canyon Mine.....	45
4.5. RO trace element rejection data for a synthetic AD sample.....	47
4.6. AD treatment data of a V-SEP module with a polyamide membrane compared to lime precipitation.....	49
4.7. Results of the RO treatment of an AD stream from an open pit brown coal mine.....	49
5.1. Estimated cost of a crossflow microfiltration system – Present value 1989 costs.....	54
5.2. Typical energy costs for the main membrane process.	55
8.1. Asarco’s Globe Plant precipitation system performance.....	62
8.2. Asarco’s Globe Plant membrane separation system performance.....	63
8.3. Cost comparison between the Asarco’s precipitation and membrane systems per 1000 gal treated wastewater.	64
8.4. Cananea pit solution composition.....	66

8.5. TRO feed and permeate composition.....	69
8.6. Performance criteria and the average performance of the SRO units of the TRO plant.....	70
8.7. Performance data for the EDR plant pretreatment process train.....	71
8.8. Performance data for the EDR stacks.....	71
8.9. Performance data for the SRO units of the EDR plant.....	72
8.10. Maximum groundwater contaminant levels and membrane treatment results at Canonsburg, UMTRA site.....	74
8.11. Heavy metal removal efficiencies of the processes tested at Black Hawk, CO.....	77
8.12. Comparative capital and operating costs for treatment of AD at Black Hawk, CO.....	78
8.13. Products and cost of production from mine drainage at Katowice, Poland.	80

LIST OF FIGURES

FIGURES

3.1. Plate and Frame Membrane System	12
3.2. Tubular modules and membranes.....	13
3.3. Spiral wound module	13
3.4. Submerged hollow fiber module	14
3.5. A typical RO/NF plant	15
3.6. SEM photo of a fouling layer deposited on the surface of a NF membrane tested with AD	19
3.7. SEM photo of a fouling layer of $MgCO_3 \cdot 2H_2O$ crystals deposited on the surface of a high rejection RO membrane tested with mine effluent	20
3.8. SEM photo of a fouling layer deposited on the surface of a high rejection RO membrane tested with a mine effluent containing an antiscalant.....	21
4.1. General schematic diagram of CANMET-MMSL bench scale membrane test system	41
8.1. Block diagram of Asarco's precipitation process.....	61
8.2. Block diagram of Asarco's membrane separation process.....	63
8.3. General diagram and performance of the Cananea membrane plant showing the average stream flows and concentrations.....	66
8.4. Block flow diagram of TRO-SRO plant for recovery of ash water.....	68
8.5. Block flow diagram of EDR-SRO plant for recovery of water from AD	70

LIST OF ABBREVIATIONS

AD – Acidic Drainage
CA – Cellulose Acetate
ED – Electrodialysis
EDR – Electrodialysis Reversal
MF – Microfiltration
NF – Nanofiltration
PES – Poly(ethersulfone)
PS – Poly Sulfone
PVDF – Poly(vinylidene fluoride)
RO – Reverse Osmosis
SS – Suspended Solids
TDS – Total Dissolved Solids
TOC – Total Organic Carbon
TSS – Total Suspended Solids
UF – Ultrafiltration

1. INTRODUCTION

The objective of this report is to provide a general overview of membrane separation technology and its application to the treatment and management of mining effluents, including acidic drainage (AD). In 2006, CANMET-MMSL conducted a review of available technologies for the treatment and management of mine water and mining effluents for Cameco Corporation, which was partially funded by CANMET-MMSL (Mortazavi *et al.*, 2005). The review covered a wide range of treatment technologies ranging from chemical treatment methods to membrane separation processes. The current report is an expanded version of the membrane separation technology section of the previous study.

Mitigation and management of saline water and wastewater as well as the management of acidic and neutral drainage are among the most important challenges faced by the mining industry. The challenge is meeting economic objectives of the mining operations while maintaining environmental performance and long-term sustainability. In recent years, increased regulatory pressures and increased emphasis on water conservation combined with other drivers such as risk and cost reduction has resulted in substantial changes in operations. As a result, the industry has become more open to adopting more innovative technologies such as membrane separation.

One of the major issues that the mining industry is facing is increased salt loading and salinity. Water, in mining and mineral processing operations, dissolves sodium, potassium, magnesium, chloride and other readily soluble salts. This results in increasingly large volumes of saline and brackish water, especially in dry and arid areas due to solution recycling at zero discharge facilities. Direct impacts of increased salt loading and salinity are increased operational costs and problems in meeting environmental discharge requirements.

Processing of industrial wastewater is a growing niche for membrane separation and therefore a continuously expanding market which is supported by the increasing pressure for water use minimization, recovery and recycle. Increased public awareness of environmental issues, more stringent environmental regulations and improved process economics, have resulted in an

increased acceptance of membrane separation technology by all sectors of the industry, even by the more conservative sectors such as the mining sector.

Wastewater treatment and waste minimization has become a rapidly growing area for membrane separation technology. Although membrane separation technology has become an established separation technique that is widely used in drinking water production; it is still considered an emerging technology in the mining industry. This technology offers many potential benefits to the mining industry, for instance, high percentages of water recovery from a wastewater will significantly reduce the volume of the stream requiring further treatment. This could translate to smaller neutralization plants with lower capital costs, particularly if small membrane plants are developed to remove contaminants where they are the most concentrated in the process.

The versatility and modularity of the membrane separation technology facilitates its introduction into practically any process with a suitable feed stream. With increasingly stringent environmental regulations, the use of membrane separation technology for achieving acceptable environmental performance may be unavoidable in the future. Although membrane separation does not always provide the ultimate solution to water and wastewater treatment, it can be economically added to conventional liquid waste treatment technologies (Weber and Bowman, 1986).

2. ACIDIC AND NEUTRAL DRAINAGE

The generation of metal bearing mine effluents from operating and abandoned mines in Canada and around the world is a major environmental concern for the government, the mining industry and the public and continues to cause serious contamination problems. The drainage from most of the coal, base metal, uranium and gold mines, where sulphidic rock and wastes are present, can be moderately to severely acidic. The acidic drainage is a result of the oxidation of the sulphide minerals (pyrite or marcasite and other metal sulphides) present in the mine workings, tailings and waste rock piles, and exposed walls in open pits. At some sites, metal bearing drainage occurs at neutral to slightly alkaline pH's. For example in precious metals mines, high levels of cyanide from tailings and cyanidation processes, and high levels of dissolved arsenic have created a great deal of concern in both Canada and elsewhere (Stewart *et al.*, 1997; Hill, 1968; Barnes and Romberger, 1968).

Acidic drainage (AD) (pH 2-4), if left untreated and unmanaged, can potentially cause serious water pollution and environmental damage and mobilize large amounts of iron, sulphate, lead, cadmium, zinc, nickel, manganese, calcium, magnesium aluminum and other heavy metals and radionuclides.

3. MEMBRANE BASED WATER AND WASTEWATER TREATMENT TECHNOLOGIES

In the most general sense, a membrane is a thin barrier that permits selective mass transport. The rate of mass transfer across a membrane depends on different driving forces that influence permeation. Membranes, depending on their composition and conditions of fabrication, can have different types of structures, but all membranes of practical industrial application are invariably of asymmetric or composite structures (Porter, 1990).

Separation in membrane processes take place as a result of differences in the transport rates of different chemical species through the membrane matrix, which for the applications of interest to the scope of this review, is usually polymeric or ceramic.

3.1. Membrane Processes

There are many requirements for separations in the mining industry but they can be classified into two major areas; 1) where materials are present in different phases, and 2) where different chemical species are present in a single phase. Membrane separation can be applied to both scenarios through their ability to; change the composition of solutions, selectively permeate certain species while rejecting others, regulate permeation of certain species and conduct electric current.

Membrane based separation processes have become viable alternatives to many of the physical methods of separation in a given process, such as selective adsorption, absorption, solvent extraction, distillation, crystallization, etc. Membranes are primarily used as a means of separation, recovery and purification, although they also have other applications that are beyond the scope of this review.

Membrane filtration is a separation process that uses a semipermeable membrane to divide a liquid or gas feed stream into two portions: a permeate, which contains the material passing through the membranes, and a retentate, which consists of the species left behind (Mallevalle *et al.*, 1996). Transport of the permeating species through the membrane matrix is achieved by the

application of a driving force across the membrane which provides a basis for the classification of membrane separation processes. This classification is based on the type of driving force which drives mass transport across the membrane, which can be mechanical (pressure), concentration (chemical potential), temperature, or electrical potential (Porter, 1990). Membrane filtration can be further classified in terms of the size range of the permeating species, the mechanisms of rejection, the driving forces employed, the chemical structure and composition of membranes, and the geometry of construction. The most broadly applied types of membrane filtration are pressure driven processes and include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF).

3.1.1. Pressure driven membrane processes

Table 3.1 gives an overview of the four pressure driven membrane processes mentioned above. It should be noted that there are more commercially available polymer choices for each of the membrane processes than those listed in Table 3.1.

Table 3.1. Comparison of the four pressure driven membrane processes (Wagner, 2001).

Membrane	Reverse Osmosis	Nanofiltration	Ultrafiltration	Microfiltration
	Asymmetric	Asymmetric	Asymmetric	Asymmetric Symmetric
Thin film Thickness	1 micron 150 micron	1 micron 150 micron	1 micron 150-250 micron	10-150 micron
Rejection of:	High and low molecular weight compounds, NaCl, glucose, amino acids	High molecular weight compounds, mono-, di- and oligosaccharides, polyvalent ions	Macromolecules, proteins, polysaccharides, vira	Particles, clay, bacteria
Membrane materials	Cellulose acetate (CA) thin film	CA, thin film	Ceramic, PS, PVDF, CA, thin film	Ceramic, PS, PVDF, CA
Pore size	< 0.002 micron	< 0.002 micron	0.02-0.2 micron	0.02-4 micron
Module configuration	Tubular Spiralwound Plate-and-frame	Tubular Spiralwound Plate-and-frame	Tubular Hollow fiber Spiralwound Plate-and-frame	Tubular Hollow fiber
Operating pressure	15-150 bar	5-35 bar	1-10 bar	< 2 bar

Reverse Osmosis (RO) or hyperfiltration is the most widely used pressure driven membrane separation process. RO membranes are the tightest membranes in liquid/liquid separation. RO is aimed at the separation of ionic solutes, metals, and macromolecules from aqueous streams such as industrial wastewaters, mine water and mill effluents. Water is, in principle, the only material that would pass through the membrane; essentially all dissolved and suspended materials, organic and inorganic, are rejected by RO membranes. The operating pressure of RO depends on the osmotic pressure of the solution and typically is in the range of 15-150 bar. Separation of species is a function of the shape and size of permeating species, their ionic charge, the membrane material properties and composition and its interaction with the permeating species. The more open types of RO membranes are sometimes confused with nanofiltration (NF) membranes.

Nanofiltration (NF) systems typically operate at lower pressures than those used for RO. NF systems have higher fluxes and their permeate quality is lower than that achieved with RO, but they have a selectivity that is not possible with RO. Since NF systems operate at lower pressures, they have lower energy consumption than conventional RO systems. True NF rejects multivalent ions and dissolved materials such as sulphate, phosphate, Mg and Ca, according to the size and shape of the molecule. The molecular weight cutoff of NF membranes is around 200 Daltons. Typical rejections with a NF membrane, at 5 bar and 2000 ppm of TDS, are 60% for NaCl, 80% for calcium bicarbonate and 98% for magnesium sulphate.

Some of the specific applications of NF are removal of Total Organic Carbon (TOC), hardness, salinity, radium, Total Dissolved Solids (TDS) and multivalent ions from surface water, groundwater and wastewater. In some plating operations, NF is used for the separation of EDTA-metal complexes and can deliver almost complete sulphate rejection from water (Scott and Hughes, 1996).

Ultrafiltration (UF) is another pressure driven membrane separation process. UF membranes are used to remove particles in the size range of 0.001-0.02 μm . Solvents and salts of low molecular weight pass through the UF membranes while larger molecules are rejected or retained. The primary application of the UF process is the separation of macromolecules, but they can be used

in mining operations for the separation of and recovery of flotation agents, surfactants and organometallic complexes or as a pretreatment to other membrane processes such as RO or NF. Osmotic effects in UF membranes are small, and the applied operating pressures of 1-7 bar are primarily required to overcome the viscous resistance of liquid permeation through the membrane matrix's pore network.

Microfiltration (MF) is a process used for the removal and separation of suspended solids. A pressure gradient is applied across the filter to maintain the flow through the polymeric filtration membrane. MF membranes are generally made of polymeric thin films with a uniform distribution of pores giving the film a porosity of approximately 80%. The method of particle retention is characterized as sieving despite the fact that the separation is affected by the interactions between the membrane surface and the solution (Scott and Hughes, 1996).

As in other membrane separation processes, a crucial element of a successful MF operation is the proper selection of membrane material. This dictates the surface properties of the membrane which, in turn, has a direct impact on the susceptibility of the membrane to fouling. It should be noted that both UF and MF have been used for the removal of Total Suspended Solids (TSS) from water and wastewater as a pretreatment to RO or NF.

3.1.2. Other membrane separation processes

There are other membrane processes, such as Electrodialysis (ED), in which pressure is not the driving force. ED is a membrane process wherein the driving force is electrochemical and ions are transported across a water swollen ion-exchange membrane under the influence of an electrical potential.

ED provides the means for selective separation of anions and cations. Ion-exchange or ion-selective membranes are used in ED applications. These membranes have fixed charged functional groups that are chemically bound into the polymer matrix to which counter ions are attached. Ion-exchange membranes can be homogeneous or heterogeneous. Heterogeneous ion-exchange membranes are prepared from ion-exchange resins. They have high electrical

resistance with low mechanical strength, especially when they are in a swollen or plasticized state due to exposure to water.

Major applications of ED are electrolyte concentration and in the dilution or de-ionizing of solutions. The latter has been the dominant application of ED in the desalination of brackish water. ED has been used in water treatment applications for the separation and recovery of ions and salinity from groundwater. In mining, ED has been utilized for AD treatment and for salt and brackish water demineralization (Schoeman and Steyn, 2001). Use of ED has also been reported for the treatment of wastewater streams from metal plating and alumina plants (Hays, 2000; Kawahara, 1994; Kanggen *et al.*, 1999).

3.1.3. Membrane filtration system selection and design

The successful use of membrane processes depends on the proper selection of membrane material and proper module design. A membrane should exhibit, at least, the following characteristics:

- high permeate flux;
- high selectivity (contaminant rejection);
- mechanical stability and durability;
- resistance to fouling and tolerance to the feed stream components;
- chemical resistance;
- manufacturing reproducibility;
- low cost; and
- high packing density; which is ability to be packaged into modules containing high surface areas.

From the above characteristics, permeate flux and selectivity determine the mass transport properties of the membrane. The permeate flux is usually defined as the rate at which permeate passes through a unit area of membrane. Selection of a membrane with a higher flux at a given driving force would result in a lower surface area for a given feed flow rate and therefore, a lower capital cost for a given membrane system. Higher selectivity is also an important property of the membrane since it yields a higher quality permeate (Pinnau and Freeman, 2000; Wiesner and Chellam, 1999).

Membrane material selection is an important part of any membrane process design. Suitability of a membrane for a given application is a function of its chemical composition and structure, the morphology of its matrix and its surface properties (Pinnau and Freeman, 2000; Wiesner and Chellam, 1999).

Organic polymers are the most widely used commercial membrane materials. They are usually constructed by coating a thin active polymeric layer onto a microporous support to provide desirable mechanical strength while having higher water permeability and chemical resistance. Table 3.2 provides a list of membrane materials used in commercial membranes. Additional information about the properties of the membranes can be found in the following references: Mallevialle *et al.* (1996), the American Water Works Association (AWWA) Membrane Technology Research Committee (1998), Matsuura (1994), Porter (1990) and Pinnau and Freeman (2000).

Table 3.2. List of common membrane materials used in the fabrication of commercial membranes and their applications.

Membrane Material	Membrane Process
Cellulose nitrate	MF
Cellulose acetate	RO, D, UF, MF, GS
Polyamide	RO, NF, D, UF, MF
Polysulfone	UF, MF, GS
Poly(ether sulfone)	NF, UF, MF
Polycarbonate	UF, MF, D, GS
Poly(ether imide)	NF, UF, MF
Poly(2,6-dimethyl-1,4-phenylene oxide)	RO, PV, GS
Polyimide	RO, NF, GS
Poly(vinylidene fluoride)	UF, MF
Polytetrafluoroethylene	MF
Polypropylene	MF
Polyacrylonitrile	RO, NF, UF, MF, D
Poly(methyl methacrylate)	UF, D
Poly(vinyl alcohol)	PV
Polydimethylsiloxane	PV, GS
RO = Reverse Osmosis, NF = Nanofiltration, UF = Ultrafiltration, MF = Microfiltration, D = Dialysis, PV = Pervaporation, GS = Gas Separation	

From a practical point of view, one of the most important membrane properties is the pore size or molecular weight cutoff (MWC), which specifies the minimum molecular weight of a solute that can be rejected. Table 3.3 summarizes the main characteristics of common membrane filtration processes. Membrane processes are suitable for simultaneous removal of a wide range of contaminants in water and wastewater treatment because of the wide range of pore sizes available.

The performance of membrane processes also depends on the use of proper module design and configurations. There are four main types of modules: plate and frame, tubular, spiral wound, and hollow fiber (Figures 3.1, 3.2, 3.3, 3.4). A comparison of the different module configurations is presented in Table 3.4. The plate and frame module (Figure 3.1) is the simplest configuration, consisting of two end plates, a flat sheet membrane, and spacers. In the tubular module configuration (Figure 3.2), the membrane is most often cast on the inside of a tubular support, the feed is pumped through the tube and the permeate is collected on the outer surface of the tube into a shell which could hold one or many tubes packed in a bundle.

The most widely used membrane module in industry for NF and RO is the spiral wound module (Figure 3.3). This module is made of flat sheet membranes sandwiched between collector and spacer sheets and wrapped around a perforated permeate collection tube (Matsuura, 1994; Mulder 1996). The feed flows on one side of the membrane at a given pressure. The permeate is collected on the other side of the membrane and spirals in towards the centre collection tube. Spiral wound modules are placed in pressure vessels into arrays and skids as shown in Figure 3.5.

Hollowfiber modules (Figure 3.4) used for seawater desalination consist of bundles of hollowfibers in a pressure vessel (Baker, 2004). They can have a shell-side feed configuration where the feed passes along the outside of the fibers and exits the fiber ends. Hollowfiber modules can also be used in a bore-side feed configuration where the feed is circulated through the fiber (Baker, 2004; Mulder, 1996). Hollowfibers used for waste water treatment and in submerged membrane bioreactors are not always used in pressure vessels. Bundles of fibers can also be suspended or submerged in a slurry or a suspended growth bioreactor such as the Zenon, Zee Weed modules, in which the permeate is collected on the lumen side by applying a vacuum.

NF and RO are typically of the spiral wound configuration (Figure 3.3) to promote turbulence, thereby reducing concentration polarization fouling and particle cake deposition. Fouling considerations, especially in waste treatment applications and in mining applications, preclude the use of hollowfiber membrane modules (Cartwright, 1997; Matsuura, 1994; Porter 1990; Mulder, 1996). Depending on the particle size distribution of the suspended solids present in the effluent and their concentrations, spiral wound modules could be used directly without a pretreatment step.



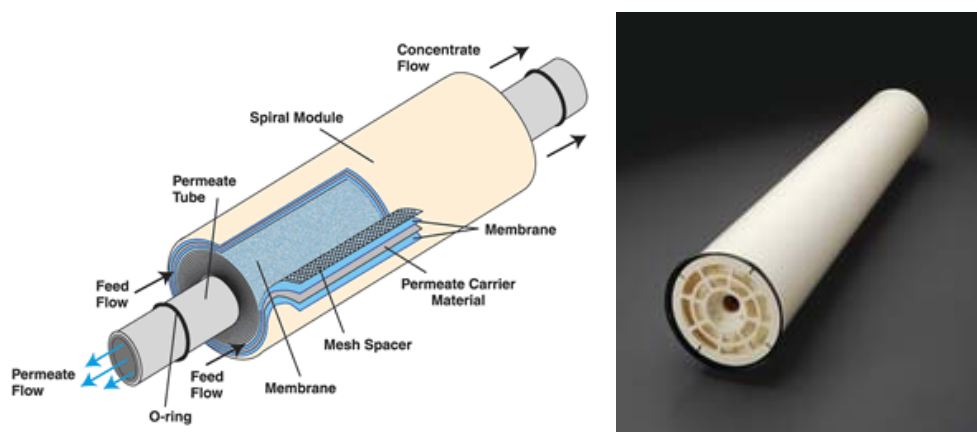
<http://www.nirosoft.com/site/picts/RP200%20module.jpg>

Figure 3.1. Plate and Frame Membrane System



http://www.berghof-filtration.de/multimedia/Bilder/BFA/Bild_188px/BFA_HyPermAE_Module_188px-width-188.jpeg

Figure 3.2. Tubular modules and membranes



<http://images.google.ca/imgres?imgurl=http://www.edstrom.com/ImageLib/www.millipore.com/catalogue.nsf/docs/CDUF050H1>

Figure 3.3. Spiral wound module



<http://www.edie.net/Products/Images/1169.jp>

Figure 3.4. Submerged hollow fiber module



<http://images.google.ca/imgres?imgurl=http://202.71.140.146/draft/waterandsewerage/202.71.140.146/.../REVERSEOSMOSIS.asp>

Figure 3.5. A typical RO/NF plant

Depending on the process conditions and the application, the energy consumption to maintain high cross-flow velocity across the surface of the membrane could be high. In recent years, many new design concepts have been introduced into the membrane market by modifying module configurations to minimize membrane fouling and reduce operating costs. When the membranes with suitable rejection and separation characteristics are identified, the next important factor in selecting the right membrane for the process depends on their cost and “throughput”, which is defined as the total volume processed before the membrane is plugged (Porter, 1990).

Table 3.3. Main characteristics of common membrane filtration processes.

Membrane	Separation size (μm)	Separation mechanism	Typical operating pressures, ΔP (MPa)	Permeate Flux
Reverse Osmosis (RO)	< 0.001	diffusion +exclusion	5-8	low
Nanofiltration (NF)	0.001-0.008	diffusion +exclusion	0.5-1.5	medium
Ultrafiltration (UF)	0.003-0.1	sieving	0.05-0.5	high
Microfiltration (MF)	> 0.05	sieving	0.03-0.3	high

Table 3.4. Comparison of different membrane configurations.

Criteria	Spiral wound	Hollowfiber	Tubular	Plate and frame	Rotating disc
Packing density (m^2/m^3)	++	+++	-	+	-
Wall shear rate	++	+	+++	+	+++
Permeate flux ($\text{L}/\text{m}^2/\text{h}$)	++	++	+++	+	+++
Holdup volume	+	++	-	+	-
Cost per area	+++	+++	-	-	-
Replacement cost	++	++	-	+++	-
Energy consumption	+	++	-	+	++
Fouling tendency	+	++	+++	++	+++
Ease of cleaning	-	+	++	+	+
Pretreatment requirement	-	+	+++	+	+++

Note: (-) disadvantage, (+) good, (++) very good, (+++) excellent

Due to the complexity of transport phenomena and interactions between membrane and contaminants in membrane filtration, the design practices of membrane filtration remain largely empirical. Consequently, site-specific bench and pilot testing are often recommended and necessary to assess treatment feasibility and to provide process parameters for plant scale-up. Common considerations and experimental protocols to conduct such tests were summarized by Mallevalle *et al.* (1996).

A membrane plant is sensitive and very specific to its feed composition and conditions. Any change in the feed composition beyond the limits set in the original plant design could have significant negative impact on its operational efficiency and performance. Lack of attention to feed characteristics, adequate pretreatment requirements and membrane module design, membrane material selection, cleaning methods and to proper selection of membrane system component materials has been the cause of numerous failed attempts in membrane separation applications.

3.1.4. Mass transport and fouling control

Membrane fouling is probably the most significant process problem that is encountered in mining applications of membrane separation and the major cause of membrane failure, and severely impacts productivity, effluent quality and membrane life. It has been observed that less soluble salts, dissolved organic compounds, colloids, fine particles, and biological growth can cause membrane fouling (Braghetta *et al.*, 1997a,b; Cho *et al.*, 1999; Fu *et al.*, 1994; Jacangelo *et al.*, 1995; Wiesner *et al.*, 1989; Zhu and Elimelech, 1995).

The major problem with the application of membrane separation to AD treatment occurs as a result of calcium sulphate and ferric hydroxide. Membrane fouling with iron can be managed by the introduction of additives and by maintaining the pH below 3. Calcium sulphate fouling has been a more challenging and limiting factor, although with high flux membranes and proper pretreatment and feed conditioning, fouling could be managed. Additionally, streams that are treated with cationic or anionic flocculants pose different and challenging fouling problems. As

the performance problems arise and escalate, operating costs increase and process economics become compromised (Zibrida *et al.*, 2000).

The type of foulant most commonly encountered in membrane separation is scaling due to inorganic precipitation and fouling. Some of the common forms of mineral scale are calcium carbonate, magnesium carbonate, calcium sulphate, calcium phosphate, barium sulphate, strontium sulphate, iron hydroxide and silicon dioxide (silica). Other types of membrane fouling include: colloidal fouling, biological fouling, and organic fouling. The latter two are not as significant in AD treatment applications.

Figure 3.6 shows the SEM photo of a deposited amorphous solid residue on a high flux RO membrane coupon that was tested at CANMET-MMSL using untreated AD, under feed pressures of 100-500 psig, without an antiscalant. The total sulphate concentration in the feed was 3500 ppm while the levels of calcium and iron were 290 ppm and 380 ppm respectively. The fouling layer shown in Figure 3.6 did not impact the permeate flux under operating pressures up to 400 psig. At 500 psig, a decline in the permeate flux and permeate quality was observed which was probably due to compaction of the cake layer. Figure 3.7 shows the SEM photo of a crystalline fouling layer, primarily $MgCO_3 \cdot 2H_2O$ crystals, which were formed during another CANMET-MMSL test. In this test, a high rejection RO membrane was tested with a mine effluent containing 13 g/L of TDS, 10 g/L of sulphate and approximately 600 ppm of magnesium at pH 9.7 and an operating pressure of 450-600 psig.

RO and NF membranes are typically able to remove 90-99% of TDS and other contaminants in an effluent. If such high rejections are combined with high water recoveries, the likelihood of membrane fouling and serious drops in water flux increases. The feed components that contribute to fouling are calcium carbonate, calcium sulphate, silica, iron, and other species that exceed the saturation index (Zibrida *et al.*, 2000; Koseoglu and Guzman, 1993).

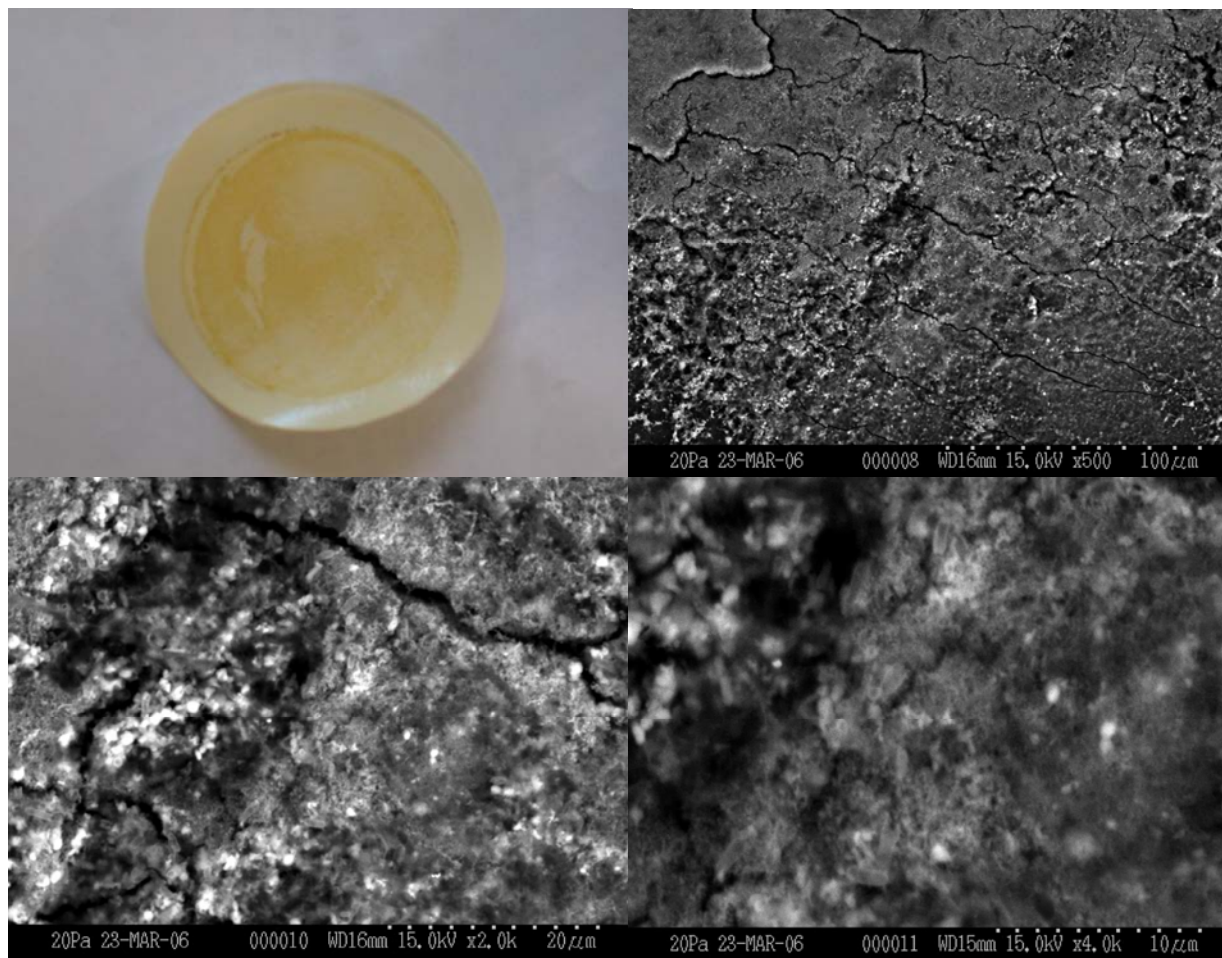


Figure 3.6. SEM photo of a fouling layer deposited on the surface of a NF membrane tested with AD containing 5.4 g/L TDS at pH 2.3

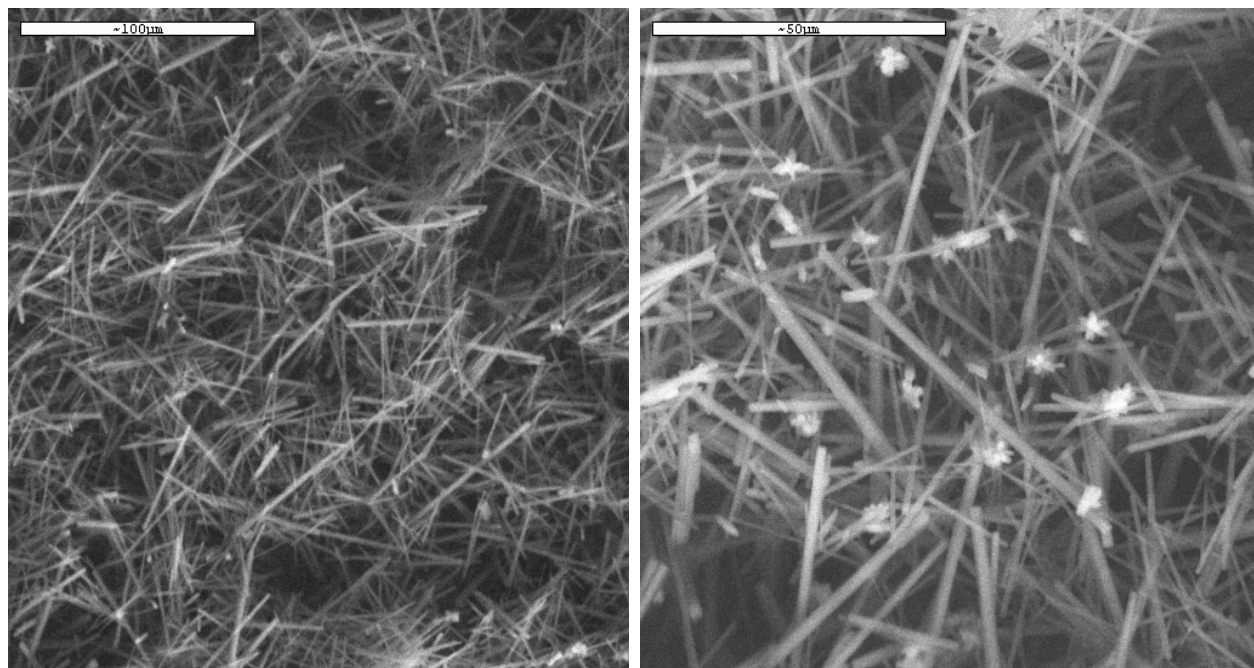


Figure 3.7. SEM photo of a fouling layer of $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$ crystals deposited on the surface of a high rejection RO membrane tested with mine effluent containing 13 g/L TDS at pH 9.66

It was demonstrated that the use of antiscalants and antifoulants help reduce the fouling potential in a membrane operation (Amjad, 1996). Polyphosphates act as threshold inhibitors and prevent precipitation of salts when their solubility limits are reached (i.e. when the feed stream becomes concentrated due to increased water recovery). In the 1930's it was discovered that the addition of polyphosphates, such as sodium hexametaphosphate (SHMP) could retard the precipitation of scale-forming salts at concentrations of 2 – 10 ppm. SHMP has shown excellent results in preventing scale formation with calcium sulphate and carbonate; however, its use could result in the generation of calcium phosphate scale. The use of SHMP is limited since it shows poor performance in suspending colloidal matter. The development of polyacrylate (PAA) based antiscalants to control fouling in RO and other membrane systems has been a significant step in making the RO process economically feasible (Amjad *et al.*, 1988; 1999; 2000, Zibrida *et al.*, 2000). Figure 3.8 shows the SEM photo of the same membrane shown in Figure 3.7 tested under the same conditions, but in the presence of an antiscalant. Although the composition and dosing of the antiscalant was not optimized, it resulted in a change in the morphology of the fouling layer and produced a complete recovery of the permeate flux.

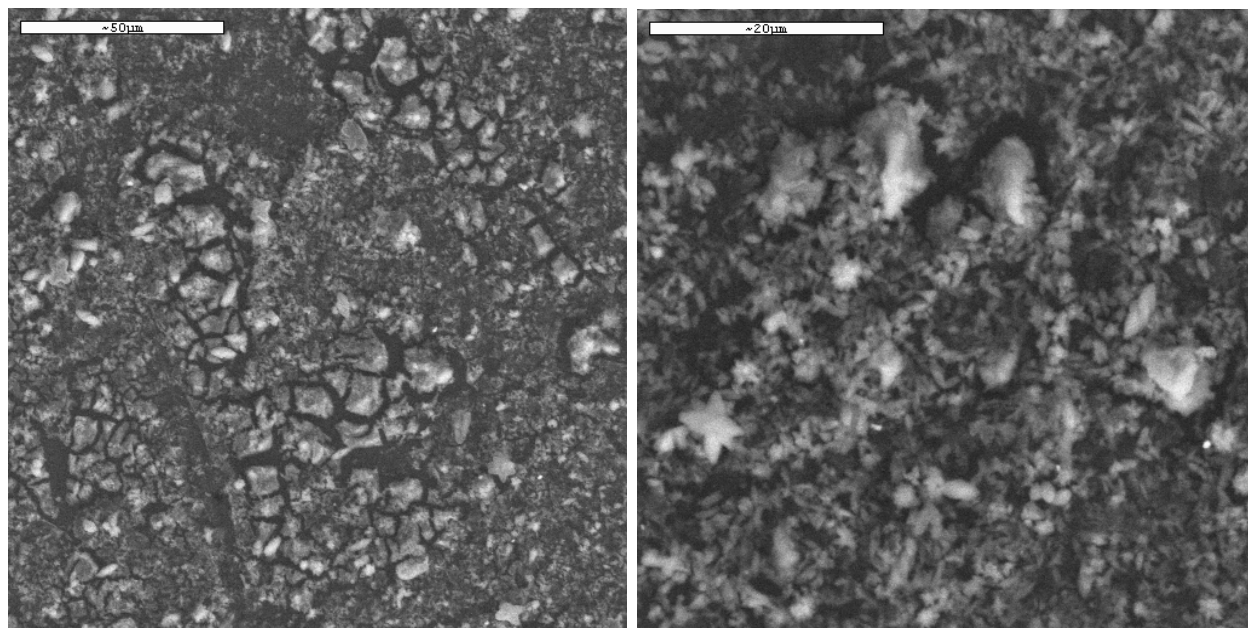


Figure 3.8. SEM photo of a fouling layer deposited on the surface of a high rejection RO membrane tested with a mine effluent containing 13 g/L TDS at pH 9.66 with an antiscalant

Adjusting the feed pH to between 4 and 6 can also help to reduce fouling and scaling. Many natural waters contain high calcium levels or are saturated in calcium carbonate. Calcium carbonate is easily rejected by RO membranes and becomes concentrated in the retentate stream during the RO process and precipitates on the surface of the membrane. Adjusting the pH to between 4 and 6 would result in the conversion of carbonate and bicarbonate ions to carbon dioxide, and would prevent carbonate precipitation.

A variety of polymer based antiscalants are now commercially available that can be used to address a broad range of fouling and scaling problems. Antiscalants, such as Flocon, King Lee, etc., are very effective and are available in formulations suitable for different feed compositions. For example, Flocon 100 (a polyacrylic acid with a molecular weight of about 3500 g/mol) (Amjad, 1985), is extensively used in the industry as a calcium phosphate precipitation inhibitor (Amjad, 1996, Amjad *et al.* 1997, 1999; Gouellec and Elimelech, 2002). Published literature shows that the performance of such antiscalants strongly depends on the composition of the polymer, its molecular weight, its dose, and the composition of the feed stream. The presence of metal ions, such as calcium, iron, zinc, manganese, aluminum, and high gypsum concentrations

in the feed water, can result in scaling problems. It has been shown that the presence of iron (II) and manganese (II) do not create fouling problems as long as they remain in solution. The presence of iron (III), even at low concentrations, has been reported to significantly impact the performance of the polymers used for inhibition of scaling by calcium phosphate. A good understanding of the fouling mechanism for different feed chemistries is an important factor in developing suitable additives and fouling prevention strategies (Amjad *et al.* 1997, 1999; Porter, 1990).

Separation and water permeation involve various mass transport steps in membrane filtration processes. Many efforts have been directed to identify and characterize basic mass transport mechanisms. For colloids and fine particles, the main transport mechanisms include convection, Brownian diffusion, shear-induced diffusion, inertial lift, gravitational settling, and lateral migration. Their relative importance depends strongly on shear rate, particle size, and, to a lesser extent, the bulk concentration of particles in the feed solution (Belfort *et al.*, 1993). Recent research has shown that mass transport is also affected by the short-range interactions between particles such as adsorption, van der Waals attraction, and electrostatic double layer repulsion. These forces become particularly significant near the membrane wall where the presence of concentration polarization and the formation of surface cake dramatically reduce the distances between particles. Consequently, any factors that could change the hydrodynamic characteristics of membrane modules and the chemical characteristics of feed solutions could affect the overall membrane performance.

It has been observed that salts with limited solubility, dissolved organic compounds, colloids, fine particles, and biological growth can cause membrane fouling (Braghetta *et al.*, 1997a,b; Cho *et al.*, 1999; Fu *et al.*, 1994; Jacangelo *et al.*, 1995; Wiesner *et al.*, 1989; Zhu and Elimelech, 1995). Consequently, five principal fouling mechanisms have been identified: (i) concentration polarization, (ii) cake formation, (iii) inorganic precipitation, (iv) organic adsorption, and (v) biological fouling. Each of these fouling mechanisms has different effects on flux recovery from backwash. Fouling inside membrane pores by salt precipitates and small colloids is often considered as an irreversible process and is responsible for irreversible declines in the flux rate,

unless they are dissolved by cleaning agents in backwash water. In contrast, flux decline due to the development of a surface cake is largely reversible.

The relative significance of these mechanisms in membrane fouling is affected by raw water quality, membrane material properties, membrane module configuration, and operating conditions. For instance, salt precipitation and dissolved organic compounds may be important causes of fouling after lime softening in water treatment, whereas their roles in wastewater treatment may be less significant. In contrast, in municipal and high-strength industrial wastewater treatment, colloidal and biological fouling will play a dominant role because of the much higher colloidal concentration and biological growth potential.

The quality of the feed stream and its composition is one of the primary considerations which could have a significant impact on the performance of the membrane plant by causing fouling. Failure to properly characterize the feed water could result in serious operational problems and elevated operating costs. Success of any measure for mitigation of fouling in a membrane process is a direct function of the operator's knowledge of the feed composition and its variability.

The presence of Al and Si in the feed water to an RO plant in a gold mine in the Australian Outback caused serious fouling of the filters and membranes in the plant. A variety of pretreatment measures were taken by the plant operators to reduce fouling, which resulted in elevated operating costs (Allenby, 2004). The purpose of the RO plant was to provide water to the mine from a highly variable groundwater source, which ranged from potable quality to hypersaline. The company failed to analyze for Al during their characterization of the feed water supply. After the plant was constructed and commissioned, the presence of high levels of Al resulted in serious clogging of cartridge filters before the membranes. The requirement for daily filter replacement and weekly full-chemical cleaning and reduced water recoveries increased the operating costs. Aluminum, at levels of 20-30 mg/L in the feed water, resulted in a white pasty and gooey deposit composed of 15% Al and 10% Si, which was predominantly Al-Si. This material coated the filter cartridges and the surface of the membranes. The attempts to remedy the fouling problem involved the addition of NaOH at a rate of 35 kg/day to precipitate the Al-Si; however, coagulation and flocculation were not sufficient to fully address the problem.

Other remedial attempts involved the use of stainless steel wire upstream of the membranes, the introduction of additional filters in the pretreatment stage, and a high strength acid wash. The company was ultimately forced to switch the feed water source to one that contained much lower levels of Al and Si (Allenby, 2004).

3.1.5. Methods of fouling control

Common fouling control strategies currently used in practice are listed in Table 3.5. These strategies include, but are not limited to; chemical membrane surface modification; physical improvement of module geometry to promote hydrodynamic shear such as the use of the Dean Vortex and the use of rotational discs; better process control; continuous adjustment of operating conditions; use of proper cleaning techniques; the pretreatment of feed streams; introduction of sponge balls for surface scrubbing and cleaning; and the addition of powdered activated carbon to form a more porous surface cake. The effectiveness of these control strategies appears to be site specific. In some applications, an integrated approach such as coupling adequate pretreatment with selection of the proper membrane module and operating conditions are essential for mitigation of fouling problems effectively and economically.

Table 3.5. Direct and indirect methods for controlling membrane fouling.

Method	Reference
Direct Methods	
Impulse feed	Boonthanon <i>et al.</i> , 1991
Periodic hydraulic or chemical cleaning	Porter, 1990
Turbulence promoter	Shen and Probstein, 1979
Rotating-vibrating membrane	Reed <i>et al.</i> , 1997; Silva <i>et al.</i> , 2000
Dean Vortex	Mallubuhotla and Belfort, 1997
Inside gas sparging	Cabassud <i>et al.</i> , 1997
Outside aeration	Silva <i>et al.</i> , 2000
Indirect Methods	
Pretreatment by coagulation-filtration	Chellam <i>et al.</i> , 1997
Selecting optimum operating conditions	Belfort <i>et al.</i> , 1993
Changing operation modes	Cote <i>et al.</i> , 1998
Membrane surface modification	Wiesner and Chellam, 1999
Pretreatment by air flotation	Braghetta <i>et al.</i> , 1997a,b

Selection of any or a combination of the options presented above would depend on the severity of fouling problem and process conditions. As indicated above, the membrane plant is quite

sensitive to its feed source quality and consistency. Lack of attention to this at the design stage, especially if large fluctuations in feed properties and composition are expected, could negatively impact process economics and result in serious operational difficulties and even failure of the plant.

3.1.6. Membrane filtration applications

Since commercial membranes are available over a wide range of pore sizes, membrane filtration technologies can effectively remove various contaminants. From a contaminant-based perspective, membrane separation applications can be grouped into three main areas: solid–liquid separation, organic removal, and inorganic removal. This distinction becomes rather blurred because the use of one membrane filtration process may remove several contaminants simultaneously. Organic removal is not within the scope of this review and will not be discussed in this report.

3.1.6.1. Solid–liquid separation

The success of membrane processes for solid–liquid separations has been demonstrated consistently over a wide range of water sources for both laboratory and full-scale applications. This is particularly important for MF and UF because they can be operated at very low pressure differentials. In water treatment, an increasing number of utilities use membrane processes to improve turbidity removal and to eliminate chlorine-resistant pathogens. In solid-liquid separation applications, the proper characterization of the suspended solids in the feed and the particle size distribution are essential to ensure a successful operation.

In wastewater treatment, membrane filtration processes have been proposed to replace clarification for the separation of suspended solids and to further polish secondary effluents (Kilega *et al.*, 1991). In the treatment of AD, a membrane filtration step could also provide significant cost savings in capital and operating costs via reducing the treatment volume and reducing the size and footprint of the conventional clarifier (precipitation/coagulation/sedimentation). The use of evaporators or crystallizers could be used for the

precipitation of the salts in which case the requirement for a clarifier in the treatment process could be eliminated. This process would result in the production of a clean permeate stream and solid precipitated salt.

Membrane processes such as UF for solid separation have been used as a pretreatment step to RO and NF membranes in order to reduce the TSS of the feed stream for spiral wound and hollow-fiber applications (Porter, 1990). UF and MF membranes have been used for solid-liquid separation in hybrid processes where an adsorbent, such as activated alumina, is initially used to adsorb a contaminant and separated by the membrane (Mortazavi *et al.*, 1999).

3.1.6.2. Inorganic contaminants

The removal of inorganic contaminants by NF and RO remains the largest application in water treatment. A survey showed that there were more than 4000 land-based RO plants worldwide in 1989 with a combined desalting capacity of approximately 3.8×10^6 m³/d (AWWA Membrane Technology Research Committee, 1992). This only includes plants with capacities larger than 95 m³/d. The feasibility of the application of RO and NF and even UF for the removal of hardness, nitrate, ammonia, heavy metals and oxyanions has been demonstrated in the published literature (Rautenbach and Groschl 1990; Waypa *et al.*, 1997). The USEPA considers RO as a best available technology to meet anticipated regulations for small surface-water plants without existing facilities and groundwater treatment plants.

3.1.7. Hybrid membrane processes

UF and MF are very effective methods of solid–liquid separation and operate at low pressures. UF and MF have been combined with other conventional treatment processes to remove dissolved species. Examples include the use of membrane filtration and powdered activated carbon, adsorption and MF. The use of polymers and resins with UF or MF and membrane bioreactors has shown great promise in water and wastewater treatment (Mortazavi *et al.*, 1998, 1999; Legault and Tremblay, 1994).

Reverse osmosis (RO) and electrodialysis (ED) are used to retrieve metals or plating compounds (in zero discharge plating operations) from wastewater. The application of RO or NF for the removal of metals from wastewater is limited by the pH range wherein the membrane is stable and for which it was designed. For instance, cellulose acetate membranes are not suitable for use in pH >7, while aromatic polyamide and polysulfone membranes are suitable for use in the pH range of 1-12. Such materials could be used for mine water with low and high pH's, as well as for treating effluents from mill and hydrometallurgical operations.

The performance of RO or NF can be impaired by the presence of colloidal matter, dissolved organics, and insoluble suspended solids. These techniques have been used in mining operations to produce low metal discharge waters, provided that adequate pretreatment is done and the appropriate membrane selected. For example, Gureli and Apak (2004) reported a process where a combination of ion exchange and membrane separation was used for the recovery of uranium from ammonium uranyl carbonate effluents.

The use of membrane processes alone or in combination with conventional treatment processes have shown that membrane processes may offer a number of advantages over conventional treatment processes in municipal and industrial mixed waste treatment processes. Some of the advantages include: (i) a high-quality effluent is produced over a wide range of raw water sources, (ii) no chemical addition is required, except when organic removal is practiced, (iii) only a small amount of solids require disposal, (iv) very compact installations, (v) simpler automation and control, and (vi) reduced operation and maintenance requirements (Chellam *et al.*, 1998; Wiesner *et al.*, 1994; Matsuura, 1994).

Other examples of hybrid processes are presented in Section 4.

3.1.8. Process conditions for membrane separation

There are some problems that could plague a membrane based approach if proper consideration and attention to the process design is not given. The most severe problems could include: highly

contaminated industrial wastes and wastewaters, corrosive wastes, abrasive wastewaters with high solids content, high temperature waste streams and mixed contaminant situations (organic and inorganic pollutants). Such cases have traditionally been treated with conventional technologies.

Significant progress has been made in membrane design and in development of polymeric and inorganic materials for membrane manufacturing and membrane treatment in the past decade (Pinnau and Freeman, 2000). The broader acceptance and demand for membrane processes has also reduced the capital and operating costs of such processes to a point that they are more competitive and, depending on the process constraints, even more cost-effective to implement than many conventional physical and chemical treatment approaches.

The most common issues in membrane based treatment processes are:

- physical and chemical stability of the membrane, which is directly related to the choice of membrane material and in the case of thin film composite membranes related to the choice of the backing material and the membrane casting process conditions;
- membrane fouling, which is related to the hydrodynamic conditions at the surface of the membrane (module design) and membrane material and surface properties;
- permeate flux and solute rejection, which are a function of the membrane porosity; and
- interaction of the permeating species with the membrane matrix and with each other.

These issues are addressed by:

- adequate pretreatment;
- operating at low water recoveries such that the concentration of the salts on the feed side would remain below saturation;
- proper membrane material selection, module design;
- by ensuring the proper flow regime within the module; and
- adequate system cleaning.

A system designed and implemented by Tiepel and Shorr (1985) applied an inert and hydrophobic, low surface energy fluorocarbon membrane which allowed them to handle high solids and abrasive feeds. The chemical stability of the membrane material allowed for the

application of aggressive cleaning reagents to the membrane in order to remove adsorbed metals and other contaminants that had precipitated on the surface of the membrane.

Finally, proper module design can ensure a high turbulent flow at the surface of the membrane which would minimize the deposition of fouling material on the membrane surface. The impact that process conditions have on membrane treatment results has been shown by many studies in the literature (Tiepel and Shorr, 1985; Nyström *et al.*, 2003; Weber and Bowman, 1986; Berg and Arthur, 1999; Prabhakar *et al.*, 1992; Chen *et al.*, 1992).

Nystrom *et al.* (2003) used NF to polish biologically treated discharge waters from a pulp mill. High fluxes were reported when fouling was minimized with the use of a hydrophilic membrane which had the least interaction with fouling agents present in the wastewater. In this application a high-shear cross-flow module was used which minimized fouling due to a highly turbulent flow along the membrane surface.

3.1.9. Limitations of membrane processes

The performance, permeate flow and membrane rejection, of all polymer-based membranes decrease over time. RO membranes are susceptible to fouling by organics, water hardness, and suspended solids in the feed stream or materials that precipitate during processing. Installing prefilters can control solids in the feed stream. Changing operational parameters, such as pH, can inhibit precipitation. Oxidizing chemicals like peroxide, chlorine and chromic acid can also damage polymer membranes. Since membranes have very poor dirt loading characteristics, consideration should be given to the use of positively charged open pore membranes as prefilters. This provides an ideal combination where most contaminants could be removed by the prefilter with the membrane acting as the final barrier for the contaminants.

In many applications, the feed solution will have significant osmotic pressure that must be overcome by the hydrostatic pressure. This pressure requirement limits the practical application of this technology to solutions with total dissolved solids concentrations below approximately 25,000 ppm (with the exception of disc tube applications and seawater desalination applications).

Membrane separation is a concentrating process in which the concentration of the solutes in the feed can be increased by several fold in the retentate stream. This high solute concentration, due to increased osmotic pressure on the feed side of the membrane, could result in the reduction of the driving force for the separation. This in turn, would lead to deterioration of product water quality, due to the increased driving force for solute transfer across the membrane and the reduced water flux (Awadalla and Kumar, 1994; Blackshaw *et al.*, 1974).

Specific ionic levels in the concentrate must be kept below the solubility limit to prevent precipitation and fouling; however, the use of proper antiscalants at the right dosage could allow for increased water recoveries. Use of other fouling control methods such as those in V-SEP (Miller, 2005) and SPARRO (Pulles *et al.*, 1992) processes have also allowed for increased water recoveries. Ionic species differ with respect to rejection percentage. Some ions such as borates exhibit relatively poor rejection rates for conventional membranes (Awadalla and Kumar, 1994; Blackshaw *et al.*, 1974).

The major problem with the application of membrane separation to AD treatment occurs as a result of calcium sulphate and ferric hydroxide. Membrane fouling with iron can be managed by the introduction of additives and by maintaining the pH below 3. Calcium sulphate fouling has been a more challenging and limiting factor, although with high flux membranes and proper pretreatment and feed conditioning fouling could be managed.

4. APPLICATION OF MEMBRANE SEPARATION FOR THE TREATMENT OF MINING EFFLUENTS

There is a continuous need for new separation techniques which selectively extract metal ions and radioactive species from wastewaters and industrial process streams. Stringent environmental regulations and possible reuse of extracted metals are incentives for the industry to search for new processes. Some conventional techniques for metal removal are: precipitation (Diamand, 1977; Choppin and Nash, 1995), solvent extraction (Diamand, 1977), and ion exchange (Choppin and Nash, 1995; Pérez de Ortiz, 1995). Conventional precipitation is not selective and not suitable for low-concentration effluents due to their low metal recovery, although some novel processes such as the BioTeq™ process might be an exception. Solvent extraction is not economical due to the loss of the extracting agent and the production of large amounts of organic waste. Moreover, the effluent might become polluted with the solvent used for the extraction process. Electrolysis is not appropriate for low concentrations. Ion exchange has been widely studied for the recovery of metal ions from diluted streams (Choppin and Nash, 1995; Pérez de Ortiz, 1995; Litovitz *et al.*, 1988; White, 1987). Commercially available ion-exchange resins show good performance but generally poor selectivity towards different metal ions (Sahni and Reedijk, 1984). High selectivity has been observed in some cases (Sahni *et al.*, 1988), but the kinetics are slow due to the hydrophobic character of the polymeric backbone (Choppin and Nash, 1995; Pérez de Ortiz, 1995; Litovitz *et al.*, 1988; White, 1987).

Wastewater from various sources can be treated to produce high quality water for reuse or discharge with little or no impact on the receiving bodies of water. As well, in some cases, valuable mining by-products can be recovered for resale or reuse from the concentrate stream of a membrane systems.

Some examples of waste streams requiring treatment include: containment pond leachate, cooling tower blowdown, concentrate and regeneration wastes, high total dissolved solids (TDS) effluents, mine water drainage, RO and NF reject, scrubber blowdown, and mill and process effluents. Another example of waste streams requiring treatment is uranium process and tailings pond effluents, which require the removal of residual uranium and other contaminants such as

As, Ra and other radionuclides. These metals are usually removed by neutralization and the TSS removal is achieved by using clarifiers and sand filtration; however, membranes could be incorporated into these processes as a tool for volume reduction and waste minimization.

A number of studies have demonstrated the effectiveness of membrane separation processes for mine water and effluent treatment; however, the effectiveness of these processes in other more complex water treatment and separation applications would suggest that there are even more applications possible for the mining sector (Bertrand *et al.*, 1997; Butler and MacCormick, 1996; Stewart *et al.*, 1997; Awadalla and Kumar, 1994; Solomon *et al.*, 1989; Bostjancic and Ludlum, 1996, Sikora and Szyndler, 2004; Tiepel and Shorr, 1985; Miller, 2005; Green *et al.*, 1993; Harrison Western, 1997, Nieuwenhuis *et al.*, 2000; Van der Graaf *et al.*, 1999).

Georgescu and Andrei (2000) reported on the application of RO for the treatment of the effluent from alkaline uranium ore processing. Typically, applied technologies for industrial effluent treatment are ion exchange, precipitation, electrochemical processes, filtration and flotation. These are not always economical and do not generate adequately low residual levels of metals and radioactive species for discharge.

Georgescu and Andrei (2000) used asymmetric cellulose acetate RO membranes prepared from a polymer with an acetate content of 39.4% in formaldehyde. The membranes were cast from 27% wt acetone-formaldehyde-cellulose acetate solution. The experiments using synthetic solutions containing uranium and molybdenum resulted in 96.46% rejection of uranium (from 4.8 to 0.17 mg/L) and 87.5% rejection of molybdenum (from 4.0 to below 0.5 mg/L) at 665 psig feed pressure. It should be noted that the results reported are specific to the performance of the specific membrane material, its casting conditions and post-treatment conditions. Any change in the aforementioned conditions could result in different outcomes for the separation processes. Screening tests should be conducted prior to a final selection of a membrane material for a specific separation process. There are likely other polymeric materials in the market that could show improved performance over the material tested by Georgescu and Andrei (2000).

According to Shapira *et al.* (1981), the application of UF and MF as alternatives to gravity separation, centrifugation and filtration would achieve practically complete removal of suspended solids and is more effective than the conventional physical treatment of wastewaters (Shapira *et al.*, 1981). The costs of crossflow MF are about half the costs of the conventional plant and therefore the selection of MF offers a cheap pretreatment option that is capable of removing TSS including colloidal particles.

The recycling of water from flotation mills can yield significant savings in reagent use. The reuse of clear overflow from flotation tailings after thickening and clarification reduced the consumption of reagents significantly in both primary and secondary grinding sections (Coulter, 1962; Awadalla and Kumar, 1994). Awadalla and Hazlett (1992) reported that the use of RO for the treatment of flotation water was effective for the removal, concentration and recovery of flotation reagents from wastewater and provided clean water for reuse in the plants. The results indicate that commercial RO membranes achieved a 95% rejection of organic carbon, calcium, and magnesium from the mill feed water. The removal efficiency with NF membranes was approximately 80%. Although the cost of operating membrane applications would be significantly higher than the biological treatment option, the biological treatment of flotation water requires residence times of 4-8 weeks. Membranes could be considered a good choice of technology due to the increasing demand for quality water in mineral processing. In addition, the legislative trend towards “zero discharge” and the adverse effects of recycling untreated water, make the RO/NF treatment option attractive for the treatment of flotation water.

Nitrate ions and ammonia in mine and mill water are generated from the degradation of cyanide in gold mill effluents and from the use of blasting compounds in mining operations (Awadalla *et al.*, 1994). The performance of RO and NF membranes have been demonstrated to be efficient for the removal of ammonia and nitrogen from actual mine effluents. The ammonium removal efficiency was > 99% using commercially available RO membranes and 66% with NF membranes in a single pass through the system. Nitrate removal from mine effluents of up to 97% has been reported with RO membranes and 43% with NF membranes. (Awadalla *et al.*, 1994). The concentrate from the RO process, containing up to 1 g/L of ammonia, could be further processed to produce ammonium compounds for fertilizer applications.

In the study by Awadalla and Kumar (1994), the removal efficiencies of ammonia and nitrate from a mining effluent using RO was 10-30% indicating that the ammonia existed as ammonium salt complexes. In this case, the size of these complexes dictates the rejection obtained by the membranes. In tests with synthetic solutions of ammonium iron sulphate, a rejection of 98% was reported with NF membranes. Separation of ammonia and nitrate with membranes in mining operations ensures production of high quality water for discharge or reuse since other metals and anions such as Ca, Fe, Zn and sulphates are also retained during the separation. There has been no report of membrane fouling concerns in the literature with ammonia and nitrate separations.

Membranes have also been used in groundwater treatment applications. Methods of minimizing groundwater contamination from in-situ uranium mining were studied by Deutsch (1985) using surface treatment methods such as RO and electrodialysis. These were found to be effective in minimizing water use but were also found to have the potential for creating conditions in the aquifer under which the redox-sensitive species were mobilized.

Groundwater treatment for the removal of radium with low pressure RO, at 70 psig, was effective and, depending on the process conditions, economical (Awadalla and Kumar, 1994; Clifford *et al.* 1988). Radium and TDS rejections of up to 91 and 97%, respectively, are possible with membranes, which is better than the performance of Ra-selective carriers (BaSO₄-loaded Al₂O₃) or ion-exchange brines.

The application of single-stage RO as a sole means for removal of uranyl sulphate (UO₂SO₄) from a mine water feed has been described by Sastri and Ashbrook (1976). In this study, metal ions Ca²⁺, Fe³⁺, Al³⁺, and U⁶⁺ were separated by a supported preshrunk cellulose acetate RO membrane. Riding and Rosswog (1979) recommended a spiral-wound RO system for economical treatment in in-situ leach applications. In this application, high water recoveries of around 85% were reported. Electrodialysis was evaluated by Garling (1981) for in-situ uranium mining. He reported the lower feed pressure requirements, the stability of membrane material over the pH range of 1 to 14, and the longer life of the membrane, as advantages of electrodialysis over RO. However, it should be noted that there has been considerable

development in membrane materials and processes since 1981 and currently available RO and NF membranes are more cost-effective and deliver more reliable performance and stability over the pH range of 1-13 depending on the material (Sirkar, 1992, Pinnau and Freeman, 2000).

Research by Prabhakar *et al.* (1992) demonstrated that membrane processes, especially RO processes, have the potential for concentrating uranyl solutions and decontaminating effluents. It was reported that a permeate concentration of <1 mg/L could be achieved with a two-stage RO process. In the treatment of uranium fluoride effluents by reverse osmosis, Chen *et al.* (1992) reported effective separation of U^{6+} and fluoride ions under acidic conditions with a continuous feedback RO process.

Uranium recovery from a 30% phosphoric acid solution was demonstrated by Stana and Glesry (1980) using a multi-stage RO system. In this method, uranium could be concentrated by passing the uranium containing feed stream through a RO system and flushing the concentrate stream with water in another RO system to further concentrate the uranium. The second concentrate stream would be treated with iron hydrogen sulfide to precipitate iron which was followed by the evaporation of the resulting stream to produce a 50-90% uranium oxide.

Visser *et al.* (2001) investigated the performance of commercially available NF membranes for the removal of sulphate and other ions from mine water under acidic conditions. These studies showed that the NF membranes are capable of sulphate rejections of 95-99% and water fluxes of 2-7 L/m².h.bar at neutral pH values. At acidic pH's, a decline in the performance of the membranes was observed due to the presence of a higher fraction of HSO_4^{-1} ions and possible change in the membrane charge. There are, however, commercial membranes available that can function at low pH values and high salt loadings. Mono and divalent ions such as calcium, sulphate, sodium and chloride were rejected at values greater than 90%. An important consideration is that these tests were performed in a dead-end filtration cell. Large-scale applications, though, are invariably cross-flow applications in which the hydrodynamics of the separation process are significantly different, therefore the results obtained might also be different.

Bertrand *et al.* (1997) reported on the use of NF for the treatment of water with a high sulphate concentration from a flooded iron mine to produce drinking water at an average rate of 125 m³/h for the town of Jarny in France. The mine water contained up to 3000 mg/L of sulphate, 2000 mg/L calcium carbonate and 400 mg/L sodium. The NF plant that was used consisted of two parallel trains with a total throughput of 75 m³/h, a by-pass flowrate of 10 m³/h and an average production flowrate of 62 m³/h. The plant maximum recovery was 75% and the membranes used were DOW NF 70-345. Pretreatment processes included precipitation, flocculation, lime softening followed by sand filtration. After sand filtration, the pH of the water was adjusted with sulphuric acid and antiscalant was added. Post treatment of the treated water included pH adjustment and chlorination prior to the introduction of the water into the distribution circuit.

Another example of the application of membranes for the treatment of AD mine water and is the joint Anglo Coal and Ingwe Collieries reclamation project. At this plant, 20 ML/day are treated for the municipality of Emalahleni in Mpumalanga, South Africa (Holtzhausen, 2006). AD collected from three mine sites is first piped to two storage facilities where it is neutralized by lime addition which removes iron, aluminum and magnesium. After the clarification step, the water is treated with UF and RO membranes. The membrane separation step is repeated three times to maximize water recovery and minimize concentrate brine volume. The process is expected to produce 100 m³/day of brine and 100 tonnes/day of gypsiferous waste. The brine is then directed to evaporation ponds for final disposal.

Treatment of mine effluents and mine waters with high calcium sulphate levels can have technical challenges because there is a high potential for scale formation. One of the approaches for treating such streams has been the use of a seeded RO process in which calcium sulphate seeds are mixed in the feed stream to prevent scaling. The seeded RO process, also known as the Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) process, was developed in the 1970's and has been the subject of many studies and has shown comparable performance to conventional RO systems with operating costs lower than EDR (Electrodialysis Reversal) and tubular RO (O'Neil *et al.*, 1981; Pulles *et al.*, 1992; Juby, 1992; Juby and Schutte, 2000; Harries, 1985; Shone and Harries, 1987; Lewis and Nathoo, 2005).

It was demonstrated in a pilot study by Pulles *et al.* (1992) and Juby and Schutte (2000) that the SPARRO process offers significant advantages for the desalination of calcium scaling type waters. Pulles *et al.* (1992) reported salt rejections of greater than 90% and water recovery of 95%; however, during the tests a significant decline in the membrane flux was reported. The reason for the decline in flux was not clear but it was suspected that high loading of quartzitic suspended solids in the feed could have been responsible for membrane fouling. Pulles *et al.* (1992) reported an estimated capital cost of R16.2 Million (1 South African Rand = \$0.14 US) for a 46.3 L/s (4 ML/day) SPARRO plant at 90% recovery and 35% per pass conversion. This cost was 5.5% more expensive than a Tubular RO plant with the same specifications and 25% more expensive than a comparable EDR plant. The estimated operating costs were, however, the lowest for the SPARRO process.

In all of the studies cited on SPARRO research, the systems were equipped with CA membranes which are susceptible to hydrolysis and degradation under effluent conditions that are normally encountered. Lifetime studies by Juby and Schutte (2000) on CA membranes were inconclusive.

The studies presented in this section have demonstrated the technical and cost-effectiveness of membrane separation for the mitigation of mine effluents and AD. There has been significant progress made in all facets of membrane separation recently, especially with respect to membrane material design, membrane fabrication, and module and system design. The challenge, however, remains in the control of fouling, pretreatment and cost-effective and environmentally benign brine disposal methods.

4.1. Membrane Separation and Treatment of Acidic Drainage

Application of different membrane separation processes for treatment of AD has been demonstrated in the literature and has been the subject of investigation since the 1970's; however, due to economic constraints, widespread application of membrane separation has not been adopted by the mining industry. As indicated previously, there has been a great deal of progress made in all aspects of membrane separation technology in the past decade. There has also been a substantial increase in demand for membrane based separation technologies in many industrial sectors. As a result, membrane based separation processes are more efficient and cost-effective than they were in the past. Membrane separation is still considered an emerging technology in the mining sector. However, with increasingly stringent environmental performance criteria imposed on the mining sector, it is gaining industry acceptance and as a result more companies are adopting the technology.

Various studies have shown successful application of Reverse Osmosis (RO), Nanofiltration (NF) and charged Ultrafiltration (UF) membranes for the treatment of acidic drainage. The literature invariably shows high rejections of metals associated with membrane applications; however, high recovery operations could be limited by calcium sulphate and/or iron fouling related problems. Membrane research examining the treatment of industrial effluents shows a progressive improvement in separation technology with the development of better membranes. Some of these advancements include: low pressure high flux RO and NF membranes; new membrane materials, both polymeric and inorganic; and better fouling control and prevention strategies (Bhattacharyya *et al.*, 1979b, 1982; Awadalla and Hazlett, 1992; Sastri, 1978, 1979; Sastri and Ashbrook, 1976; Valenzuela *et al.*, 2005; Neiuwenhuis *et al.*, 2000; Lorax, 2003). A summary of some of the applications of membrane separation for the mitigation of AD is presented in this section and two case studies are presented in Section 8.

The removal of pollutants from acidic drainage can be accomplished by a number of methods. As an example, iron and manganese easily form insoluble hydrates that can be removed by neutralization, aeration and settling; however, other dissolved salts such as sulphate, calcium, and magnesium are not removed and high quality water cannot be produced. In this case, the

discharge water would still have elevated amounts of dissolved solids. Almost complete removal of TDS from AD can be achieved by ion exchange, distillation and RO. All of these generate a high quality water stream that can be either reused or discharged with minimal impact on the receiving environment.

Using RO for the recovery of potable water from AD was reviewed by Awadalla and Hazlett (1992). The RO treatment of AD often generates considerable volumes of concentrate that needs further treatment and subsequent disposal. It should be noted that the concentrate stream contains much higher levels of metals and has gone through volume reduction, which can improve the efficiency of chemical treatment. If the levels of metals or components of interest in the concentrate stream are sufficiently high, it could be further processed and generate revenue to cover part of the costs of the treatment operation (Riedinger and Schultz, 1996; Wilmoth, 1973; Hill *et al.*, 1971; Awadalla and Kumar, 1994).

RO or NF can also be utilized after lime treatment and neutralization as suggested by Awadalla and Hazlett (1992). A cost analysis is required to determine the optimal arrangement of the RO and the neutralization steps. A combination of ion exchange and RO can also be utilized for the treatment of AD or any other water with extreme pH values and high metal content. This combination of processes could overcome the limitations arising from the high concentrations of calcium sulphate and/or iron which could create serious fouling problems (Hill *et al.*, 1970, 1971; Blackshaw *et al.*, 1976).

For applications where complete demineralization of the wastewater is not required, the use of a UF process can yield adequate rejections of contaminants and provide a lower cost option to a RO or NF. Bhattacharyya *et al.* (1979a) utilized a negatively charged noncellulosic UF membrane for treating AD. Use of a UF process provides a broadly applicable technique that can simultaneously reject various inorganic metal ions present in wastewaters and effluents. A high UF permeate recovery rate with good water flux and low calcium sulphate and iron concentrations are essential for the purposes of water reuse. Using a single stage UF process without an intermediate settling step, a water recovery of only 90% was reported. A pH of 4 and a channel velocity of 200 cm/s (Reynolds number of 6000), was determined as the optimal

conditions to minimize membrane fouling. The flux loss was reported to be less than 30%, even at TDS levels of 16 g/L. High iron and aluminum rejections of 98% and 85% respectively were reported, but calcium and magnesium rejections were only 50% and 73% respectively (Bhattacharyya *et al.*, 1979a).

Water recoveries of up to 97% and improved UF permeate quality can be achieved with an inter-stage settling step. The study by Bhattacharyya *et al.* (1979a) consistently produced permeate with calcium sulphate concentrations considerably below the saturation level whereas in the lime neutralization process, the treated water was very high in calcium sulphate. The cost for treating 1000 US gallons of AD with UF with inter-stage settling was estimated at \$1.33 USD which included the cost for membrane replacement, pumping and lime. A case study discussed later in the report shows significant cost savings for this treatment process compared to the conventional clarifier system (coagulation, flocculation and sedimentation) with significant improvement in the removal efficiencies for Cd, Cr, Pb, Mg and Zn (Bhattacharyya *et al.*, 1979a).

CANMET-MMSL used a polyethersulfone (PES) UF membrane, with a molecular weight cut-off of 5000 daltons, to test an AD with a total TDS of 5.4 g/L using a bench scale system as shown in Figure 4.1 (Mortazavi and Chaulk, 2008). During these experiments the membranes were tested at operating pressures of 200 to 400 psig. Higher operating pressures were tested to determine the point at which membrane fouling would become a problem by affecting the permeate flux and permeate quality.

Tables 4.1a and 4.1b show the results of the experiments in terms of percent rejection (%R) and the feed and permeate compositions. The results presented are the averages of duplicate experiments. The tables show sulphate removals of as high as 74%, corresponding to a sulphate concentration of 782 ppm in the permeate stream, and metals removals between 66% and 86%. Although the treated permeate would not meet the MMER discharge criteria, depending on the operation and the application of the permeate stream within the process, UF could be an effective and lower cost tool, compared to NF and RO.

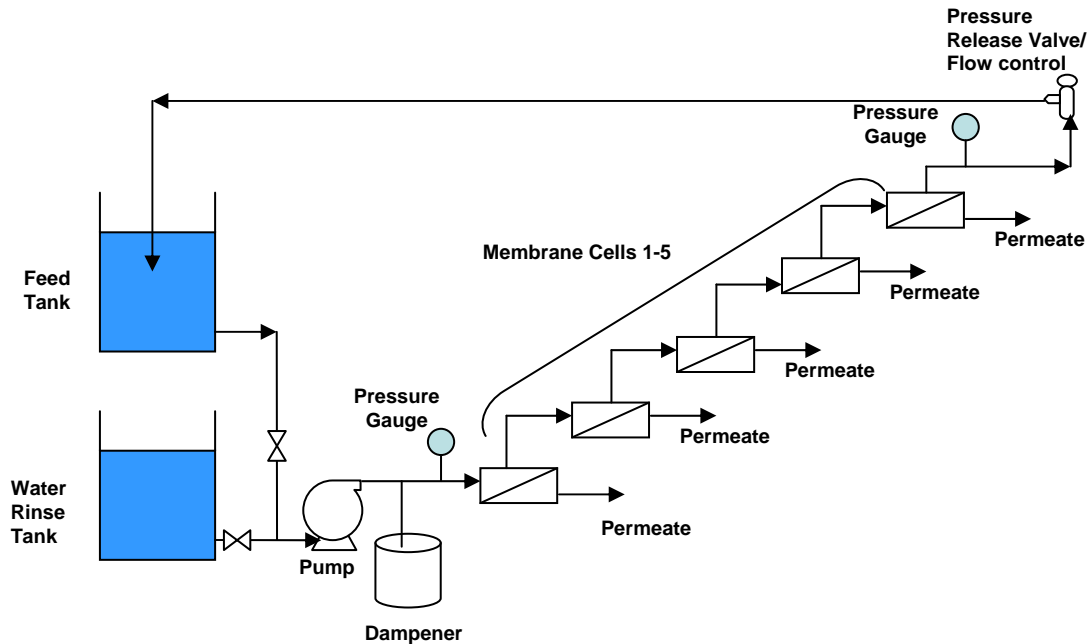


Figure 4.1. General schematic diagram of CANMET-MMSL bench scale membrane test system

Table 4.1b show permeates fluxes of $99.72 \text{ L/m}^2\cdot\text{h}$ at 200 psig and $144.72 \text{ L/m}^2\cdot\text{h}$ at 400 psig. Such high permeate fluxes would have a positive impact on the pump sizes in a large scale operation and the energy costs related to pumping energy consumption.

Table 4.1a. Rejection data for a PES UF membrane tested with actual AD sample at 200 and 400 psig.

Pressure (psig)	% Rejection	
	200	400
Al	69.04	86.46
Ca	47.92	69.25
Cu	43.61	66.00
Ni	41.71	68.56
Fe	61.80	80.99
Mg	48.51	70.52
Mn	46.34	68.73
S _{total}	58.80	74.43
Zn	44.71	68.37
SO ₄	54.38	74.33

Tables 4.2a and 4.2b show the results of the experiments in terms of percent rejection (%R) and the feed and permeate compositions for a PES NF membrane tested with the same AD sample tested at feed pressures of 200-500 psig. The tables show sulphate concentrations of as low as 384 corresponding to a percent rejection of 88%. Rejection values in the range of 82% to 99.99% were achieved for the different metals present in the solution.

Table 4.1b. AD solution feed and permeate compositions obtained from a UF membrane test at 200 and 400 psig.

Pressure (psig)	200		400	
	Feed	Permeate	Feed	Permeate
pH	2.32	2.38	2.33	2.55
Conductivity (mS/cm)	4.18	2.78	4.17	2.05
Al (ppm)	118.80	36.78	117.10	15.86
Ca (ppm)	252.70	131.60	249.50	76.72
Cu (ppm)	3.05	1.72	3.50	1.19
Ni (ppm)	0.40	0.23	0.40	0.13
Fe (ppm)	400.30	152.90	395.20	75.11
Mg (ppm)	133.60	68.79	131.30	38.71
Mn (ppm)	12.17	6.53	12.09	3.78
S_{total} (ppm)	1038.00	427.70	1021.00	261.10
Zn (ppm)	1.55	0.86	2.09	0.66
SO₄ (ppm)	3071	1401	3046	782
Permeate Flux (L/m².h)		99.72		144.72

Table 4.2a. Rejection data for a PES NF membrane tested with actual AD sample at 200 and 400 psig.

Pressure (psig)	% Rejection		
	200	400	500
Al	85.17	93.98	91.44
Ca	75.32	85.60	84.26
Cu	72.95	83.36	82.78
Ni	93.43	99.99	99.99
Fe	81.46	91.76	89.82
Mg	74.33	85.51	82.62
Mn	74.33	84.83	82.16
S_{total}	78.49	88.14	86.89
Zn	64.52	83.17	82.32
SO₄	78.64	88.42	87.12

Table 4.2b. AD solution feed and permeate compositions obtained from a NF membrane test at 200 to 500 psig.

Pressure (psig)	200		400		500	
	Feed	Permeate	Feed	Permeate	Feed	Permeate
pH	2.28	2.57	2.38	2.76	2.11	2.45
Conductivity (mS/cm)	4.10	1.67	4.05	1.23	4.07	1.269
Al (ppm)	114.20	16.94	113.70	6.85	111.6	9.55
Ca (ppm)	242.70	59.91	240.70	34.67	239.2	37.65
Cu (ppm)	3.90	1.06	4.22	0.70	4.67	0.804
Ni (ppm)	3.85	0.25	0.37	ND	0.522	ND
Fe (ppm)	384.80	71.34	381.80	31.47	384.5	39.16
Mg (ppm)	127.80	32.80	126.80	18.37	126.7	22.015
Mn (ppm)	11.90	3.06	11.80	1.79	12.05	2.15
S _{total} (ppm)	992.70	213.55	989.00	117.25	991.7	130.05
Zn (ppm)	2.60	0.92	3.03	0.51	3.49	0.617
SO ₄ (ppm)	2950	630	2937	340	2982	384
Permeate Flux (L/m ² .h)		14.85		24.588		25.12

Nanofiltration and RO were used successfully at the Kennecott Utah Copper's Bingham Canyon Mine, currently a Rio Tinto property, to treat acidic drainage and contaminated groundwater. This mine has been in operation for over 100 years and more than 70 years of active leaching (20,000 – 70,000 gpm) has created a large groundwater contamination problem, including 62 million m³ of acidic water with a pH of <4.0 and 247 million m³ of sulphate water with sulphate levels of 1.5 to 9.2 g/L. Table 4.3 presents the results of the application of NF to wastewater treatment in Bingham Canyon Mine.

The water at the site contains high levels of Al, Ca, Cu, Fe, Mg, Mn, Zn, SO₄, TDS and pH's of ~ 2.9 to 3.4. The highest levels of contaminants reported were; 92,000 ppm of TDS, 73,800 ppm of sulphate, 9,900 ppm of Mg, 5,960 ppm of Al. The rest of the contaminants were in the range of 150-500 ppm (Bayer, 2004).

The leach water and the acidic groundwater were prefiltered to remove solid particulates and were pumped directly to the NF membrane following the addition of an antiscalant agent. The

permeate was discharged and partly recycled, the wash water and the concentrate were returned via scavenger cells and tailings lines to the tailings impoundment. The water from a sulphate plume was directly treated with an RO system and the permeate was combined with the NF wash water and permeate stream and then discharged. Table 4.3 presents the typical leach water NF results showing greater than 97% solute retention. The NF and RO systems used were single pass units. The concentrations of some contaminants, such as Cu, Zn and pH, are over the limits of the Canadian Metal Mining Effluent Regulations (<http://www.ec.gc.ca/nopp/docs/regs/mmer/>), however, it was reported that they met the process objectives.

Table 4.3. Typical stream compositions from the NF treatment of leach water from the Bingham Canyon Mine (Bayer, 2004).

Parameter	Feed (ppm)	Permeate (ppm)	Concentrate (ppm)	R (%) - Solute Retention
Al	5,959	119	8,780	98.0
Ca	488	12	726	97.5
Cu	153	2	250	98.7
Fe	420	11	640	97.4
Mg	9,910	229	14,750	97.7
Mn	472	12	720	97.5
Zn	228	6	350	97.4
SO ₄	73,796	1,690	109,940	97.7
TDS	92,000	2,095	137,500	97.7
pH	2.9	2.5	3.0	-

The primary difficulty was gypsum scaling inside the pressure vessels and the concentrate lines which was resolved after the addition of a proper antiscalant to the feed stream.

Before being fed to the RO system, the sulphate plume water was treated with UV for disinfection and pre-filtered. The permeate was partly chlorinated and added to the drinking water system at the site. Table 4.4 shows the results of the RO treatment process at Bingham Canyon Mine.

Table 4.4. Typical stream compositions from the RO treatment of the sulphate plume water from the Bingham Canyon Mine (Bayer, 2004).

Parameter	Feed (ppm)	Permeate (ppm)	Concentrate (ppm)	R (%) - Solute Retention
Ca	438	1	1,743	99.8
K	5	0.01	20	99.8
Mg	144	0.4	574	99.7
Na	74	0.2	296	99.8
Cl	157	0.5	624	99.7
SO ₄	1,291	4	5,139	99.7
TDS	2,355	7	9,372	99.7
pH	6.7	5.5	6.8	-

The important considerations for the treatment process were: feed water characterization, pretreatment requirements, membrane selection, array design, flowrates, recovery, permeate flux, antiscalant selection, membrane cleaning (chemicals, temperature, pH, cleaning duration and frequency) and post-treatment requirements. This was an example of a successful large scale membrane operation where > 99% solute rejection was achieved to generate a high quality discharge stream despite high potential for membrane scaling and fouling which was managed by the addition of an antiscalant.

A number of studies by Riedinger and Schultz (1996), and Wilmoth (1973) assessed the feasibility of the production of potable water from AD. The mine water feed to the system was at pH < 3.0 and TDS of 100 mg/L. The tests were conducted with a variety of membranes including cellulose acetate (CA) high rejection membranes. At present, there are commercially available materials superior to CA for AD treatment applications. Metal rejections of 98 to 99% were achieved and no significant sulphate or iron related scaling problems were reported. The operating pressures for the tests ranged from 4.1 to 5.5 MPa (595-798 psig). Water recoveries of up to 92% were achieved during short periods of operation. It is expected that similar tests with

high flux, low pressure RO membranes (in the range 200-300 psig) would be more energy efficient.

In similar tests with an AD feed containing ferrous iron conducted by Wilmoth (1973), iron fouling was observed, this was remedied by the addition of a 5% sodium hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$) solution to remove the iron precipitate from the membrane surface. The iron fouling was prevented by maintaining a lower pH.

Bhattacharyya *et al.* (1979b; 1982) studied the rejection of metal species and different anions in membrane treatment of AD. In these tests, which were conducted at pH 3.0, virtually no metal hydroxide precipitation was observed and the metals rejected were dissolved. Increasing the pH to 4.0-4.5 resulted in 95% of iron and 30% of the total Al precipitating, thus allowing for simultaneous separation of precipitated and dissolved metals. Proper hydrodynamics in the membrane module and proper sizing of the spacer in a spiral wound module could allow for the separation of TSS without a loss of flux. Also, UF pretreatment could greatly improve the results.

Sastri (1978) and Malaiyandi and Sastri (1981) applied RO to synthetic and actual mine effluent and studied the separation of Ca, Zn, Mg, Mn, Cu, Ni, Al, and Fe as nitrates, chlorides, and sulphates and achieved metal rejections in the order of 95-99%. Table 4.5 presents the results obtained by Wilmoth *et al.* (1978), studying the recovery of trace elements from AD by RO.

Other studies have warned against fouling due to the precipitation of calcium sulphate and severe reduction in the permeate flux (Harries, 1985; Jarusutthirak *et al.*, 2007). The use of the antiscalant sodium hexametaphosphate prior to the RO unit was shown to be effective in dealing with this issue.

Table 4.5. RO trace element rejection data for a synthetic AD sample (Wilmoth *et al.*, 1978).

Parameter	Feed (mg/L)	Permeate (mg/L)	Concentrate (mg/L)	Rejection (%R)
As	2.29	0.01	3.58	99.6
B	2.01	0.88	3.08	56.2
Cd	0.83	0.006	1.22	99.3
Cr	0.54	0.01	0.82	98.1
Cu	6.18	0.01	9.12	99.8
Hg	0.28	0.06	0.17	78.6
Ni	0.74	0.01	1.10	98.6
P	1.50	0.32	1.93	78.7
Se	1.17	0.11	1.83	90.6
Zn	6.25	0.06	9.63	99.0
pH	2.2	2.0	3.6	-
Acidity	1340	130	2070	90.3
Al	5.0	0.20	7.8	96.0
Ca	370	0.60	590	99.8
Fe ²⁺	150	<0.10	230	99.9
Fe _{Total}	170	0.30	270	99.8
Mg	110	0.20	180	99.8
Mn	5.0	0.05	7.1	99.0
Na	400	0.30	640	99.9
Specific Conductance (µmhos/cm)	5,980	60	8,540	99.0
SO ₄ ²⁻	2,990	22	4,610	99.3
TDS	4,040	24	6,290	99.4

A more effective approach to mitigation of AD would be the use of a membrane separation stage (UF, NF or RO) in combination with a conventional neutralization process. Application of membranes in high flow situations, such as that normally encountered in mining operations, could result in the production of considerable volumes of concentrate which must undergo further treatment before disposal. The neutralization of the concentrate stream produces sludge with high levels of metal hydroxides and a clarifier stream that cannot be discharged into surface waters because of high TDS levels. Part of the RO concentrate can be combined with the raw AD feed to the RO plant which would reduce the volume of contaminated water (Hill *et al.*, 1970; Blackshaw *et al.*, 1976). An alternative to the above approach would be to place the membrane unit after the AD pretreatment processes which are likely to include neutralization, aeration, coagulation and flocculation.

Treatment of AD with conventional static or cross-flow membrane filtration, even with the use of properly selected antiscalants at the right dosage, is susceptible to colloidal fouling and mineral scale formation, especially at high TDS concentrations and in the presence of sulphates and carbonates. New Logic Research Inc. (<http://www.vsep.com>) has developed a Vibratory Shear Enhanced Processing System (V-SEP). V-SEP technology utilizes vibrational oscillation of the membrane surface with respect to the liquid phase which prevents the build up of suspended solids or precipitated colloidal particles on the membrane surface. The shear created by the lateral movement of the membrane surface keeps the colloidal particles in suspension. The result is improved relative throughput per area of membrane. The vibrational shear combined with the laminar flow of the feed solution across the membrane surface allows for a very high recovery. Water recoveries of up to 97% have been achieved with the treatment of AD in a single V-SEP pass (Miller, 2005). A single V-SEP unit has a throughput capacity of 5 to 200 US gallons per minute with a footprint of 20 square feet and a power consumption of 15 hp.

In a typical V-SEP operation, the AD feed is pH adjusted to precipitate calcium sulphate and other low solubility mineral salts. The feed is heated to reduce the viscosity of the water and is pumped into the V-SEP pack. The concentrate which could be as high as 15% of the feed volume would still need treatment and disposal. Table 4.6 shows the permeate composition from a V-SEP system in comparison to the discharge stream from a lime treatment process. The membrane that generated these results was a polyamide RO membrane with a nominal salt rejection of 99% and a maximum pressure and temperature of 600 psig and 60 °C. The life expectancy of a V-SEP module is 2 years. The throughput of a V-SEP unit at 20 gfd (US gallons/sq ft/day) is reported as 10,500,000 gal/year, with an annual power cost of \$7,180 US and system maintenance and cleaning costs of \$8,640 US (Miller, 2005).

Table 4.6. AD treatment data of a V-SEP module with a polyamide membrane compared to lime precipitation (Miller, 2005).

Component	Feed (mg/L)	Lime Precipitation (mg/L)	V-SEP Permeate (mg/L)
TDS	10,000	3,000	240
pH	2.7	8.5	8.5
Ca	490	600	36
Mg	420	350	18
Na	70	70	6
Fe	1,100	0.1	<0.1
Mn	182	3.6	<0.1
Cu	186	<0.1	<0.1
Zn	550	<0.1	<0.1
SO ₄	8,000	2,000	100

Pisa and Gulikova (2005) presented the results of field testing of RO for the treatment of AD from an open pit brown coal mine in the Czech Republic. This site had high concentrations of sulphates, calcium, iron, manganese, hydrocarbons, ammonium and suspended solids. High contaminant rejections were achieved and high quality water was recovered. Three AD streams were treated with a RO membrane system and permeate recovery rates of 0.8 m³/h at 65 bar (940 psig) were achieved. The results of one set of RO treatment tests are presented in Table 4.7.

Table 4.7. Results of the RO treatment of an AD stream from an open pit brown coal mine.

Parameter	Feed Composition (mg/L)	Permeate Composition (mg/L)	Concentrate Composition (mg/L)
pH	6.8	4.3	6.3
Fe _{total}	10.5	<0.1	21.6
Mn	2.2	<0.05	5.7
SO ₄ ²⁻	1,020	7	2,960
Dissolved Solids	1,700	116	4,830
Ca	290	0.4	700
Mg	112	0.09	260
NH ₄ ⁺	11.5	0.9	28
Zn	<0.04	<0.04	0.34
V	0.02	<0.006	0.06
Ba	0.05	<0.006	0.10

Pisa and Gulikova (2005) noted that the RO concentrate would require treatment before disposal, but did not present any results for the processes used. The brine treatment process proposed

involved the addition of ash from the desulphurizing process flue gas, which was obtained from an onsite power plant, and this ash contained 30% free CaO. Laboratory tests indicated that the soluble ions in the RO concentrate were bound to the ash particle and the precipitate remained stable when disposed of in designated areas in the open pit.

The studies presented in Sections 4 and 4.1 demonstrated the technical and cost effectiveness of membrane separation for the mitigation of mine effluents and AD. Significant progress has been made in all facets of membrane separation, some of the most important advances were made in membrane material design, membrane fabrication, and module and system design. The challenge, however, remains in the control of fouling, reducing pretreatment and developing cost-effective and environmentally benign brine disposal methods.

4.2. Post Treatment and Brine Disposal

Some of the commercially available methods of brine treatment for disposal are lime neutralization, chemical precipitation, and vapor compression crystallization. These can be combined, in the process, with other technologies such as a brine concentrator, evaporator, or a seeded-slurry falling film evaporator. Some brine treatment options could be more site specific depending on the mining operation and the nature of the infrastructure and facilities available on site. For instance, some sites may use the ash from desulphurizing of the flue gas from a power plant as reported by Pisa and Gulikova (2005) or in cold climates the brine could have application in drilling operations in permafrost regions as a source of saline drilling water.

An investigation of technologies for the treatment of underground mine water discharged by Grootvlei Proprietary Mines in South Africa, assessed RO (Schoeman and Steyn, 2001). The TDS in the feed was 2000-4500 mg/L. It was reduced to potable water standards at 85% water recovery. The flowrate of the brine stream for an 80 ML/d plant at 85% recovery was estimated to be 12 ML/d. The brine disposal option considered was the use of evaporation ponds, although forced evaporation was also considered as an option. The estimated capital costs for a brine flow rate of 12 ML/d was \$14.7M US dollars for unlined evaporation ponds (based on \$1222/1000L

of brine), \$57.1M for lined evaporation ponds, \$18M (based on \$1222/1000L of brine) and \$75.3M for ocean disposal.

Treating AD, mine effluent or other contaminated streams in mining operations with membrane separation creates a concentrated stream which, depending on the water recovery, could be highly saline. Despite the fact that in some membrane applications water recoveries in the range of 80% to 95% could be achieved, the range of flow rates encountered in mining operations and processes can be high and the volumes of highly saline or brine streams would be quite large. If for operational reasons the water recoveries cannot be maximized, the cost of brine disposal could become prohibitive.

5. MEMBRANE PROCESS ECONOMICS

The capital and operating costs presented in this section are general guidelines. The materials for construction of the plant (i.e., the alloys used for piping, types of welds, pumps, plant operating pressure, instrumentation, CIP system, plant configuration (single *versus* double pass, *etc.*)) would have a large impact on the capital cost of the plant. On the other hand, plant control options such as constant pressure, constant retentate or constant concentration factors, membrane cleaning frequency and cleaning chemicals, membrane life and replacement would impact the operating costs of the system. Also, the capital and operating costs associated with pretreatment, post-treatment and brine or concentrate disposal and measures for membrane fouling control can be large.

Some examples of general components of a membrane plant are:

System components:

Pretreatment

- pH Adjustment System;
- Antiscalant Mixing and Dosing System;
- Hydrocyclone Separator (If feed is from surface water);
- Multi-Media Filtration (MMF) System with rubber lining and flange connections; and
- Cartridge Filtration System (316L SS).

Primary Treatment

- RO/NF/UF System: Side-Port pressure vessels;
- Feed and permeate piping;
- Membranes module elements;
- Pumps with Energy Recovery Turbine (ERT);
- Concentrate piping; and
- Fully automated Clean In Place (CIP) system.

Post Treatment

- pH Adjustment System; and
- Chlorination System.

Other

- NEMA 4 enclosed control panel;
- Instrumentation;
- Control system: SCADA with VIEW interface;
- Epoxy coated 304SS frames for mounting components; and
- Drip Pans.

5.1. Membrane System Capital Costs

The capital costs include the following components (Scott and Hughes, 1996):

- Construction and Civil Engineering Costs – Only large plants have associated high civil engineering costs. When membrane processes are compared to alternative competing processes, cost savings are often available on the civil engineering costs of the plant since these plants are compact and have small footprints and can be built on flat slab foundations in standard single story industrial buildings or skid mounted for small, temporary operations.
- Mechanical and Electrical Costs - Membrane Modules – Costs of the membrane modules vary significantly from well over \$2500 Cdn/m² for advanced ceramic membranes to below \$50 Cdn/m² for reverse osmosis polymeric membranes. Also the module configuration is a determining factor for the membrane costs. The costs usually increase in the following order: MF < UF < NF < RO. RO is the most widely utilized membrane separation process in the world due to its application water desalination for drinking water supply. For small scale systems, membrane module costs could account for about 10% of the system cost. This percentage will increase for processes with throughputs of 100 m³/day and above, and one could expect the cost of modules to increase by up to 40% of the overall system cost.
- Other Mechanical Equipment – The costs of other components could vary. Membrane systems are provided with the pumps, pipe work, valves, etc., however, the treatment conditions determine the materials of construction for the pumps, valves, pipe work, etc. On a large system, mechanical equipment other than the membrane modules could account for up to 40-45% of the overall system cost.
- Electrical Control and Instrumentation – As a rough guideline, electrical and control systems and instrumentation account for 10-15% of the overall system cost.
- Installation and Commissioning – The installation of the system is normally not less than 55% of the overall cost of the system.

The primary determining factor in costing a membrane plant is the total surface area and the throughput of the system and the potential for fouling. Table 5.1 shows the cost of a crossflow

microfiltration plant (Sirkar, 1992). The cost of filtration media is only a small fraction of the total installed cost (15% to 25%). The total installed cost does not include the civil engineering and plant construction.

Table 5.1. Estimated cost of a crossflow microfiltration system – Present value 1989 costs.

Material	Cost of Media (\$/m²)	Cost of Installed system (\$/m²)
Polymers	65-969	1,722-6,997
Ceramics	861-3,229	2,476-7,535
Metals	646-1,292	2,152-9,688

5.2. Membrane System Operating Costs

The operating cost of a membrane system varies depending on the type of feed and the requirement and frequency for cleaning as well as the energy consumption for pumping. The main operating cost considerations are:

- Membrane replacement – In many applications, membrane replacement is the major operating cost. Membrane life expectancy varies from less than six months under aggressive waste processing conditions to over five years for potable water treatment applications. Ceramic membranes have a much longer lifetime than polymeric membranes under similar treatment conditions. The longer life of the ceramic membranes balances their higher costs.
- Energy – The main energy cost for membrane systems is the energy expended for pumping. Table 5.2 shows typical energy costs for the main membrane process (Scott and Hughes, 1996).
- Operating Labor – Labor is primarily required to conduct the membrane exchange and general plant maintenance, as well as for performing the cleaning cycles and data logging. In general, the labor costs for a membrane plant operation are lower than competing processes.

- Cleaning – This refers to the costs of cleaning chemicals and their disposal which are generally in the order of 5-10% of the overall operating costs.

Table 5.2. Typical energy costs for the main membrane process.

Process	Driving Pressure (bar)	% Recovery	Typical Energy Consumption (kWh m⁻³)
Dead End Microfiltration	0.5	90	0.05
Crossflow Microfiltration	1.0	5	1.1
Ultrafiltration	2.0	10	1.1
Nanofiltration	5.0	70	0.4
Brackish Water Reverse Osmosis	20	70	1.6
Sea Water Reverse Osmosis	40	50	4.4

6. ARSENIC AND SELENIUM REMOVAL TECHNOLOGIES

This section provides a brief discussion on the arsenic and selenium removal technologies. Several technologies appear to hold promise for arsenic and selenium removal from mine effluents in the $\mu\text{g/L}$ range, e.g., $<10 \mu\text{g/L}$. These processes include:

- adsorption;
- ferrihydrite adsorption;
- conventional water treatment;
- ion exchange;
- membrane separations including: reverse osmosis, emulsion liquid membranes and nanofiltration;
- reduction;
- ferrous hydroxide; and
- biological reduction, such as *Pseudomonas stutzeri* bacteria/immobilized alginate enzymes, *Clostridium* Bacteria and Biological Anaerobic Reactors.

Success in achieving effective selenium removal will depend on the site-specific characteristics of the individual wastewater to be treated. Those technologies that appear to hold promise for effective selenium removal include: ferrihydrite adsorption, RO and NF, iron reduction and biological reduction.

Hybrid membrane separation processes such as the combination of adsorption on activated alumina or binding to a selective polymer followed by microfiltration, has been successful for effective removal of As and Se from contaminated water and groundwater for concentrations from several hundred mg/L to $< 10 \mu\text{g/L}$ (Mortazavi and Cooper, 1998). It has been shown that the presence of competing ions at high concentrations could reduce the adsorption capacity of the adsorbent. The adsorbent can be regenerated and reused, generating a highly concentrated solution of As or Se, which could then be extracted if justified by their market price.

Macintosh (2002) reports the use of hybrid membrane process for the removal of arsenic from mine water at Bendigo Mining in Australia. The mine water was a complex mixture of salts, H₂S, metals such as As, Hg, Zn and Fe, with a pH of 5-6 and TDS level of 5,100 ppm. The focus of the treatment was to address the removal of H₂S in a controlled fashion, prepare the stream for oxidation of As and achieve conditions suitable for adsorption of As by flocculation. The stream was then pre-filtered and desalinated by RO.

7. BIOLOGICAL TREATMENT OF MINE EFFLUENT AND WATER

7.1. Membrane Bioreactors

Metal contaminated wastewaters usually contain compounds that may be toxic or inhibit the growth of micro-organisms. These streams are often saline or exhibit extreme pH values and are suitable for treatment using extractive membrane bioreactors.

In recent years, membrane bioreactors; coupled membrane system to a bioreactor; have attracted a great deal of attention both in the industry and academia. This has been due to the advantages this process offers over conventional biological wastewater treatment systems alone (Van Houten *et al.*, 2001; Visvanathan *et al.*, 2000). Membrane bioreactors (MBRs) have emerged as viable alternative wastewater treatment processes in areas where space (*e.g.* settling ponds) and water resources are limited. MBRs are also gaining popularity as alternatives to treat industrial wastewaters with high total dissolved solids, where settling and clarification are often a problem (Enegeess *et al.*, 2003; Van der Roest *et al.*, 2001). Membrane bioreactors have also been applied to the treatment of AD.

In membrane bioreactors biomass is used to degrade contaminants and membrane filtration is applied to separate the biomass from the water (Scott and Ollis, 1995). As a result, in these systems the settling characteristics of biomass are no longer important in determining effluent quality which makes it possible to operate with a higher biomass concentration. Presently, this hybrid process has been applied to the treatment of: high-strength wastewaters (Boman *et al.* 1991; Brindle *et al.* 1999), disinfection of treated water, trace xenobiotic contaminant removal and nitrate removal (McCleaf and Schroeder, 1995). More information can be found in the reviews written by Brindle and Stephenson (1996) and the AWWA Membrane Technology Research Committee (1998).

Wider acceptance of membrane bioreactor technology has been hindered primarily by the high susceptibility to biofouling and the system's relatively high pumping energy requirements for

recirculating wastewater through membrane modules. This problem can and has been partially alleviated by utilizing submerged membranes (Yamanoto *et al.*, 1989) in which the filtration is vacuum driven. A further improvement to reduce membrane fouling may be the use of air scrubbing outside the membrane surface. From an engineering perspective, this technology can be easily implemented without the installation of separate containers containing the membrane modules and thus can be used in plant retrofitting to increase water production and improve water effluent quality. Zenon ZeeWeed™ is an example of such a system (Zenon, 2004). Another consideration with the application of MBRs is the temperature sensitivity and operation in colder environments.

8. CASE HISTORIES

Several summaries of large scale and pilot processes have been presented above. The selected case studies in this section provide examples of membrane separation performance, associated capital and operating costs, where available, and a comparison of membrane separation with conventional treatment options.

These case studies cover different membrane applications in various scenarios and provide comparative examples of membrane and conventional wastewater and effluent treatment technologies. All the examples show that the application of membrane separation technology to mitigation of AD and water management in mining and metal processing operations provides opportunities for water recovery and recycle. As well, the examples show that membrane separation could provide the possibility of improving process economics and performance while exceeding environmental water discharge criteria.

8.1. ASARCO Inc. Globe Plant in Denver Colorado

This case study presents a summary of a feasibility study conducted at Asarco's Globe Plant to reduce the operating costs, sludge volume and discharge water quality of the existing wastewater treatment facility. A number of process configurations were examined including a membrane separation polishing system (Green *et al.*, 1993).

Asarco Inc. is a large producer of non-ferrous metals such as copper, zinc, lead, silver and gold. The Asarco Globe plant has been a metal refining facility since 1886, producing a wide range of non-ferrous metals. In 1986, the company installed and operated a chemical precipitation system to treat wastewaters containing arsenic, selenium, lead, zinc, cadmium, nickel, iron, manganese, copper, chromium and silver.

The Asarco Globe Plant system utilized ferric sulphate to first remove arsenic and selenium followed by lime addition for the removal of manganese, cadmium and zinc. The pH is adjusted

to from 4 to 9.8. The system operating temperature was maintained at 10-20°C. No complexing agents were added to the wastewater.

The wastewater feed entered the process train into a surge/blend tank where sodium carbonate was added (1), followed by ferric sulphate (2), the sludge was then filtered in press filters and dewatered and sent to sludge processing. Lime and sodium sulphide at pH 9.8 were added (3), followed by filtration and sludge dewatering. The final effluent water pH was adjusted to pH 7.5 before final discharge. The total operating cost of the wastewater treatment, including the depreciated initial capital cost was \$58.34 USD (in 1993) per 1000 US gal of treated wastewater. Figure 8.1 shows the block diagram of the precipitation process. Table 8.1 shows the concentration of the contaminants in the feed and the discharge water from the precipitation system.

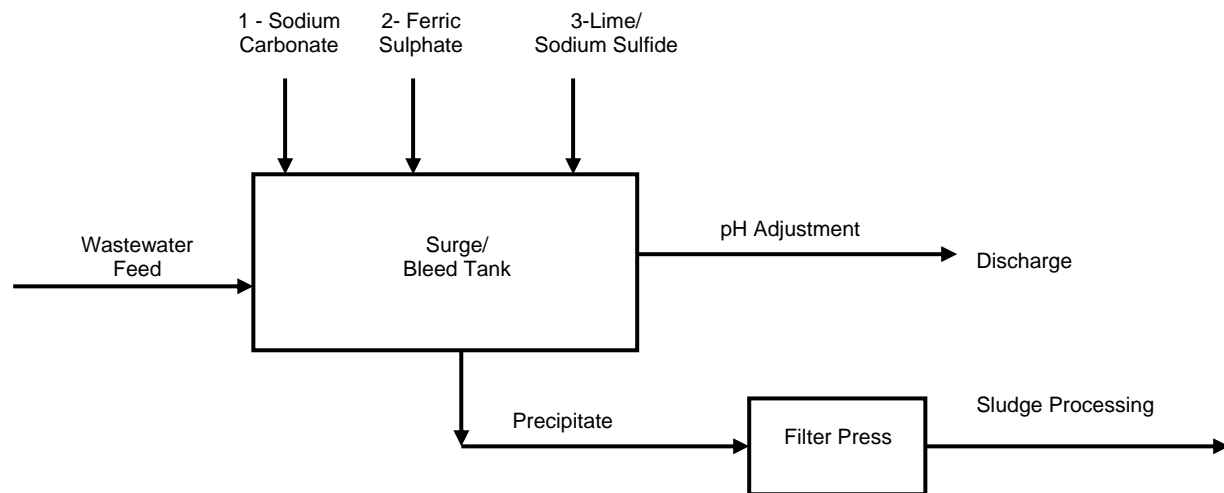


Figure 8.1. Block diagram of Asarco's precipitation process

Table 8.1. Asarco's Globe Plant precipitation system performance.

Component	Wastewater Feed (mg/L)	Treated Water (mg/L)
pH	4.0	~7
TDS	3000-10000	<3000
As (mg/L)	10.1	0.024
Se (mg/L)	0.056	<0.010
Cd (mg/L)	14.5	0.10
Zn (mg/L)	35.5	0.35
Pb (mg/L)	3.07	<0.050
Ni (mg/L)	0.060	0.025
Fe (mg/L)	0.986	0.100
Mn (mg/L)	3.33	0.120
Cu (mg/L)	0.07	0.020

In 1991, the company investigated the use of various types of encapsulated biomass for the extraction of the contaminants present in the Asarco wastewater; however, the biomass did not have the capacity for the levels of contaminants present. In a full-scale pilot plant study, the wastewater, after pretreatment, was first subjected to a membrane separation stage for reduction of all contaminants. This was followed by a biomass media extraction stage for heavy metal polishing, and finally a mineral media extraction stage for arsenic and selenium polishing. The final concentrate, which had a significantly reduced volume, was then put through the existing precipitation system that primarily treated the concentrate from the membrane stage and the stripping solution from the biomass polishing stage. Figure 8.2 shows the block diagram of the membrane separation system. Table 8.2 shows the compositions of the feed and the discharge water produced from the membrane separation system.

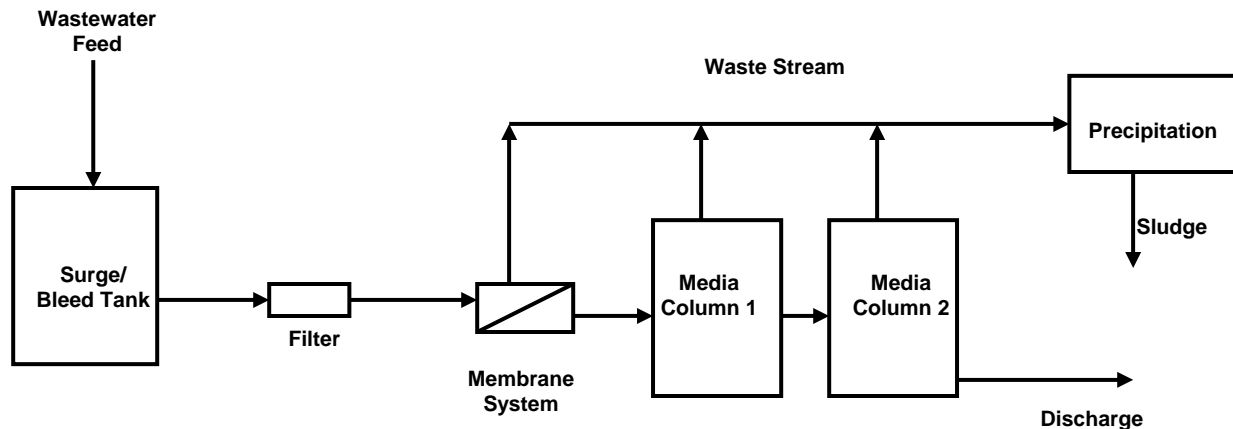


Figure 8.2. Block diagram of Asarco's membrane separation process

Table 8.2. Asarco's Globe Plant membrane separation system performance.

Component	Wastewater Feed (mg/L)	Treated Water (mg/L)
pH	4.0	~7
TDS	3000-10000	<1000
As (mg/L)	10.1	0.006
Se (mg/L)	0.056	<0.010
Cd (mg/L)	14.5	0.02
Zn (mg/L)	35.5	0.010
Pb (mg/L)	3.07	0.050
Ni (mg/L)	0.060	0.050
Fe (mg/L)	0.986	0.10
Mn (mg/L)	3.33	0.050
Cu (mg/L)	0.07	0.012

Water recovery from the treatment process was 80% and the treated water was discharged with contaminant levels below the discharge standards. The concentrated water from the membrane separation stage and the metal stripping from the biomass polishing stage were treated in the existing precipitation system. An overall 85% sludge reduction was realized.

Some of the difficulties encountered were; the variability of the feed water metal, the variability of contaminant concentrations and the presence of algae and bacteria in the feed water. These issues were handled by providing adequate pretreatment through the addition of an antiscalant and by adjusting the frequency of bio-medial regeneration cycles.

The operating cost of treating 1000 US gal of wastewater with the membrane system, including the depreciated capital costs, was reduced to \$15.67 USD (1995) from \$58.32 USD (1993).

Table 8.3 presents the costs and benefits of the precipitation and membrane system.

Table 8.3. Cost comparison between the Asarco’s precipitation and membrane systems per 1000 US gal treated wastewater. Costs are based on 1995 dollars unless otherwise specified.

Costs Items	Precipitation System	Membrane Separation System
Water Quality	Meets Discharge Criteria	Meets and Exceeds Discharge Criteria
Capital Cost (USD)	\$1,000,000 (1986)	\$300,000 (1993)
Reagent Cost (USD) (per 1000 US gal)	\$9.88	\$0.93
Direct Operating Cost (USD) (per 1000 US gal)	\$10	\$3.33
Sludge production (per 1000 US gal)	160 lbs	24 lbs
Total Treatment Cost (USD) (per 1000 US gal)	\$58.34 (1993)	\$15.67 (1995)

As the above table shows the membrane system reduced the amount of the generated sludge by 85% and reduced the operating cost by 73%, while producing better discharge water quality than the precipitation system.

8.2. Mexicana de Cananea mine in Cananea, Mexico

Open pit mines can accumulate enormous amounts of water, even in dry areas, from water run off, rain and snow melt and intrusion of ground water. Water accumulation can severely impact the hydrogeology of the area, can create a risk of flooding and may result in an interruption of mining operations. This situation was observed at the Berkley pit in Butte, Montana.

The Mexicana de Cananea mine, located in northern Mexico, was facing closure due to insufficient water and a threat of flooding of the operational parts of the mine because of an accumulation of water in the Cananea pit. The Cananea pit started accumulating water in the

1980's. At the beginning of mine operation, the company leached minerals directly in the pit and then utilized it as a reservoir for the pregnant leachate from dump leaching operations around the pit. As well, in the years prior to the study, the pit was used to hold the excess water from the hydrometallurgical system which was transferred to the pit in order to avoid spills. Eventually, the pit solution volume reached 17 Million cubic meters (4.49×10^9 US gal) with an average copper concentration of 0.70 g/L. At this point, pit water levels and evidence of channeling within the pit had jeopardized the operation of the mine (Harrison Western, 1997).

The mine decided to install a full-scale membrane plant to control the water levels. The plant was successfully 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 Cananea pit to the copper extraction plant, remove excess water from the leach circuits, and produce clean water for mine process water application. The membrane system was able to; dewater the leach solution, increase its copper concentration, recover clean water for reuse, reduce acid costs, and recover copper from excess raffinate and electrowinning electrolyte.

In 1995, initial pilot tests were completed with a small 10 - 15 US gpm membrane system to assist with the design of a system for a 4000 US gpm membrane plant capable of generating a 2000 US gpm concentrate stream with 1.6 g/L copper and 2000 US gpm of clean permeate suitable for reuse. The objectives of the large scale membrane plant were to; improve the feed copper concentration in the feed to SX/EW plant, increase the cathode copper production by more than 14%, create savings of \$212K in process water cost and \$27K in sulphuric acid costs, and reduce the pit water level.

Table 8.4 shows the concentrations of different components in the Cananea pit solution. The pit solution was processed in a full scale 4000 US gpm membrane plant. The pit solution was at pH 1.1, with a total TDS of 113,000 mg/L.

Table 8.4. Cananea pit solution composition.

Component	Concentration (mg/L)
Al	4400
Ca	220
Cu	800
Fe	21600
Mg	220
Zn	110
SO ₄	85500

The full scale membrane plant was commissioned in February 1997. Figure 8.3 shows the general diagram of the membrane plant and its performance with average stream flows. The copper recovery from the pit solution was reported to exceed 99% and the water recovery was about 43%. The concentrate solution reached an average copper concentration of 1.2 g/L. The permeate from the membrane plant was combined with the tailings solution and sent to the grinding and ore flotation circuit. 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.

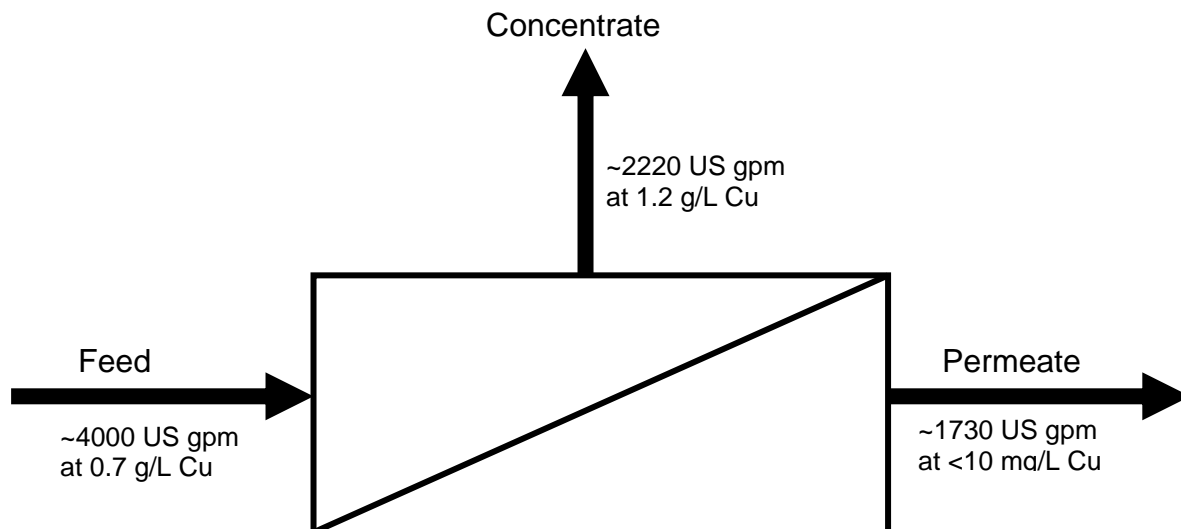


Figure 8.3. General diagram and performance of the Cananea membrane plant showing the average stream flows and concentrations

Process Economics

The typical capital cost for the membrane plant according to Harrison Western (1997) was \$1.5-\$2.5 USD/US gal/day. The operating costs included; power consumption, prefiltration and pretreatment operations, chemicals, membrane cleaning, and membrane replacement. Operating credits were the value of the copper increase in the feed to the SX/EW plant and the recovered permeate. The typical operating costs were \$1.00-\$2.00 USD/1000 US gal water recovered. The payback period for the plant was 1-3 years. The cost for a lime precipitation system, accounting for the loss of copper, would be approximately \$5.00 USD/1000US gal removed.

8.3. Desalination and Reuse of Acidic Drainage and Ash Water

This case study reviews the membrane plant put in place at the Sasol Technology Limited operation in Secunda, Republic of South Africa. At this plant, Tubular and spiral RO and EDR were used to treat AD and ash water and production of boiler feed water (Nieuwenhuis *et al.*, 2000). Sasol Technology Ltd. was able to design and operate a successful membrane operation which reduced water intake volumes.

The processes that were installed consisted of a tubular RO (TRO) system followed by a second RO system with spiral wound modules (SRO) for the recovery and treatment of ash water. For the treatment of AD, a combination of EDR and SRO was used to successfully convert AD to boiler feed water. The operating costs of the two processes were similar at R3.50/m³ of the final boiler feed water.

System Design

TRO-SRO system Design

Figure 8.4 shows a block flow diagram of the process used for the recovery of ash water and boiler feed water production.

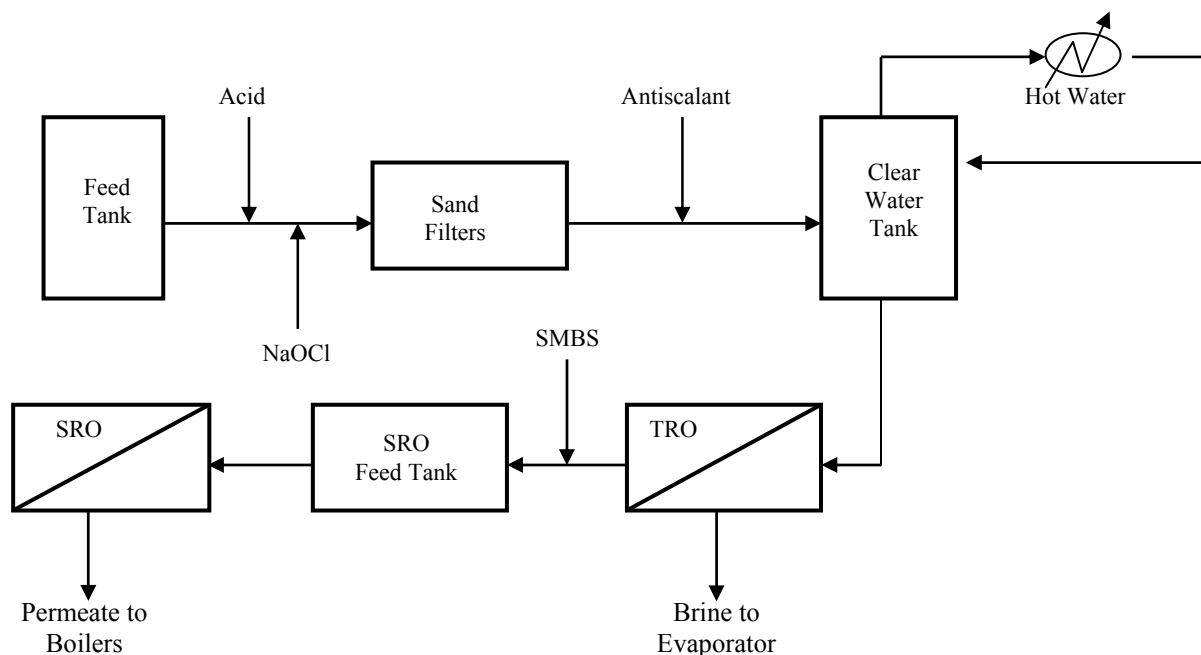


Figure 8.4. Block flow diagram of TRO-SRO plant for recovery of ash water

In this process the pretreatment of the feed included pH adjustment to pH 3.0 to 6.5 with sulphuric acid. Suspended solids (SS) were then reduced to 40 mg/L by sand filtration and an antiscalant was added. Chlorination was used and the ash water was heated to 27°C to minimize biofouling.

The membrane plant (TRO) consisted of 11 units, each of which was made up of 80 parallel branches with 10 modules in series, for a total of 800 modules with a total capacity of 230 m³/h. Flow reversal and sponge balls were used in thirty minute intervals for system cleaning. The plant was operated at a constant water recovery rate. Each unit in the plant produced 23 m³/h of permeate. The concentrate stream was treated using three falling film evaporators.

The permeate from the TRO plant was further treated with the SRO units. The SRO units had a production capacity of 128 m³/h and were operated at 90% recovery. The membranes used were high rejection polyamide RO membranes in a 10:5:3 configuration.

Performance criteria for the pretreatment process included targets for pH, SS removal, feed temperature and microbial counts. The operation did not always meet the performance criteria and problems were reported with sand filtration and hypochlorite dosing. During the operation, large variations in the SS concentrations in the feed stream were encountered with an average SS concentration of 146 ± 33 mg/L achieved. The sand filters were able to remove an average of 50% of the SS content of the feed stream.

TRO performance criteria included targets for permeate quality, salt rejection, standard membrane flux (flux at 4000 kPa (580 psig) and at 25°C) and CIP frequency. The feed to the TRO had a great deal of variability and the concentrations of feed constituents such as organic compounds, chloride, sodium, barium and calcium were at a higher concentration than the plant's original design values. The TRO was, however, effective in treating the feed and generating a permeate of a relatively constant quality. Table 8.5 shows the feed and permeate compositions and variability. The TRO system's standard flux was 524 ± 65.5 L/m².day. The reported variation in flux was due to the feed variation. No membrane fouling was observed and the average salt rejection, calculated based on conductivity measurements, was 94.5%. It was seen that the operation of an effective CIP regime was effective in preventing fouling in the TRO plant. The high TOC levels in the feed were an issue with respect to biofouling; however, the risk was managed by the introduction of an inorganic biocide.

Table 8.5. TRO feed and permeate compositions.

Component	Feed Concentration (mg/L)	Permeate Concentration (mg/L)
TDS	3998 ± 786	96 ± 38
Ca	422 ± 94	4.6 ± 3.2
Ba	0.2 ± 0.09	>0.2
Na	917 ± 79	48 ± 7
Cl	828 ± 238	44 ± 4
SO ₄ ²⁻	3254 ± 842	7.5 ± 5.1
F	18 ± 4.9	2 ± 0.3
TOC	52 ± 14	<10

The permeate from the TRO units was sent to the SRO units for further upgrading of the permeate to boiler feed water. Table 8.6 illustrates the performance criteria for the SRO plant.

Table 8.6. Performance criteria and the average performance of the SRO units of the TRO plant.

Component	Target	Average
Water Recovery (%)	90	88 ± 8.8
Conductivity (µS/cm)	<30	26 ± 6.1
CIP/Train/month	1	2.4
Flux (L/m ² .h)	25	23.5 ± 1.7
Feed Pressure (kPa)	1350	1390 ± 159

The major issue that was reported with the standard CIP was that it was not completely effective in mitigating biofouling which resulted in the lower reported flux in the SRO plant.

EDR-SRO system Design

The EDR-SRO plant was designed for the treatment of AD and the generation of boiler feed water. Figure 8.5 presents the process block diagram of the EDR-SRO plant.

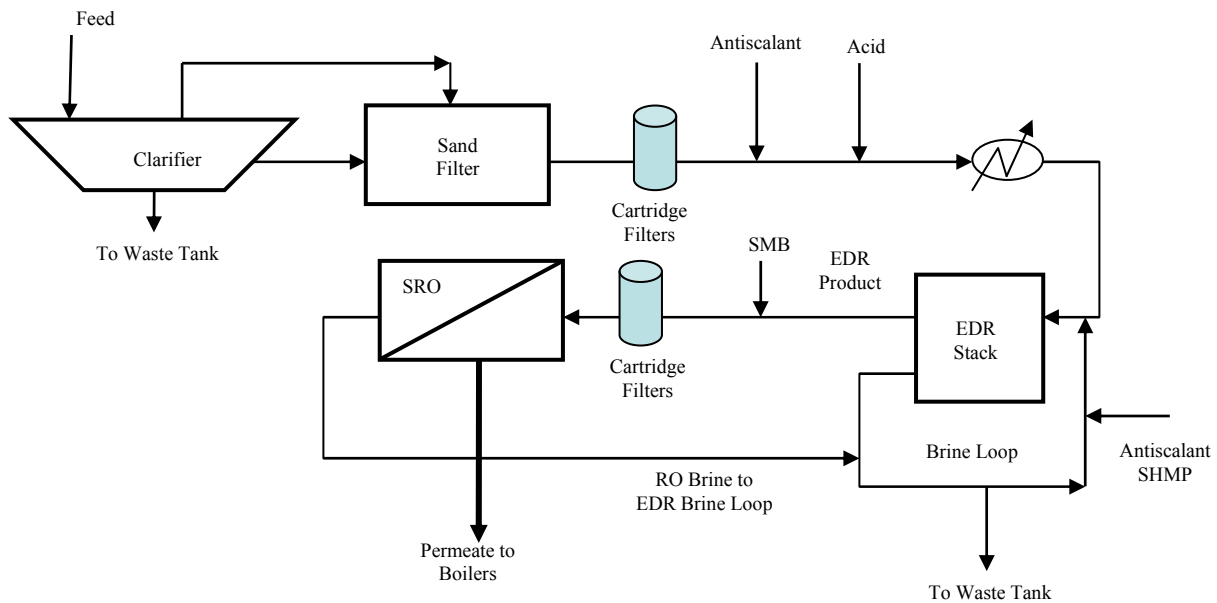


Figure 8.5. Block flow diagram of EDR-SRO plant for recovery of water from AD

Performance criteria for the EDR pretreatment processes were based on Silt Density Index (SDI) and on the iron and manganese concentrations leaving the cartridge filters units. The pretreatment train was able to produce an EDR feed with an SDI of less than 5. However the iron and manganese concentrations were higher than the design values, which was related to a decrease in mine water pH from 7.9 to 5.8, this issue was resolved by the addition of soda ash. Table 8.7 shows the targets and the average performance of the pretreatment train.

Table 8.7. Performance data for the EDR plant pretreatment process train.

Factor	Target	Maximum Value (mg/L)	Average (mg/L)
Fe input		0.62	0.37
Fe output	0.2	0.18	0.1
Mn input		0.81	0.42
Mn output	0.1	0.53	0.03
SDI	<5	>5	3.9

The EDR performance criteria were based on the frequency of EDR stack cleanings, salt rejection and water recovery. Table 8.8 shows the performance data for the EDR stacks. Based on the data presented, the EDR stacks performed well but the salt rejection was lower than the design target value which suffered because of higher water recovery.

Table 8.8. Performance data for the EDR stacks.

Component	Feed Concentration (mg/L)	EDR Permeate Concentration (mg/L)
TDS	3998 ± 786	1435 ± 438
Ca	422 ± 94	36 ± 15
Na	917 ± 79	358 ± 151
Cl	828 ± 238	121 ± 42
SO ₄ ²⁻	3254 ± 842	701 ± 487
TOC	2.12 ± 1.1	1.98 ± 0.4

The permeate from the EDR stacks was then sent to the SRO units. The performance criteria for the SRO units were permeate quality, water recovery, CIP frequency and permeate flux. Table

8.9 shows the performance data for the SRO section of the EDR plant. Given the calcium and sulphate content of the SRO feed, a CIP was implemented that used 1% EDTA, 1% tri-sodium-polyphosphate, and sodium-dodecyl-sulphate at pH 10.5 and 35°C.

Table 8.9. Performance data for the SRO units of the EDR plant.

Component	Target	Average
Water Recovery (%)	85	79 ± 1.6
Conductivity (µS/cm)	80	33 ± 9
CIP/Train/month	1	2.5
Flux (L/m ² .h)	25	20.1 ± 3.2
Feed Pressure (kPa)	1350	1350

The overall EDR plant water recovery was 76%. The SRO concentrate was recycled to the EDR stacks as brine makeup.

8.4. Canonsburg, Pennsylvania Uranium Mill Tailings Remedial Action Program (UMTRA) Site

Tiepel and Shorr (1985) applied their system design to a wide number of treatment scenarios including the groundwater clean-up of operation at the Canonsburg, PA, Uranium Mill Tailings Remedial Action Program (UMTRA) site.

Site Description

The Canonsburg site was operated as a vanadium and radium processing facility from the 1900's through to the 1920's. In 1933, the facility was utilized to extract uranium, vanadium and radium from various residues, ores and concentrates. It primarily processed uranium for the U.S. Atomic Energy Commission (AEC) until 1953 and solid and liquid wastes were deposited and discharged at different locations on the site. Some remedial action was performed on site by burying solid waste under a layer of steel mill slag.

Remedial Action

The remedial action consisted of the identification of all contaminated areas and excavation of the contaminated soils into a central engineered encapsulation cell. Groundwater from the contaminated soil and tailings excavation area and any surface runoff from the exposed

contaminated soils were collected in a lined holding pond. A system consisting of a combination of chemical treatment and membrane filtration was implemented to treat the contaminated discharge.

The system consisted of three chemical pretreatment steps followed by membrane filtration. The study does not provide detailed information on the membrane step but from the results it seems that RO or a tight NF membrane was likely used.

The first two steps involved the precipitation of the radioactive elements, uranium and radium and the removal of arsenic and selenium using reduction and co-precipitation followed by settling. In the third pretreatment step, the remaining metals were precipitated by lime addition. The stream was further polished and treated by membrane filtration. The treatment system consistently met the discharge limits of the time and a flux of 250 US gal ft⁻² membrane area per day (425 L m⁻²) was maintained for a 200 US gpm unit design. Table 8.10 provides the concentrations of the different species in the three membrane streams. No capital or operating cost data were reported in the study.

Table 8.10. Maximum groundwater contaminant levels and membrane treatment results at Canonsburg, UMTRA site (Tiepel and Shorr, 1985).

Metals and other Assays	Concentration (mg/L)				
	Groundwater	Feed	Concentrate	Permeate	Discharge Limit*
Ra	690	1.00	3.60	0.6	3.00
U	13	6.40	2.60	0.001	2.00
Ag	- ^{***}	0.03	0.03	0.01	0.01
Cd	12	0.076	0.012	0.01	0.20
Cr	5.5	4.60	5.40	0.06	0.05
Cu	16	2.00	2.00	0.03	0.20
Fe	-	14.80	350	0.04	3.00
Mn	-	1.61	1.70	0.02	4.00
Ni	18	0.21	0.13	0.06	0.20
Pb	12	1.00	1.0	0.10	0.20
Zn	2	0.16	6.80	0.008	0.40
Se	36	-	-	-	-
As	10	-	-	-	-
pH	6-8	6-8	10	6-9	6-9
TSS	20-3,000	-	-	-	-
TOC	13	-	-	-	-

*Monthly average discharge limit; ** pCi/L; *** data not reported

8.5. Black Hawk Colorado Pilot

Ultrafiltration ceramic and polymeric membranes were used to clean-up the acidic drainage/heavy metal contamination (Stewart *et al.*, 1997).

Site description

Since the late 1850's, the areas around the towns of Black Hawk and Central City, Colorado, have been mined for gold, silver, lead, zinc and copper. In the late 1980's, the area was classified as a Superfund site by the US Environmental Protection Agency. Early placer mining, followed by underground mines resulted in the disposal of large volumes of waste rock and tailings over a large and wide area. This resulted in the discharge of heavy metals from the waste rock and mine tailings stored at the area into the surface water streams. Over 800 abandoned mines and tunnels still exist in the area and many are still discharging acidic mine water containing high concentrations of heavy metals.

Process description

The goal of the study was to identify an efficient and cost-effective treatment system for the removal of heavy metals without the expense of a clarifier system. Due to the site constraints, a system with a minimized footprint was also required. A comparison was made between a conventional clarifier, a ceramic membrane system and a polymeric membrane system. The cost data from the study were normalized to a 250 US gpm sized system for the purposes of comparison.

The first system consisted of a general clarification step with pH adjustment followed by flocculation and sedimentation in a rectangular clarifier. This system was able to remove approximately 70-80% of the heavy metals but required a large land area in order to accommodate the required retention times for coagulation/flocculation and sedimentation.

The second system was a polymeric membrane system that had a footprint of only 10% of that required for the conventional system. This system had significantly better performance than the first system with removal rates of over 90%. After several months of operation the polymeric

membranes became brittle and failed. The system throughput was 10 US gpm and the trans-membrane pressure was 35-40 psig. No information was provided on the system maintenance requirements. Any pH adjustment was made prior to the membrane skids and the concentrate stream was neutralized and the sludge was pressed and landfilled.

The third system was a tight ceramic MF membrane system developed by BASX systems with a pore size of 0.2 μm . The system was more robust than the polymeric system and yielded heavy metals removal of over 99% in most cases, and the operating costs were reduced by 30%. The system throughput was 10 gpm and the trans-membrane pressure was 35-40 psig. Table 8.11 shows the heavy metal removal efficiencies of the three described processes.

Process economics

The capital costs calculated and presented here were calculated over a 10-year life of the system. The reported values are the present value for 1997 and the cost data as mentioned earlier were normalized to represent a 250 US gpm system. It should be noted that the capital and operating costs could vary widely based on the effluent stream conditions and compositions as well as the site conditions. Table 8.12 provides the capital and operating costs of the three systems that were tested.

Table 8.11. Heavy metal removal efficiencies of the processes tested at Black Hawk, Colorado.

Process	Metal	Removal Efficiency (%)
Clarifier	Cadmium	0-85
	Chromium	> 99
	Lead	90-95
	Manganese	0-3
	Zinc	0-90
Polymeric Membrane System	Cadmium	85-95
	Chromium	>99
	Lead	>99
	Manganese	50-80
	Zinc	85-95
Ceramic Membrane System	Cadmium	90-99
	Chromium	>99
	Lead	>99
	Manganese	70-90
	Zinc	90-95

Table 8.12. Comparative capital and operating costs for treatment of AD at Black Hawk, Colorado.

Capital Costs (\$US)			
Cost Item	Ceramic Membrane System	Polymeric Membrane System	Conventional Treatment (coagulation/flocculation/sedimentation) System
Estimated capital costs for a 250 gpm treatment plant	1,900,000	1,800,000	4,200,000
Annual Operating Costs (\$US)			
General building and equipment maintenance	20,000	20,000	100,000
Treatment chemicals	60,000	78,000	255,000
Sludge disposal	20,000	20,000	25,000
Operator labor	30,000	90,000	120,000
Monitoring costs	18,000	18,000	18,000
Power costs for pumping	80,000	80,000	0.0
Membrane replacement cost	0.0	100,000	0.0
Contingency (15%)	34,200	60,900	77,700
Total costs	262,200	466,900	569,800
Present value annual costs (1997) for the 10 year life of the plant	1,611,105	2,868,898	3,660,319

The cost data show that even if an investment had been made in a conventional system, a switch to ceramic membrane system would result in a lower cost over the 10 year life of the system.

8.6. Debiensko Coal Mines, Katowice, Poland

Mine water treatment and recovery for zero liquid discharge at Polish mines were described in detail by Solomon *et al.* (1989), Bostjancic and Ludlum (1996), and Sikora and Szyndler (2004).

A brief summary of the integrated treatment process extracted from the above publications is provided below.

Polish mines discharge a massive amount of contaminated mine water each day, an estimated 2,500 m³/min or approximately 3.6x10⁶ m³/d. The water contains approximately 600 mg/L to 120,000 mg/L total dissolved solids, which is mostly common salt (NaCl). About 60% of this drainage can be recovered and used for drinking water or in agriculture and/or other industries. The remaining, approximately 1.44x10⁶ m³/d, are saline waters that are discharged directly to local rivers causing substantial damage to Polish water reservoirs.

At the Debiensko Coal Mines a plant was constructed to treat this brackish water. It was designed by Polish engineers and scientists using water treatment technologies from the U.S. and Sweden. The plant recovered 10,500 m³/d of drinking and process water, ~ 4,500 m³/d of distilled water, 250 tonnes/d of pure sodium chloride for sale, and ~ 25 tonnes of calcium sulphate.

The water purification was conducted in the following five stages: pretreatment, membrane filtration using reverse osmosis (RO), brine concentration, salt crystallization and purge treatment. The cost for the entire desalination plant was about \$60 million USD. The pretreatment system accounted for about 40% of the cost. Table 8.13 shows the products and costs of production of the desalination plant at Katowice.

Table 8.13. Products and cost of production from mine drainage at Katowice, Poland. The prices are in U.S. Dollars (adapted from Sikora and Szyndler, 2004).

Product	Quantity per day	Price
Products from mine drainage		
Distilled water	4,500 m ³	\$0.8 per m ³
Drinking water	9,800 m ³	\$0.2 per m ³
Salt tablets for water softening	150 tonnes	\$40 per tonne
Bag and bulk salt	250 tonnes	\$40 per tonne
Products from crystallizer purge		
Lower quality salt (animal feed)	30 tonnes	\$15 per tonne
Iodine to chemical industry	54 kg	\$4 per kg
Bromine to chemical industry	280 kg	\$0.3 per kg
Carnallite for fertilizer	12.5 tonnes	\$90 per tonne
Magnesium chloride for bricks	13 tonnes	\$60 per tonne

The pretreatment section prevented the fouling of the RO membranes in the reverse osmosis section. It consisted of the following components:

- Feed water dosing with an algaecide;
- Sedimentation with polymer dosing;
- Disinfection, chlorination and intermittent shock treatment with sodium bisulphate;
- Flocculation with alum and acid dosing for pH control;
- Filtration in dual media sand, anthracite and granular activated carbon filters; and
- Sludge thickening and disposal.

The pretreated water was purified in a reverse osmosis system consisting of the following stages.

- A two-stage microfiltration section containing 50 µm washable / reusable steel baskets and 5 µm disposable cartridge filters;
- A RO system consisting of spiral wound RO membranes contained in more than 500 vessels and pressurized to approximately 6-7 MPa (870 – 1000 psig). The RO system concentrated the saline water to ~ 80,000 – 90,000 mg/L total dissolved solids (TDS);
- The permeate was used as drinking water after de-carbonation, chlorination and lime treatment; and

- The RO membranes were cleaned periodically with a prepared acidic solution, which was neutralized after washing.

The concentrate or reject from the RO section was concentrated further in brine concentrators, which were vertical tubes with falling film evaporators driven by vapor compressors. The falling film design gave a high heat transfer coefficient. The feed water was concentrated to near the point where sodium chloride would normally precipitate. Calcium sulphate crystals were added as seeds to the input feed solution at the startup, which gave the precipitating salt a place to attach and remain in suspension without crystallizing.

In the crystallizer circuit, about 60% of the saturated brine from brine concentrators, concentrated to approximately 260,000 mg/L total dissolved solids (TDS) and 3000 mg/L total suspended solids (TSS) was sent to the pre-heater of a forced-circulation, submerged-tube crystallizer. The remaining 40% of the feed was sent to the elutriation leg of the crystallizer. The salt was allowed to crystallize and the circuit is purged periodically.

The crystallizer purge treatment, using chemical and thermal methods, was used for the recovery of chemicals and distilled water. The following technologies were used to recover chemicals from the crystallizer purge:

- Calcium sulphate precipitation;
- Thermal pre-concentration and additional sodium chloride crystallization, iodine and bromine desorption and adsorption;
- Final stage thermal concentration and sodium chloride crystallization;
- Carnallite crystallization; and
- Magnesium chloride crystallization.

Using these integrated water treatment processes, the following products were recovered from the mine water:

- Distillate – approximately 65 m³/d;

- Sodium chloride – approximately 30 tonnes/d;
- Carnallite – approximately 4,200 tonnes/year;
- Magnesium chloride – approximately 4,400 tonnes/year; and
- Iodine and bromine – approximately 110 tonnes/year.

8.7. Newmont - Gold Leaching Operation in Peru

Another example of a membrane application in mining operations is a full-scale plant operated by Newmont Mining Corporation in Yanacocha, Peru.

The gold mine produces approximately 3 Million oz. gold per year. It utilizes a cyanide heap leaching process for gold and silver recovery. The company faces tight environmental discharge criteria which were deemed to be too costly to meet individually using chemical treatment options for excess water from the gold leaching operation during the wet season. Additional constraints for the company were limitations in cyanide concentrations which could be chemically treated prior to discharge of excess water, which resulted in reduced gold and silver production and gold lost during release of the treated water. Newmont commissioned a 1500 US gpm membrane plant, manufactured by Harrison Western Group, in 2004 that allowed the company to meet its discharge requirements, contain gold losses and significantly reduced its water treatment costs. The membrane system also increased precious metal recovery.

The feed to the membrane plant is from the Merrill-Crowe barren solutions, which is a diatomaceous earth filtered feed. The permeate contains some residual free cyanide, which is treated by alkaline chlorination and neutralization of the effluent and the membrane concentrate returns some of the free cyanide, the bulk of the metal cyanide complexes, metal oxyanions and nitrates to the leaching process. Some preliminary problems with fouling, due to a mercury amalgam forming on the surface of the membranes from trace residual gold precipitate passing through the filters, were solved utilizing a cyanide washing protocol. The plant is fully automated and has run unattended at the site during road blockage incidents.

Due to the success of the process, the company installed an additional 6000 US gpm capacity in 2005 (Newmont, 2007; Harrison Western, 2007). Detailed information on the process and its economics was not available.

9. RESEARCH AND TECHNOLOGY REQUIREMENTS

One of the important factors that separate the mining related membrane applications from many other industrial applications is the highly scaling streams such as AD and higher flow rates encountered in mining.

The important areas of research and development of membrane applications for mitigation of acidic drainage and other effluents in mining are:

- Development of fundamental understanding of factors that affect the long-term performance of membrane separation and the limiting steps, which are primarily the understanding of fouling mechanisms, and the related membrane surface properties that reduce fouling and scaling and the chemistry involved in restoring the performance of the membrane after cleaning. Although there has been significant progress in the area of membrane fouling there is still much room for improvement.
- Development of adequate pretreatment processes that are economically non-prohibitive. This would take into account particulate matter and dirt loading (TSS), organic and biological matter and their potential for downstream fouling.
- Development of high flux low fouling membranes and membrane materials. This would include: membrane material development to improve existing polymeric materials; the development of new polymers that would have suitable chemical, physical and mechanical surface properties; and module and system design.
- Strategies to deal with membrane process concentrates, which could include extraction and recovery of chemicals and metals of value and water recovery for safe discharge or further use. The concentrate stream volume and salinity would be an important factor to consider given the magnitude of the flow rates that are normally encountered in mining applications.

Although some of the above issues have been addressed to some extent for other applications, there is still significant room for progress in each of the above mentioned areas within the mining context. A successful process should integrate:

- feed stream quality;
- water and environmental quality targets;
- final concentrate treatment and environmental impacts of disposal;
- regulatory restrictions; and
- factors that have direct or indirect impact on the economics of the process.

The most important objective for pretreatment is to reduce its costs by the appropriate choice of technology, process integration and optimization. This involves the assessment and evaluation of conventional physical and chemical treatment technologies as pretreatment for membrane plant feed streams and replacing or complementing conventional filtration techniques with micro- or ultra-filtration. Improvement of the MF and UF processes, through the removal of particulates such as fine clays and colloidal metal precipitates, is another approach for improved RO or NF performance. Another aspect of pretreatment is the addition of appropriate anti-scalants, anticoagulants and anti bio-foulants at the right dosage. Proper conditioning of the feed stream can minimize the frequency of cleaning, reduce fouling, maintain the flux and increase the life of the membrane.

The objective in using solute rejection is to develop cost-effective processes for TDS removal, while maintaining high water recovery rates, high flux and high rejection rates, while at the same time minimizing fouling effects through module and system design. This also involves the development of new membrane materials with chemical, physical and mechanical properties suitable for mining applications. Consideration should also be given to applications where organic solvents and other organic materials such as surfactants could be present (e.g. in some uranium mills where trace kerosene may be present). The development of membranes with surface properties that are resistant to fouling could result in operating cost reductions through prolonged membrane life and reduced frequency of cleaning. The water recoveries for the best case average around 85%, although higher recoveries have also been reported. Development of high flux, low-pressure membranes has resulted in reduced energy consumption of membrane processes, especially for RO applications; however, energy recovery systems could further improve process economics.

Brine recovery and mitigation, in cases where very high flow rates are encountered, could become a serious issue. A variety of methods for brine management have been investigated which include: evaporation ponds; use of crystallizers and evaporators; and precipitation of metals. Depending on the geographic location of the treatment facility, feasibility options such as deep-well injection could also be considered. One way to approach brine management is through brine minimization by volume reduction.

Generation of a concentrated stream could bring about the opportunity for the recovery and recycling of concentrate components of value, such as metals, flotation agents, etc. There is a high potential for niche membrane applications at high concentrations and low flow rates within gold refinery operations where contaminants could be bled out of the process, cyanide and gold recovered and the permeate could be used as a more efficient solvent for gold recovery from activated carbon.

10. CONCLUSIONS

The information presented in this review shows that membrane separation is an efficient and cost-effective technology for acidic drainage and mine effluent treatment. Comparison with conventional treatment technologies has also shown that membrane separation, if properly designed and operated, can provide superior discharge water quality and much improved treatment results while offering lower capital and operating costs. Membrane separation, however, cannot completely replace conventional treatment technologies and is not a stand-alone treatment option. Membranes can be a powerful tool for volume reduction and waste minimization, allowing for the recovery and recycle of water and other potentially valuable by-products from AD and other effluents such as acid, gypsum, heavy metals and sulphur. Because of the volume reduction that membrane separation offers, the footprint and capital costs of the accompanying conventional treatment options such as clarifiers and other chemical treatments could be substantially reduced.

Due to the composition of AD and other mining streams that require treatment, the most significant issue encountered with membrane separation in mining applications is membrane fouling and brine disposal. Some of the technical issues that drive membrane research and technology development, with the goal of improving the performance and reducing cost, are as follows:

- Membrane fouling – lowering membrane replacement costs, maximizing recoveries;
- Pretreatment as a measure of fouling control;
- Maximizing water recoveries; and
- Brine disposal or treatment and minimizing its associated costs.

11. REFERENCES

- Allenby M., Aluminum Compounds Cause Operational Problems in a Reverse Osmosis Plant, Chemical Treatment, *Materials Performance*, May 2004.
- Amjad Z., Applications of Antiscalants to Control Calcium Sulfate Scaling in Reverse Osmosis Systems, *Desalination*, Vol 54, p.263, 1985.
- Amjad Z., Butala D. and Pugh J., The Influence of Recirculating Water Impurities in the Performance of Calcium Phosphate Inhibiting Polymers, *Corrosion 99*, Paper No. 118, San Antonio, Texas, NACE International Conference, 1999.
- Amjad Z., Controlling Metal Ions Fouling in Industrial Water Systems, *Ultrapure Water*, Vol. 17(4), 2000.
- Amjad Z., Hooley J. P. and Workman K., Copolymer-Based Reverse Osmosis Water Treatment Programs New Developments Which Expand Their Application Areas, National Water Supply Improvement Association Conference, 1988.
- Amjad Z., Pugh J., Zibrida J. and Suhl R., Polymer Performance in Cooling Water: The Influence of Process Variables, *Materials Performance*, Vol. 36(1), 1997.
- Amjad Z., Scale Inhibition in Desalination Applications: An Overview, NACE-96-230, Corrosion 96, The NACE National Conference and Exhibition, Paper 230, 1996.
- Awadalla F.T. and Hazlett J. D., Application of Membranes for the Treatment of Mining Metallurgical Effluents, in proceedings of *International Symposium on Processing and Recycling*, at the 31st Annual Conference of Metallurgists, Edmonton, Alberta, Canada, pp. 87-103, 1992.
- Awadalla F.T. and Kumar A., Opportunities for Membrane Technologies in the Treatment of Mining and Mineral Process Streams and Effluents, *Sep. Sci. Technol.* 29, 1231-1250, 1994.
- Awadalla, F.T., Striez C. and Lamb K., Removal of Ammonium and Nitrate Ions from Mine Effluents by Membrane Technology, *Separation Science and Technology*, 29(4), 483-495, 1994.
- AWWA Membrane Technology Research Committee. Committee Report: Membrane Processes in Potable Water Treatment. *J. Am. WaterWorks Assoc.* 84(1): 59-67, 1992.
- AWWA Membrane Technology Research Committee. Committee Report: Membrane Processes. *J. Am. WaterWorks Assoc.* 90(6): 91-105, 1998.
- Baker R.W., *Membrane Technology and Applications*, 2nd Ed., John Wiley & Sons, Ltd., Chichester, 2004.

Barnes H.L. and Romberger S.B., Chemical Aspects of Acid Mine Drainage, *J. Water Pollut. Control. Fed.*, 40 (3), 371, 1968.

Bayer H., Water Treatment at Kennecott Utah Copper, Proceedings of the 2004 Ontario MEND Workshop, Sludge Management and Treatment of Weak Acid or Neutral pH Drainage, Sudbury, Ontario, May 26 and 27, 2004.

Belfort G., Mikulasek P., Pimbley J.M. and Chung K. Y., Diagnosis of Membrane Fouling using a Rotating Annular Filter. 2. Dilute Particle Suspensions of Known Particle Size, *Journal of Membrane Science*, vol.77(1), pp. 23-39, 1993.

Berg G. and Arthur B., Proposed Mine Water Treatment in Wisconsin, Sudbury 99 Mining and the Environment II; vol. 2, Sudbury, Ontario, 1999.

Bertrand S., Lemeitre I. and Wittmann E., Performance of a Nanofiltration Plant on Hard and Highly Sulphated Water During Two Years of Operation, *Desalination*, Vol. 113, pp. 277-281, 1997.

Bhattacharyya D., Farthing S.S., and Cheng C.S., Multiple-Pass Water Reuse, *Environmental Progress* Vol. 1(1), pp. 65-72, 1982.

Bhattacharyya D., Grieves R.B and Shelton S., Charged Membrane, Low Pressure Ultrafiltration to Treat Acid Mine Drainage Waters (PB-297-209, W7907424 OWRTB-050-KY(1)), Office of Water Research and Technology, Washington D.C., 1979a.

Bhattacharyya D., Shelton S. and Grieves R.B., Charged Membrane Ultrafiltration of Multisalt Systems: Application to Acid Mine Waters, *Separation Sci. and Tech.*, Vol. 14, pp. 193-208, 1979b.

Blackshaw G. L., Pappano A. W. and Avakali V. S., Pilot Plant Treatment of AMD by Reverse Osmosis Based Techniques, Proceedings of the 5th Symposium on Coal Mine Drainage Research, Louisville, Kentucky, 1974.

Blackshaw G. L., Pappano A. W., Thomas Jr. G. E. and Cheng S. Y., Feasibility of Using Reverse Osmosis to Treat Acid Mine Waters, *Symp. Coal Mine Drainage Res.*, Vol. 6, pp. 113-130, 1976.

Boman B., Ek, M., Heyman, W., and Frostell, B., Membrane Filtration Combined with Biological Treatment for Purification of Bleach Plant Effluents. *Water Sci. Technol.* 24(3/4): 219-228, 1991.

Boonthanon S., Hwan, L.S., and Vigneswaran, S., Application of Pulsating Cleaning Technique in Crossflow Microfiltration. *Filt. Sep.* 28 (May/June): 199-201, 1991.

Bostjancic J. and Ludlum, R., Getting Zero Discharge: How to Recover That Last Bit of Really Bad Wastewater. In the Proc., 57th Annual International Water Conference, Bellevue, Washington, U.S.A. Oct 21-23, 1996.

Braghetta A., DiGiano, F.A., and Ball, W.P., Nanofiltration of Natural Organic Matter: pH and Ionic Strength Effects. *J. Environ. Eng. ASCE*, 123: 628–641, 1997a.

Braghetta A., Jacangelo, J.G., Chellam, S., Hotaling, M., and Utne, B.A., DAF Pretreatment: Its Effect on MF Performance. *J. Am. Water Works Assoc.* 89(10): 90–101, 1997b.

Brindle K., and Stephenson, T., The Application of Membrane Biological Reactors for the Treatment of Wastewaters. *Biotechnol. Bioeng.* 49: 601–610, 1996.

Brindle K., Stephenson, T., and Semmens, M.J., Pilot-Plant Treatment of a High-Strength Brewery Wastewater using a Membrane Aeration Bioreactor. *Water Environ. Res.* 71: 1197–1204. 1999.

Butler R. and MacCormick T., Opportunities for Decentralized Treatment, Sewer Mining and Effluent Re-use, *Desalination*, vol. 106(1-3), pp. 273-283, 1996.

Cabassud C., Laborie, S., and Lainé, J.M., How Slug Flow can Enhance the Ultrafiltration Flux in Organic Hollow Fibres. *J. Membr. Sci.* 128: 93–101, 1997.

Cartwright P. S., Industrial Effluent Applications of Membrane Separation Technologies, Chang, Y., and Benjamin, M.M., Iron Oxide Adsorption and UF to Remove NOM and Control Fouling. *J. Am. Water Works Assoc.* 88(12): 74–88, 1997.

Chellam S., Jacangelo, J.G., Bonacquisti, T.P., and Schauer, B.A., Effect of Pretreatment on Surface Water Nanofiltration. *J. Am. Water Works Assoc.* 89(10): 77–89, 1997.

Chellam S., Serra, C.A., and Wiesner, M.R., Estimating Costs for Integrated Membrane Systems. *J. Am. Water Works Assoc.* 90(11): 96–104, 1998.

Chen Y., Chu M. L. and Shieh, Effect of pH on the Separation of Uranium Fluoride Effluents by the Reverse Osmosis Process, *Sep. Sci. Technol.*, vol. 27(5), pp. 557-571, 1992.

Cho J., Amy, G., and Pellegrino, J., Membrane Filtration of Natural Organic Matter: Initial Comparison of Rejection and Flux Decline Characteristics with Ultrafiltration and Nanofiltration Membranes. *Water Res.* 33: 2517–2526, 1999.

Choppin G.R. and Nash K.L., *Radiochim. Acta*, 225, 70–71, 1995.

Clifford D., Vijjeswarapu W., and Subramonian S., Evaluating Various Adsorbents and Membranes for Removing Radium from Ground Water, *J. Am. Water Works Assoc.*, 80(7), 94-104, 1988.

Cote P., Buisson, H., and Praderie, M., Immersed Membrane Activated Sludge Process Applied to the Treatment of Municipal Wastewater. *Water Sci. Technol.* 38(4/5): 437–442, 1998.

Coulter R. F., Beneficiation of Ores at the Flin Flon Concentrator, *CIM Bull.*, vol. 55(602) pp. 375-389, 1962.

Deutsch W., Martin W. J., Eary L. E. and Serne R. J., , Methods of Minimizing Ground Water Contamination from In Situ Leach Uranium Mining, Final Report PNL-5319, NTIS *Energy Res. Abst.* Vol. 10(12), No. 22460, 1985.

Diamand R.M.E, Environmental Chemistry, Plenum Press, New York, 1977.

Enegeess D., Togna A. P. and Sutton P. M., Membrane Separation Applications to Biosystems for Wastewater Treatment. *Filtr. Separat.* 40 (1) 14-17, 2003.

Fu P., Ruiz, H., Thompson, K., and Spangenberg, C., Selecting Membranes for Removing NOM and DBP precursors. *J. Am. Water Works Assoc.* 86(12): 56–72, 1994.

Garling R. A., *Evaluation of Electrodialysis for Process Water Treatment for In Situ Mining*, Presented at the 5th Uranium Seminar, Albuquerque, New Mexico, AIME, Society of Mining Engineers, Littleton, Colorado, 1981.

Georgescu D. P. and Anderi L., Treatment of Tailings Water from Uranium Ore Processing by reverse Osmosis, Uranium 2000 International Symposium on the Process Metallurgy of Uranium, Eds. Özberk E. and Oliver A. J., The 30th Annual Hydrometallurgical Meeting of the Metallurgical Society of CIM, Saskatoon, Saskatchewan, Canada, September 9-15, 2000.

Gouellec Y. A. and Elimelech, Control of Calcium Sulfate (Gypsum) Scale in Nanofiltration of Saline Agricultural Drainage Water, *Environ. Eng. Sci.*, Vol 19(6), pp. 387-397, 2002.

Green D. H., Speakman L. L., Yantorno D., and Ramachandran V., A Technical and Economical Comparison Between Conventional Precipitation and Membrane-Media Treatment of the Wastewater at ASARCO Globe Plant, Denver, Colorado, Provided by HW Process Technologies, Advanced Industrial Water Treatment Systems, 1208 Quail Street, Lakewood, CO 80215, July 1993.

Gureli L. and Apak R., *Sep. Sci. Tech.*, 39(8), pp.1833-1856, 2004.

Harries R. C., A Field Trial of Seeded Reverse Osmosis for the Desalination of Scaling Type Mine Water, *Desalination*, vol.56, pp. 227-236, 1985.

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

Harrison Western, Personal Communication, Jay Lombardi, HW Process Technologies, 2007.

Hays J., Iowa's First Electrodialysis Reversal Water Treatment Plant, *Desalination*, vol. 132, pp. 161-165, 2000.

Hill R.D., Wilmoth R. C., and Scott R. B., Neutrolysis Treatment of Acid Mine Drainage, 26th Annual Purdue Industrial Waste Conference, Lafayette, Indiana, 1971.

Hill R.D., Wilmoth R.C., Roger C., and Scott R. B., High Recovery Treatment of Acid Mine Drainage by Reverse Osmosis Neutralization, Norton Mine Drainage Field Site, FWQA, Norton, West Virginia, 1970.

Hill R.D., Mines Drainage Treatment State of the Art and Research Needs, U.S. Department of Interior, Federal Water Pollution Control Administration, Mine Drainage Control Activities, Cincinnati, Ohio 45226, December 1968.

Holtzhausen L., From Toxic to Tap: Mine Water Becomes Commodity, *Water Wheel*, May 2006.

Jacangelo J.G., Adham, S.S., and Laine, J.M., Mechanism of *Cryptosporidium Parvum*, *Giardia Muris*, and MS2 Virus removal by MF and UF. *J. Am. Water Works Assoc.* 87(9): 107, 1995.

Jarusutthirak C., Mattaraj S. and Jiratananon R., Influence of Inorganic Scalants and Natural Organic matter on Nanofiltration Membrane Fouling, *Journal of Membrane Science*, vol.287(1), pp. 138-145, 2007.

Juby G.J.G. and Schutte C. F., Membrane Life in Seeded-Slurry Reverse Osmosis System, *Water SA*, vol. 26(2), pp. 239-248, 2000.

Juby G.J.G., Membrane Desalination of Service Water from Gold Mines, *J. S. Afr. Inst. Min. Metall.*, 92(3), 65-69, 1992.

Kanggen Z., Qixiou Z., Aiping L., Chunsheng F., Jihong S., Ming L., Weiqing H. and Xiaoqing Z., Treatment of Industrial Wastewater from an Alumina Plant by Membranes, *Journal of Central South University of Technology*, Volume 6, Number 2 / November, 1999.

Kawahara T., Construction and Operation Experience of a Large-Scale Electrodialysis Water Desalination Plant, *Desalination*, vol. 96, pp. 341-348, 1994.

Kilega M., Grohmann, G.S., Chiew, R.F., and Day, A.W., Disinfection and Clarification of Treated Sewage by Advanced Microfiltration. *Water Sci. Technol.*, 23: 1609–1618, 1991.

Koseoglu S.S. and Guzman G. J., Reverse Osmosis: Membrane Technology, Water Chemistry and Industrial Applications, Chapter 10, Amjad Z. (Ed.), van Nostrand Reinhold Publishing, New York, USA, 1993.

Legault A.S. and Tremblay A. Y., Arsenic Removal by Polymeric Binding and Membrane Separation, Proceedings of the 11th Technical Seminar on Chemical Spills, Vancouver, British Columbia, 1994.

Lewis A. and Nathoo J., Prevention of Calcium Sulphate Crystallisation in Water Desalination Plants Using Slurry Precipitation and Recycle Reverse Osmosis (SPARRO), Project No. 1372, Water Research Commission, Pretoria, South Africa, 2005.

Litovitz T.A., Macedo P.B. and Hojaji H., WO8803915, 1988.

Lorax Environmental, 2003. Treatment of Sulphate in Mines Effluent. INAP Report. October 2003.

Macintosh P., Treating Arsenic Mine Water Using a Hybrid Membrane Plant, *Australian Water and Wastewater Association*, 29(2), 84-86, 2002.

Malaiyandi M. and Sastri V.S., Reverse Osmosis Separation of Sulphate, Nitrate and Ammonia from Mining Effluents, *Separation Science and Technology*, Vol. 16(4), pp. 371-376, 1981.

Mallevalle J., Odendall, P.E., and Wiesner, M.R., *Water Treatment Membrane Processes*. McGraw-Hill, New York, 1996.

Mallubhotla H., and Belfort, G., Flux Enhancement During Dean Vortex Microfiltration: 8. Further diagnostics. *J. Membr. Sci.* 125: 75, 1997.

Matsuura T., *Synthetic Membranes and Membrane Separation Processes*, CRC Press, London, 1994.

McCleaf P.R., and Schroeder, E.D., Denitrification using a Membrane-Immobilized Biofilm. *J.Am. Water Works Assoc.*, 87(3): 77-86, 1995.

Miller J. V-SEP Filtration of Acid Mine Drainage – A Cost Effective and Efficient Processing Solution, New Logic Research Inc., http://vsep.com/downloads/case_studies_application_notes.html, April 20, 2005.

Mortazavi S., Dave, N and Zinck, J., Uranium Mine/Mill Effluent – Zero or Minimal Discharge, CANMET-MMSL Internal Report #05-038/CR, November 2005.

Mortazavi S. and Cooper D., Application of Activated Alumina on the for the Removal of Selenium from Water, Proceedings of the 15th Technical Seminar on Chemical Spills, Edmonton, Alberta, 1998.

Mortazavi S., Tezel F. H. and Tremblay A. Y., Effect of pH on the Uptake of Arsenic from Contaminated Water by Activated Alumina, *Advances in Environmental Research*, vol. 3(1), 1999.

Mortazavi S. and Chaulk J., Application of Membrane Separation to Sulphate Removal and TDS Reduction, CANMET-MMSL Internal Report No. 08-005(TR), 2008.

Mulder, M., Basic Principles of Membrane Technology, Kluwer Academic Publishers, London, 1996.

Newmont, 2007, Personal Communication, Charles Bucknam, Newmont Metallurgical Service, 2007.

Nieuwenhuis J. G., Steytler B., Vijoen A. J. and van der Merwe I. W., Sasol's Experience in the Desalination and Re-Use of Acid Mine Drainage and Ash Water, Special Publication, ISSN0206291, vol. 249, pp. 211-218, 2000.

Nyström M., Pihlajamäki A., Liikanen M. and Mänttari M., Influence of Process Conditions and Membrane/Particle Interaction in NF of Wastewaters, *Desalination*, vol. 156, pp. 379-387, 2003.

O'Neil T.M., Kirchner O. E. and Day W. J., Achieving High Recovery from Brackish Water with Seeded Reverse Osmosis Systems, 42nd Annual Meeting, International Water Conference, Pittsburgh, Pennsylvania, 1981.

Pérez de Ortiz E.S., Ion Exchange, Science and Technology, Martinus Nijhoff Publishers, Dordrecht, 1986.

Pinnau I. and Freeman B. D., Formation and Modification of Polymeric Membranes: Overview, Chapter 1, in Membrane Formation and Modification, Pinnau I. and Freeman B. D., Editors, ACS Symposium Series 744, 2000.

Pisa V. and Gulikova E., Desalting of Acid Mine Drainage by Reverse Osmosis Method – Field Test, 9th International Mine Water Congress (IMWA 2005), September 5-7, 2005, Asturias, Spain, 2005.

Porter, M.C., Handbook of industrial membrane technology. Noyes Publications, Park Ridge, N.J. pp. 136–259, 1990.

Prabhakar S., Panicker S. T., Misra B. M., and Ramani S. P. S., Studies on the Reverse Osmosis Treatment of Uranyl Nitrate Solution, *Sep. Sci. Technol.*, 27(3), 349-359, 1992.

Pulles W., Juby G. J. G., and Busby R. W., Development of the Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) Technology for Desalinating Scaling Mine Waters, *Wat. Sci. Tech.*, vol. 25(10), pp.177-192, 1992.

Rautenbach M. and Groschl, A., Separation Potential of Nanofiltration Membranes. *Desalination*, 77: 73–84, 1990.

Reed B.E., Lin, W., Viadero, R., Jr., and Young, J., Treatment of Oily Wastes using High-Shear Rotary Ultrafiltration. *J. Environ. Eng. ASCE*, 123: 1234–1242, 1997.

Riding J.R. and Rosswog F. J., *Restoration of Ground-Water Quality after In Situ Uranium Leaching* (Contract J0275028), U.S. Department of Interior, Bureau of Mines, Washington, D.C., 1979.

Riedinger A. B. and Schultz J., Acid Mine Water Test at Kittaning, Pennsylvania, R&D Report No. 217, Office of Saline Water, Washington, D.C., 1996.

Sahni S.K., Driessen W.L., Reedijk J., *Inorg. Chim. Acta* 154, 141, 1988.

Sahni S.K. and Reedijk J., *Coord. Chem. Rev.* 59, 1984.

Sastri V.S., Reverse Osmosis of Metal Ions in Acid Mine Waters, *Separation Sci. and Tech.*, Vol. 14(18), pp. 711-719, 1978.

Sastri V.S., Reverse Osmosis of Nickel from Dilute Solutions, *Separation Sci. and Tech.*, Vol. 14, pp. 193-208, 1979.

Sastri W.S. and Ashbrook A. W., RO Performance of Cellulose Acetate Membrane in the Separation of Uranium from Dilute Solutions, *Sep. Sci. Technol.*, 11(4), 361-376, 1976.

Schoeman J.J. and Steyn A., Investigation into Water Treatment Technologies for the Treatment of Underground Mine Water Discharged by Grootvlei Proprietary Mines Ltd. into the Blesbokspruit in South Africa, *Desalination*, vol. 133, pp. 13-30, 2001.

Scott K. and Hughes R., *Industrial Membrane Separation Technology*, Blackie Academic & Professional, New York, 1996.

Scott J.P., and Ollis, D.F., Integration of Chemical and Biological Oxidation Processes for Water Treatment: Review and Recommendations. *Environ. Prog.* 14(2): 88-103, 1995.

Shapira N.I., Baranski J., and Kurzweg, Removal of Heavy Metals and Suspended Solids from Battery Wastewaters, EPA600/2-81-147, 1981.

Shen J.J., and Probst, R.F., Turbulence Promotion and Hydrodynamic Optimization in an Ultrafiltration Process. *Ind. Eng. Chem. Process Design Dev.* 18(3): 547-554, 1979.

Shone R.D.C. and Harries R.C., Desalination of Mine Water, *Journal of Mine Ventilation of South Africa*, vol. 40(3), pp. 29-35, 1987.

Sikora J. and Szyndler, K., Desalination Plant at Debiensko, Poland: Mine Drainage Treatment for Zero Liquid Discharge. Ionics Incorporated publication. www.ionics.com. 2004.

Silva C.M., Reeve, D.W., Husain, H., Rabie, H.R., and Woodhouse, K.A., Model for Flux Prediction in High-Shear Microfiltration Systems. *J. Membr. Sci.*, 173: 87-98, 2000.

Sirkar K., Membrane Handbook, 1st Edition, Springer, 1992.

Solomon R., Masarczyk, J., Hansson, C. and Hallmans, B., Desalination Plant at KWK Debiensko, Poland: Advanced Mine Drainage Water Treatment Engineering for Zero Discharge. International Desalination Association, 1989.

Stana R.F. and Glesry J.G., “Recovery of Uranium by a Reverse Osmosis Process,” U.S. Patent, 4,206,049, 1980.

Stewart D., Norman T. and Cordery-Cotter S., Utilization of a Ceramic Membrane for Acid Mine Drainage Treatment, *Tailings and Mine Waste '97*, Balkema, Rotterdam, 1997, ISBN 9054108576, 1997.

Tiepel E.W. and Shorr, J., Application of Advanced Membrane Filtration to Industrial Wastewater Treatment and Groundwater Clean-up, Proceedings of: The International Water Conference, 46th Annual Meeting, pp. 35-43, November 1985.

Valenzuela F., Fonseca C., Basualto C., Correa O., Tapia C. and Sapag J., Removal of Copper Ions from a Waste Mine Water by a Liquid Emulsion Membrane Method, *Minerals Engineering*, vol.18(1), pp. , 33-40, 2005.

Van der Graaf J.H.J.M., Kramer J. F., Pluim J., de Koning J. and Weijts M., Experiments on Membrane Filtration of Effluent at Wastewater Treatment Plants in the Netherlands, *Wat. Sci. Tech.*, Vol. 39 (5), pp. 129-136, 1999.

Van der Roest H., Leenen J., Hofstra M., Boeve J. and van der Vlist, The Dutch Contribution to the MBR Development in Perspective, *H2O*, pp. 7-9, 2001.

Van Houten R., Evenblij H. and Keijmel M., Membrane Bioreactors Hit the Big Time – Ten Years of Research in the Netherlands, *H2O*, pp. 26-29, 2001.

Visser T.J.K., Modise S.J., Krieg H.M. and Keizer K., The Removal of Acid Sulphate Pollution by Nanofiltration, *Desalination*, vol. 140(1), pp. 79-86 20 October 2001.

Visvanthan C., Ben A. and Parameshwaran K., Membrane Separation Bioreactors for Wastewater Treatment, *Crit. Rev. Environ. Sci. Technol.*, vol. 30(1), pp. 1-48, 2000.

Wagner J., Membrane Filtration Handbook – Practical Tips and Hints, second edition, revision 2, GE Osmonics, www.gewater.com/pdf/1229223-%20Lit-%20Membrane%20Filtration%20Handbook.pdf, 2001.

Waypa, J.J., Elimelech, M., and Hering, J.G., Arsenic Removal by RO and NF Membrane. *J.Am. WaterWorks Assoc.* 89(10): 102–114, 1997.

Weber W.F. and Bowman W., Membranes Replacing Other Separation Technologies, Chemical Engineering Progress, Vol. 82(11), 1986.

White D.A., European Patent 0,266,945, 1987.

Wiesner M.R., and Chellam, S., The Promise of Membrane Technology. *Environ. Sci. Technol.* 33: 360A–366A, 1999.

Wiesner M.R., Clark, M.M., and Mallevalle, J., Membrane Filtration of Coagulation Suspensions. *J. Environ. Eng. ASCE*, 115: 20–40, 1989.

Wiesner M.R., Hackney, J., Sethi, S., Jacangelo, J.G., and Laine, J.- M., Cost Estimates for Membrane Filtration and Conventional Treatment. *J. Am. WaterWorks Assoc.* 85(12): 33–41, 1994.

Wilmoth B.C., Baugh T.L. and Decker, D.W., Removal of Selected Trace Elements from Acid Mine Drainage Using Existing Technology, Proceedings of the 33rd Purdue Industrial Waste Conference, pp. 886-894, Purdue University, 1978.

Wilmoth R. C., Application of Reverse Osmosis to Acid Mine Drainage Treatment (EPA 670/2-73-100), U.S. Environmental Protection Agency, Cincinnati, Ohio, 1973.

Yamanoto K., Hiasa, M., Mahmood, T., and Matsuo, T., Direct Solid–Liquid Separation using Hollowfiber Membrane in an Activated Sludge Aeration Tank. *Water Sci. Technol.* 30(4): 43–54, 1989.

Zenon, Product Information: Zenon Zee Weed 500,
http://www.gewater.com/products/equipment/mf_uf_mbr/zeeweed_500.jsp 2008.

Zhu X., and Elimelech, M., Fouling of Reverse Osmosis Membranes by Aluminium Oxide Colloids. *J. Environ. Eng. ASCE*, 121: 884–892, 1995.

Zibrida J.F., Amjad Z., Zuhl R. and Lewis J., Advances in Reverse Osmosis Application in Water Reuse, Corrosion 2000, Paper No. 00314, 2000.