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REVIEW

Opportunities for Membrane Technologies in the Treatment of Mining and Mineral Process Streams and Effluents*

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ABSTRACT

The membrane separation technologies of microfiltration, ultrafiltration, nanofiltration, and reverse osmosis are suitable for treating many dilute streams and effluents generated in mining and mineral processing. Membrane technologies are capable of treating these dilute streams in order to produce clean permeate water for recycle and a concentrate that can potentially be used for valuable metals recovery. Membrane technologies can be utilized alone, or in combination with other techniques as a polishing step, in these separation processes. A review of potential applications of membranes for the treatment of different process streams and effluents for water recycling and pollution control is given here. Although membranes may not be optimum in all applications, these technologies are recognized in the mining sector for the many potential advantages they can provide.

Key Words. Membrane; Microfiltration; Ultrafiltration; Nanofiltration; Reverse osmosis; Streams; Effluents; Mining and metallurgical processes; Permeate; Concentrate; Recycled; Metals, Recovery; Polishing technique

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INTRODUCTION

Large quantities of process water are used by mining and mineral processing industries in a variety of operations such as metal leaching, ore washing, flotation, as a process medium, boiler make-up, and in extraction-resin regeneration (1). Wastewater that is generated by both the processes and mine dewatering contains heavy metals, oxidants, reducing agents, salts, and suspended solids. The treatment of such dilute streams is sometimes designated for recovering metal values and at other times for controlling environmental pollution.

Recycling of process water in mining and mineral operations is gaining importance since the use of fresh water might be taxed according to new environmental regulations under consideration in many jurisdictions. Also, water from acid mine drainage and cyanide ponds has to be treated at many sites to avoid contamination of groundwater. Therefore, there is a need for producing high quality water from these streams for recycling or discharging in a safe way. Recycling of pond water by decantation alone is becoming increasingly unattractive due to the adverse effects on the process induced by changed water chemistry. On the other hand, lime precipitation-settling technology (2) is not suitable to provide in plant reuse of the effluent water, due to the insignificant separation of arsenic and selenium oxyanions and the presence of high concentrations of calcium sulfate and metal hydroxide precipitates. Although, lime neutralization technology is considered as the "best available technology economically achievable," it is no longer considered an environmentally acceptable process due to the low level contamination of heavy metal which cannot be separated. In addition, the solid waste product is classified as toxic which requires transportation to special dumps at considerable expense.

A brief description of some of these technologies will aid to understand their application for pollution control in the mining industry.

Membranes are microporous barriers of polymeric, ceramic, or metallic materials which are used to separate dissolved materials (solutes), colloids, or fine particulate from solutions. Pressure-driven membrane processes are generally classified into four categories based on the mean pore size of membranes: hyperfiltration (HF) or reverse osmosis (RO) which typically separates materials less than 0.001 μm in size such as the separation of monovalent salts from water as practiced in the desalination of seawater and brackish water; nanofiltration (NF) which separates larger size molecules such as sugars and divalent salts while allowing passage of monovalent salts; ultrafiltration (UF) which is used to separate materials in the 0.001 to 0.1 μm range (10–1000 Å) such as proteins or colloids; and finally microfiltration (MF) which is used for sterilization by removing insoluble particulate materials (microbes) ranging in size from 0.1 to 10.0 μm (1000–100,000 Å).

Membrane modules are used in systems which contain pressure vessels, pumps, and control instruments. These systems are operated by various degrees of sophistication of automated control. Operating pressures are determined by the type of separation to be performed. There are schematically four types of modules of industrial significance for UF/NF applications: tubular, plate and frame, spiral, and hollow fiber. More information on membrane fundamentals, including the features of modules, is described elsewhere (3, 4).

Tangential or crossflow filtration allows for continuous processing of liquid streams. In this mode of operation the bulk solution flows over and parallel to the filter surface, forcing the permeate to flow tangentially across the surface of the membrane. This provides a sweeping action which minimizes the accumulation of particulate matter on the filter, facilitates continuous operation of the system, and increases membrane productivity.

Modest energy consumption is one of the main advantages of membrane processes over many other conventional processes. The other inherent advantages of membranes include their ability to separate both inorganic and organic solutes from solution by the removal of solvent, to offer the possibility of permeate water recycle, to provide a concentrate for use as a make-up solution when the waste contains a costly chemical, and to eliminate the use of regenerating chemicals. In addition, the process is simple, capable of continuous operations, requires low capital, and needs relatively little floor space. However, separation by membrane systems is a concentrating process whereby solutes in the feed stream may be concentrated severalfold. The high solute concentration leads to several problems including high osmotic pressure, which lowers the effective driving force for separation, deterioration of product water quality, shortening of membrane life, and concentration of sparingly soluble salts which can lead to precipitation on the membrane (membrane fouling), causing an increased resistance to product flow. Membranes can now tolerate a wide pH range (1–13) and temperature range (up to 200°F), which makes RO treatment more amenable for waste treatment. Direct treatment of the waste stream with no additional pretreatment steps such as pH adjustment and temperature control can be performed. Improvements in membranes have also resulted in greater recoveries of contaminants, thereby minimizing waste produced. They have provided a high degree of treatment in meeting more stringent discharge requirements.

APPLICATIONS

The application of ultrafiltration or microfiltration as alternative separation techniques which include gravity separation, centrifugation, and filtration achieves virtually complete removal of suspended solids and is more effective than conventional physical treatment of wastewater (5). In addition, higher concentration sludges than with conventional clarifiers are produced in membrane separation processes. The costs of crossflow microfiltration are about half of those incurred in a conventional plant. Therefore, the selection of microfiltration as a cheap pretreatment system capable of removing suspended matter, including colloids, is considered a viable option.

The following examples illustrate the suitability of membrane technologies for treating various mining and mineral dilute streams and effluents for pollution control and recycling of process water.

Treatment of Acid Mine Drainage (AMD)

Drainage of contaminated water from mining operations has caused some serious pollution problems (6). The primary pollutants present in acid mine drainage include iron, manganese, calcium, magnesium, and sulfate ions (7). Removal of these pollutants from acid mine drainage can be accomplished with a variety of processes. For example, iron and manganese easily form insoluble hydrates that can be removed by neutralization, aeration, and settling. However, these processes do not remove the other dissolved salts such as sulfates, calcium, and magnesium, and therefore do not produce a high quality water since they continue to carry significant amounts of dissolved solids. An almost complete removal of dissolved solids in AMD could be accomplished by ion exchange, distillation, and reverse osmosis to produce high quality water which can be used by municipalities or industry.

Acid mine drainage in most coal mining operations is principally caused by oxidation of iron sulfide minerals in the presence of air to form ferrous sulfate and sulfuric acid. Through subsequent hydrolysis more sulfuric acid is produced along with ferric hydroxide. The resulting acid water dissolves various metals from the surrounding strata and produces highly contaminated water. This contaminated water contains toxic metals such as copper, zinc, and arsenic which are harmful to vegetation and pollute the surface and groundwater.

Utilization of RO to recover a potable water product from AMD has been reviewed (8). However, RO treatment of AMD often produces a considerable volume of concentrate which must undergo further treatment and subsequent disposal. To produce high quality water for a particular purpose, the RO unit would likely be utilized as an adjunct to neutralization processes. The concentrate in this case subsequently would be treated in the neutralization/clarifier train before discharge to surface waters. However, if it were desirable or necessary to alleviate concentrate disposal problems, a portion of the neutralized RO brine might be recycled back to the RO unit where it can be mixed with raw AMD for additional treatment. The name "neutrolosis" was therefore applied to the coupled process in which the RO concentrate was neutralized by lime and recycled back to the RO unit (9–11). Lime neutralization followed by RO processes for AMD treatment has also been suggested (8). The potable water could be produced in the permeate while the concentrate in this system could be recycled back to the neutralization step. However, a cost comparison study is required to justify whether the neutralization step would be conducted before or after the RO process. A coupled ion-exchange/reverse osmosis (IX/RO) system can also be used to treat AMD waters in order to overcome the limitations arising due to the presence of a high concentration of calcium sulfate and/or iron fouling problems (12, 13). It was clearly demonstrated that given a specific AMD treatment task utilizing RO, a once-through separation process at maximum permissible recovery was superior to any neutrolosis mode (two separation processes) which could be devised in terms of ease of operation and cost (13).

For applications requiring water reuse in which completely demineralized water is not required, a charged membrane ultrafiltration process utilizing negatively charged noncellulosic membranes was applied (14). This type of filtration provides a unique and broadly applicable technique for the simultaneous separation of various inorganic metal ions present in industrial wastewaters. An application involving reuse of acid mine water for coal conversion processes has been reported (15). High ultrafiltrate recovery with good water flux containing low concentrations of $CaSO_4$ and iron are essential for the purpose of water reuse. With a single-stage ultrafiltration process having no intermediate settling operation, only 90% water recovery could be achieved (15). Water recovery up to 97% and improved ultrafiltrate quality can be achieved by introducing an interstage settling step. Among the various commercially available, charged ultrafiltration membranes that were evaluated in a continuous flow unit, PSAL membranes (Millipore type of noncellulosic skin on cellulosic backing) of initial water flux of 8.2×10^{-4} to 17.3×10^{-4} cm/s at a pressure of 5.6 $\times 10^5$ N/m^2 were found to be the best suited for the treatment of acid mine drainage (14). At the optimum operating pH of 4.0 to 4.5, a channel velocity of 200 to 250 cm/s was sufficient to minimize fouling. Even with a concentrated acid mine water containing 16,000 mg/L total solids (including high $CaSO_4$ concentration), the flux drop was less than 30%. The charged membrane ultrafiltration process consistently produces water with calcium sulfate concentrations considerably below the saturation concentration, whereas, with the lime neutralization technique, the treated water will be very high in $CaSO_4$ concentration. Although the reverse osmosis process produces water highly suitable for reuse, membrane compaction and water recovery problems must be minimized. The cost to treat 1000 gallons of acid mine water utilizing an ultrafiltration unit with interstage settling was estimated at $1.33, including the membrane replacement cost, pumping cost, and lime cost (14). Membrane technology for AMD treatment is an attractive technique since newly developed membranes can operate over a wide range of pH and hence no adjustment of pH is required.

Treatment of Flotation Water

The recycling of water from flotation mills can result in a considerable saving in the consumption of reagents. It has been reported that the reuse of clear overflow from flotation tailings after dewatering and clarification in a thickener has reduced the consumption of reagents considerably in both primary and the secondary grinding sections (16). In another plant the use of wastewater in the flotation of copper-lead-zinc sulfide ore decreased the consumption of individual reagents (17). However, flotation reagents could build up in the recycled water and have detrimental effects on the flotation operation. For example, the addition of cationic collector to a concentrate containing Pb-Zn ore causes the build up of amines in the recycled water, and this enhances the flotation of slimes and lowers the grade of the concentrate. In order to avoid problems caused by the recycling of water containing the breakdown products of collector-frother reagents, the flotation water has to be purified before recycling to mining operations (18).

Several methods were reported (18) for the treatment of flotation water such as lime precipitation, ozonation, adsorption on activated carbon, and biological treatment. However, each of these methods suffers from one or more drawbacks. For example, the natural biological treatment, which is considered the most economical treatment for flotation water, takes

4–8 weeks and the quality of the treated water is not always very good. The success of biological treatment depends on climatic conditions, the influence of toxic heavy metals, and the proper supply of nutrients for microorganisms. Unexpected pressures on pond usage and potential hazards (e.g., groundwater contamination, run-off, etc.) make this process less attractive.

It has been reported (8) that the use of RO for the treatment of flotation water was demonstrated to be a useful technique for the removal, concentration, and recovery of flotation reagents from wastewater and to provide clean water for reuse in flotation plants. The results indicated that commercial RO membranes removed in excess of 95% of the organic carbon, calcium, and magnesium from the mill water feed. The removal efficiency for the more open nanofiltration membrane was approximately 80%. Although the cost estimate for such RO treatment would be considerably higher than the biological treatment, RO treatment could be considered a good choice due to the increasing demand for quality water in mineral processing. In addition, the legislative trends toward "zero discharge" and the adverse effects of recycling untreated water make RO treatment attractive for this application. A detailed study on the use of the RO process for this treatment by carrying out a large-scale test is then required to determine the factors affecting the process as well as the extent of producing a good quality water without encountering serious fouling problems arising as a result of concentration of scaling and organic species. The economics of using RO in the flotation process versus other processes (which have been previously reported in Ref. 6) should be explored to evaluate the possibilities of using RO to purify flotation water on a large scale.

Copper Smelting and Refining Wastewater

Low-pressure ultrafiltration with negatively charged noncellulosic membranes has been shown to be feasible for the treatment of acid processing water from selenium-tellurium plant streams as well as for scrubber blowdown water from a primary copper smelting plant (19). The selenium plant water requires the adjustment of pH to 10 and a settling step prior to ultrafiltration. Membrane rejections of As and Se were 85 and 95%, respectively. On the other hand, ultrafiltration of the scrubber blowdown water containing As, Se, and several other heavy metals was effectively performed at a lower pH of 4.5 and without any presettling treatment. The maximum possible buildup of dissolved metals was quite low, even at a large number of recycle stages. A detailed study for arsenic removal from wastewater by membrane technology is essential since effluents containing arsenic are very toxic. The study will include the screening of various commercial membranes for greater percentage removals of arsenic, the effect of initial pH of solution on arsenic separation, enlargement of arsenate ion by complexation prior to ultrafiltration, and optimization of the process parameters. In a recent study (20) it was claimed that arsenic effluent could be treated with the reverse osmosis process to produce a clean permeate. The arsenic-contaminated aqueous waste was first treated by ultrafiltration to minimize the presence of materials which would reduce the efficiency of the RO membrane. Next, arsenic-contaminated water free of particulate matter was adjusted to pH range from about 6 to about 8 by chemical treatment. The filtrate was then subjected to an RO process at a pressure of about 300–1000 psig. The RO process was used as a polishing technique to produce 50–90% of the water as a permeate stream having less than 50 ppb arsenic.

The treatment of copper streams produced from dump leaching operations or plating rinse was also possible using membrane filtration. Ultrafiltration was chosen as a good candidate for acid pretreatment and then direct electrowinning. Reverse osmosis could also be used for further concentration of both copper and acid prior to electrowinning and recycling of the acid stream (21). The total process costs for the treatment of rinse streams was estimated to be approximately US$3.5/1000 gallons of rinse water recycled. This compared quite favorably with current rinse water costs which vary from US$10 to US$25/1000 gallons. However, a large-scale test is required in order to optimize the process parameters, to identify the problems encountered during a long-term operation, and to propose the appropriate solution for these problems.

Mill Wastewaters

Wastewater associated with brass wire production contains toxic metals such as Cu, Zn, Pb, Cr, and Ni. These contaminants are present as a result of the standard production process which involves heat treatment, chemical removal of oxides, and a drawing step. Removal of heavy metals, primarily copper and zinc from wire mill wastewaters, has been investigated in both bench-scale and full-scale tests using neutralization of the waste with caustic soda followed by membrane filtration (22, 23). The membrane filtration system was operated in a crossflow model using 25-mm diameter tube geometry. The tubular geometry was preferred due to its resistance to fouling. Cleaning the membranes with dilute HCl maintained permeate rates of 375 to 450 L/min without adding additional membranes. A high quality effluent was produced by this treatment. The use of liquid caustic soda avoided the formation of excess solids associated with lime neutralization of acid-bearing waste. Based on the results of pilot-plant studies, neutralization followed by an ultrafiltration scheme was selected as the preferred treatment process. Metal removal efficiencies of over 99% for Cr^{3+}, Cu, and Zn and above 90% for Ni and Pb were achieved. Process economics were evaluated, and the waste treatment costs for the modified process, including pretreatment, were reduced by US$43,200/y (22).

On the other hand, excellent rejections of dissolved solids were achieved by reverse osmosis and electrodialysis for the treatment of primary aluminum mill wastewater (24). The product waters were suitable for nonpotable reuse applications. The pilot study indicated that after an initial flux decline, no significant decline occurred over the rest of the study. The membrane life would be expected to meet or exceed the 3-year performance period given by the manufacturer. However, several types of different commercial membranes need to be tested in order to compare their performances and costs.

Removal of Ammonium and Nitrate Ions

Ammonium and nitrate ions in mine and mill water are generated from degradation of cyanide in gold mill effluents and from the use of ammonium nitrate–fuel oil blasting agents in mines. RO and NF membranes proved to be efficient membranes for the removal of ammonium and nitrate ions from actual mine effluents (25). More than 99% ammonium ion removal was reported by using commercial RO membranes while about 66% removal was reported using commercial NF membranes. Nitrate removal, however, reached up to 97% by RO membranes (25). The concentrate containing an appreciable amount of ammonium ions (about 1 g/L) could be further processed to produce ammonium compounds to be used as fertilizers. An extended laboratory-scale test should be done in order to investigate the effect of various operating parameters, including the concentration effect, on the performance of membranes over a longer period of time. Also, concentration tests should be done in order to collect a certain volume of concentrate to be tested for the possibility of producing a fertilizer product.

In the fertilizer industry, the main waste constituents are ammoniacal nitrogen and phosphate along with urea. Different parameters have been studied for the application of RO in fertilizer industry waste treatment (26), but the alkalinity of the feed and low urea separation by the cellulose acetate membrane has restrained its application. However, cellulose triacetate RO membranes showed better performance for the separation of ammonium ions in the form of chloride, sulfate, and phosphate from fertilizer industry waste (26). Rejections of ammonium chloride and ammonium sulfate up to 95 and 97%, respectively, were reported. An even higher rejection of 99.5% for diammonium phosphate was also reported. The high rejection of sulfates and phosphates as compared to chlorides is attributed to the differences in molecular sizes. The possible treatment of wastewaters generated from fertilizer plant effluent with a hybrid method including binding of target metal ions by a polyelectrolyte such as polyethylenimine (PEI) and subsequent ultrafiltration has been demonstrated (27). The polymer binding/ultrafiltration process allows significant reduction in the volume of solution treated due to better retention of the complexes by membranes. A fertilizer effluent containing heavy metals (concentration in mg/L: Co 21, Cu 3.6, Mn 2.6, Ni 3.3, and Pb 13.5) was treated by this method to achieve a volume reduction ratio of 20 along with metal enrichment. However, the use of other types of membranes such as polysulfone membranes for such treatment is missing in the literature and therefore needs to be investigated.

Phosphatic pond water from fertilizer plants could also be treated by reverse osmosis in order to produce a clean water for irrigation (28). Initial treatment of the pond water involved a combination of liming, biological activity, and aging, which significantly reduced the level of contaminants, including phosphate, fluoride, ammonia, and dinitrotoluene (DNT), in the water. A reverse osmosis unit of spiral-wound cellulose acetate membranes (CA) provides the final polishing stage of the process, removing most of the remaining dissolved solids. The permeate produced from CA membranes had a dissolved solids (TDS) content of 150–200 mg/L compared with the feed TDS of 5427 mg/L. As a result of the process, no pond water would be discharged to the river. However, the concentrate stream of the RO process, which represents about 15% of the total feed, remained to be treated or stored until a final storage or disposal method has been developed. This treatment also included many steps which would contribute to increasing the total costs of the treatment. Other types of membranes should be tested for the removal of contaminants from phosphate pond water in order to identify the appropriate candidate that can clean pond water effectively.

Membrane Technology in the Aluminum Industry

The recovery of aluminum hydroxide from bauxite ore by the Bayer process is achieved by digesting the ore with caustic liquor under high pressure and temperature. The undissolved constituents, which are often referred to as red mud, are removed from the sodium aluminate liquor by decantation and filtration. The aluminum hydroxide is separated from the supersaturated liquor by precipitation, and the resulting spent sodium aluminate liquor is recycled to be mixed with incoming bauxite in the digester.

It is well known that the presence of organic and inorganic impurities in a caustic sodium aluminate liquor lowers liquor productivity and reduces the purity of the alumina produced. The possibility of removing organic impurities by membrane filtration has been explored (29–31). For example, results obtained using sulfonated polysulfone hollow fiber ultrafiltration modules indicated an increase in Bayer liquor whiteness of 75–90% due to the removal of colored humate species. As a result, the purity of aluminum hydroxide product was significantly improved (29, 30). A recent study (29) indicated that laboratory cast Radel-R membranes with pore sizes in the nanofiltration range are capable of removing the color of humate species from spent Bayer liquor in excess of 70% at 50–70°C and at an operating pressure of 100 psig.

Contaminated alkaline groundwaters associated with abandoned storage or aluminum industry treatment sites of spent potlinning solutions contains fluorides and cyanides. RO treatment could also be an attractive technique for such contaminated groundwaters. Pilot studies are required to identify the most reliable and cost effective commercial membranes for this application and to allow estimating appropriate flow rates, degree of membrane fouling, membrane life, equipment and operating costs.

Treatment of Groundwaters

Removal of humic substances from ground and drinking waters by membrane technology has been reported (32–34). For example, membrane filtration of highly colored river water that was rich in humic acids reduced the chemical oxygen demand (COD) by about 50% after membrane treatment (32). In other investigations it was reported (35) that membrane treatment of a groundwater source containing significant levels of color and disinfection by-products was found to be more effective than treatment by the ozonation process. Groundwater containing volatile organic compounds (VOC) was treated by membranes and achieved a VOC removal of 85–90% (36). Methods of minimizing groundwater contamination from in-situ leach uranium mining were reported (37). Surface treatment methods such as reverse osmosis and electrodialysis were found effective in decreasing the amount of water used, but they also had the potential for creating conditions in the aquifer under which the redox-sensitive contaminants would be mobile. Radium removal from groundwater by reverse osmosis (RO) at low pressure (70 psig) was fond effective and probably economic (38). Radium and total dissolved solid rejection reached up to 91 and 87%, respectively, which was better than Ra-selective carriers

($BaSO_4$-loaded Al_2O_3) or ion-exchange brines. More research in this field is required to explore the advantages of utilizing membranes as a replacement technique with a cost-effective treatment to produce a recyclable water.

Treatment of Uranium Wastewater

The use of single-step reverse osmosis as the sole means to remove uranyl sulfate (UO_2SO_4) from mine water feed has been described in the literature (39). The metal ions Ca^{2+}, Fe^{3+}, Al^{3+}, and U^{6+} were separated by using supported preshrunk "tight" cellulose acetate perm selective membranes having rejection rates of between 50 to 90% of NaCl. The spiral-wound cellulose acetate RO membrane was recommended for economical treatment in in-situ leach applications because it could be operated at high water recoveries (85%) and could be easily cleaned (40). On the other hand, the restoration method for in-situ mining has been evaluated using the electrodialysis technique (41). The lower feed pressure required, the stability of membrane material over a pH range of 1 to 14, and the longer life of the membrane are the main technical advantages of electrodialysis over reverse osmosis.

Recent studies on the reverse osmosis treatment of uranyl nitrate solution (42) indicated that membrane processes, particularly reverse osmosis, have a potential for the concentration/decontamination of uranyl solutions. Permeate concentrations to less than 1 mg/L could be achieved if a two-stage reverse osmosis process was employed. In a treatment of uranium fluoride effluents by reverse osmosis (43), separation of fluoride and U^{6+} ions under acidic conditions with a continuous feedback RO process was reported.

A uranium recovery method from aqueous solutions with a combination of reverse osmosis processes has been described (44). In this method uranium in phosphoric acid solution (30% P_2O_5) could be concentrated by passing a feed solution containing uranium through at least one reverse osmosis membrane system and then flushing the concentrated uranium solution with water in another reverse osmosis membrane system to further concentrate the uranium. The uranium concentrate was treated by hydrogen sulfide gas to remove iron in the form of iron sulfide precipitate, followed by evaporation of the uranium concentrate to produce 50–95% uranium oxide.

Treatment of Dilute Gold Cyanide Solutions

Dilute gold cyanide solutions are obtained as a result of leaching gold-containing ores with an alkaline solution of NaCN. There are two methods for gold recovery from such solutions: by cementation with zinc powder (Merill-Crowc process) and adsorption on activated carbon followed by subsequent elution. The concentrated gold cyanide solution is then subjected to electrolysis to obtain gold in the pure form. The use of reverse osmosis has been investigated as an alternative method to concentrate dilute gold cyanide solutions (45, 46) as well as to reduce the volume of gold mill barren bleed for cyanide recovery (47). Reverse osmosis has advantages over other volume reduction technologies, and these advantages suggest its suitability in this application. For example, the RO process offers high energy efficiency, particularly when compared to evaporation. RO is capable of producing an environmentally acceptable effluent as a by-product of the concentration process. RO is also well suited to automatic operation.

There is limited information in the literature on the application of RO for gold mine barren bleed. However, successful application of RO technology to metal finishing operations, including gold and cyanide solutions, has been documented (48). For example, with Filmtec, FT-30 membranes, rejections of free and combined cyanides CN^-, $[Cu(CN)_4]^{2-}$, and $[Zn(CN)_4]^{2-}$ were in the range of 91 to 99% (49). The cyanide rejection was found to be highly pH dependent, as reported in the literature (50), to be 90–95% and 99% for CN^- and $[Fe(CN)_6]^{3-}$, respectively.

An RO process for concentrating gold, silver, and copper cyanide complexes in aqueous cyanide solutions has been described (51). The membranes employed were a nitrogen-containing aromatic condensation polymer. The particular cyanide complexes concentrated by this process are one or more of the following species: $Ag(CN)_2^-$, $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, and $Cu(CN)_4^{3-}$. Cyanide complexes were obtained as a result of leaching gold-bearing ores with aqueous sodium cyanide, potassium cyanide, or calcium cyanide solution. The results indicated that a high metal percentage was retained by the RO process under different pressures (51).

Preliminary laboratory investigations indicated that a reverse osmosis process for concentrating gold cyanide solution is possible (45). The feed concentration was approximately tripled as a result of removing about 70% of the original feed volume, and a low gold content permeate was obtained.

Other studies performed by Zenon Environmental Inc. (47) on the applicability of RO technology to cyanide recovery from a gold mill barren bleed indicated that the cyanide rejection decreased from 93.4 to 90% while CNS^- rejection increased from 93.3 to 98.9% over a tenfold concentration. The rejection of anions and metals remained virtually the same. In the case of water from the acidification/volatilization/reneutralization (AVR) process, developed for the recovery of cyanide from gold mill barren bleed (52), the CN^- rejections increased from 35.3 to 70.1% while CNS^- rejections decreased from 94.2 to 84.2% over a tenfold reduction in volume.

Membrane desalination of service water from a gold mine in South Africa has been investigated (53). The operating costs associated with tubular reverse osmosis were expected to be about 50 cents/1000 L for a plant of 50 L/s capacity in order to produce quality water.

The opportunity for utilizing membrane technology in this area is great due to the benefit of concentrating cyanide ions for recycle instead of their destruction as practiced by other processes. A pilot-scale study utilizing appropriate membranes is necessary to identify the optimum operating parameters as well as the cost of membrane processes.

Recovery of Zinc from Pond Water

The production of Zn from zinc ores starts with roasting Zn-containing ores to increase the Zn content in the ores followed by a leaching and conversion step. During the leaching and conversion step, calcined ore is heated with sulfuric acid to dissolve zinc, cadmium, copper, and iron. Iron is precipitated out of solution as an ammonium jarosite crystal by adjusting the pH of the leach solution with ammonia. Jarosite can be separated from the solution by thickening. The overflow from the thickeners is pumped to the purification section where cadmium, copper, and other impurities are removed by cementation with zinc. The pond overflow is recycled back to the leaching step for further treatment. The zinc in solution is then recovered by electrolysis and cast into molds (54).

Preliminary investigation on the possibility of using membrane technologies to increase the concentration of zinc in industrial pond overflow before recycling back to the process and at the same time to provide water for washing the jarosite has been performed (55). The results indicated that the treatment of the industrial pond water containing zinc was technically and economically feasible by RO or nanofiltration (NF). Pilot-scale trials of RO and NF spiral-wound modules were also evaluated (56). Both membranes demonstrated acceptable performance for zinc recovery from the pond water. A high quality permeate (<1 g/L Zn) was produced while in excess of 99% of the zinc was recovered in the membrane concentrate. An extended pilot-scale trial of a staged process has been recommended to produce a concentrate with a high zinc content using a small membrane area (56). However, the maximum concentration attained by RO was in the range of 60 to 65 g/L Zn. In order to further increase the concentration of Zn to the degree which could be suitable for recovery (120 g/L), it has been suggested that an electrodialysis unit should be combined with the

RO unit. An electrodialysis process will be feasible for a preconcentrated stream produced by RO, whereas the RO process will be limited by the high osmotic pressure of a concentrated solution. A more detailed cost analysis of this process is required.

Rare Earth's (RE) Concentration

The RE in raw ores can be dissolved in certain electrolyte solutions and enriched by reverse osmosis (57). The separation of RE^{3+}/Na^+ in the $RECl_3$–NaCl system by one stage or three stages of RO showed that more than 90% NaCl could be removed. RO could also be used to concentrate $RE_2(SO_4)_3$–$(NH_4)SO_4$ in a feed solution from raw ores (57). The results obtained showed that RE concentrated to about eight times and that RE recovery was about 89%. The advantages for concentration by RO include a shortened process with simple treatment, no consumption of chemicals, and no environmental pollution burden.

Separation of rare-earth ions from each other is difficult since they have similar ionic radii and chemical properties. However, the magnetic moments of these ions differ appreciably, which might be useful in a possible RO treatment. Results on separation of RE ions from aqueous solution by a hydrous Fe oxide–cellulose composite membrane (58) showed higher rejection compared to a hydrolyzed cellulose acetate as a support membrane. In addition, the composite membrane did not show a flux decline with time compared to a cellulose acetate membrane. This is a new area where membrane processes could be suited for the concentration and recovery of rare earths. Research investigations should be expanded to benefit from the application of membranes for the recovery of these valuable metals.

Separation of Selenium from Barren Solution

The removal of copper and gold from process streams produces a barren solution containing a considerable amount of heavy metals which cannot be disposed of safely. Magnesium hydroxide addition followed by $FeCl_3$ is used to neutralize and precipitate heavy metals from barren solutions. Although the filtered barren solution meets environmental regulations by this treatment, the filter cake is contaminated with selenium and must be disposed of by using a costly procedure. The possibility of using membrane separation techniques to remove selenium from the barren solution was examined in order to reduce the amount of selenium in solids generated in the filtration process (44, 57). The high concentration of sulfuric acid in the barren solution and the similar sizes of the selenite and sulfate ions limited direct treatment of the barren solution with RO or nanofiltration. Therefore, size enlargement and chelation of selenium was attempted with thiourea and polyethylene glycol (59) to achieve improved separation. The results of these tests indicated that thiourea combined with ultrafiltration can reduce the amount of selenium in the barren solution to 1.5 mg/L. However, the formation of selenourea compounds would complicate the disposal of the filter cake. Selective recovery of selenium by membrane technology from barren solution needs to be investigated further.

CONCLUSION

Membrane technology could be suitable for treating wastewaters in various mining and mineral sectors where water reuse is effective; for example, metal leaching solutions, ore washing, flotation process water, acid mine drainage, refinery operations, etc. This technology would be attractive to the mining sector due to the advantages it offers: the permeate stream produced can be recycled whereas the valuable chemicals in the concentrate stream could be recovered, the energy consumption is low compared with many other conventional processes, and the treated effluent could meet the ever-increasing stringent requirements of environmental regulations. Also, membrane technology could be a useful technique to concentrate and/or recover precious metals such as gold and silver as well as rare earth metals, from dilute solutions. However, the increase in solute concentration due to membrane operation over a long period of time causes problems of high osmotic pressure which lowers the effectiveness of the driving force for separation, deteriorates the product water quality, and shortens the membrane life. Therefore, pretreatment stages are required prior to membranes separation in order to overcome these difficulties. More research is required for each of these areas to implement new ideas for pretreatment; for example complexation of metallic species through binding with polymer and then coupling with ultrafiltration in order to reduce the cost of RO membranes.

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