MEMBRANE TECHNOLOGIES FOR MINING AND REFINERY PROCESSING IMPROVEMENTS

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SUMMARY

Membrane technology has been available for over 30 years, but has been used sparingly in the general mining industry. However, recent developments in polymer chemistry, spiral wound element construction, pretreatment equipment and techniques and an expanded understanding of membrane fouling and cleaning techniques have dramatically improved the reliability and robustness of membrane based systems in the mining industry. These improvements have expanded the use of "new" technology to enhance the use of membrane technologies to separate metals from large volume heap leach mining solutions containing copper, zinc, iron, gold or silver. Moreover, membrane technologies are ideally suited to fractionations that add value to processing fluids from refineries like separating metals from acids or concentrating acids and producing high quality process fluids. Finally, wastewater from Acid Mine Drainage (AMD) can be cost effectively processed to meet surface discharge standards.

Polymeric membranes, specifically thin-film composites, have been developed that will purify, fractionate or concentrate copper, zinc, nickel, gold or silver. Recent applications have been developed for spiral wound modules that operate across the pH spectrum from 0 to 14. Systems using membranes have been constructed that operate on feed streams from 200° C to 3000 centipoise. Most recently, processes have been developed and pilot tested to successfully purify solvents, like LIX.

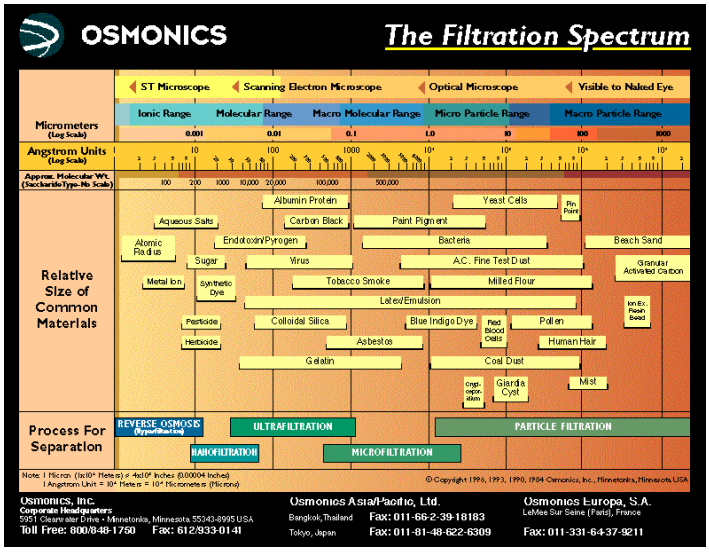
Opportunities exist to apply membrane technology to concentrate copper, zinc, nickel, silver or gold using either thin film composite Nanofiltration (NF) membranes or very tight Reverse Osmosis (RO) membranes. Both membrane types can opeate across the spectrum from low pH <2 acid applications to high pH > 10 cyanide applications. Incorporating membrane technologies into current mining operations could allow one to increase production because the membrane technology would be used to pre-concentrate heap leach solutions, and therefore, increase utilization of existing extraction and refinery capabilities. Furthermore, because of the unique selectivity of thin-film composite membranes the permeate streams from NF membranes streams will contain purified acid devoid of metals or in the case of RO membrane permeate streams will contain purified high pH cyanide also devoid of metals.

INTRODUCTION

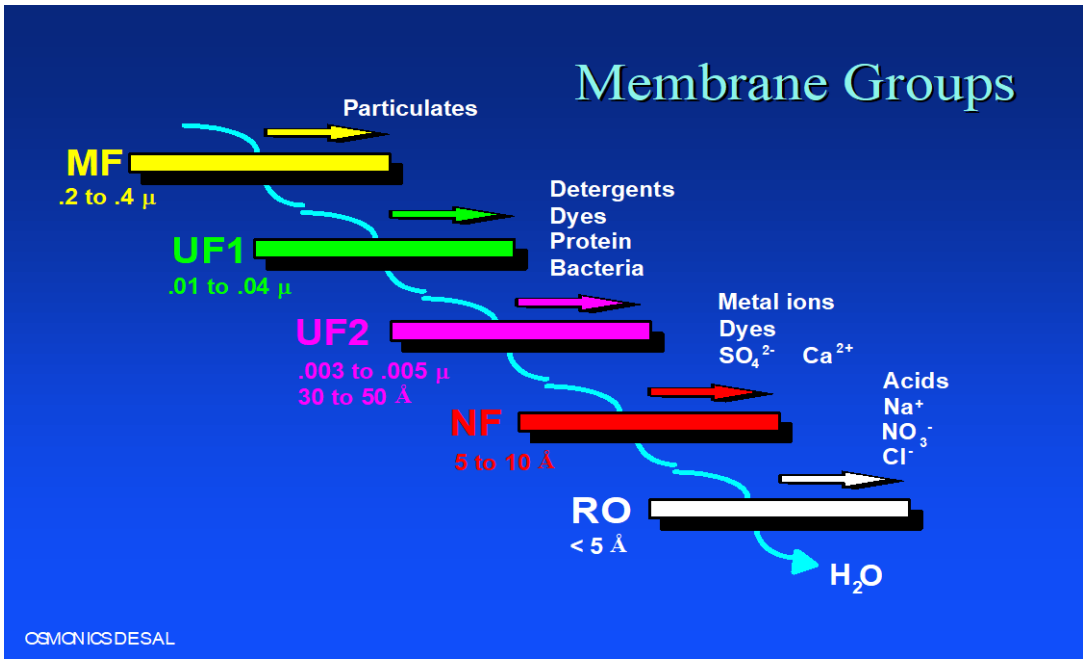
This paper will initially give a brief summary of membrane types and their configurations in spiral wound modules. Then, I shall give specific details concerning recent membrane applications developments that detail the different separations currently being used or pilot tested by the mining industry. The processes vary from the fractionation of pregnant leach solutions (PLS) in the copper and gold industries, to fractionation and concentration of metals and acids in the refineries and finally waste water treatment cost savings that combine membrane and precipitation processes. Finally, general costs (capital, operating and maintenance) of each application will be included with its respective process description.

MEMBRANE TECHNOLGOY

Membrane technology is best explained by addressing a spectrum of pore sizes (microns) and Molecular Weight Cut-Off (MWCO) values for various polymeric and thin-film composite types. The classification of membranes generally starts with the largest pore size membranes, which would be Microfiltration (MF). This membrane type would consist of symmetric or asymmetric polymers from .1 to 3 microns. Next would be a group of asymmetric polymers that form the family of Ultrafiltration (UF) membranes. This group varies across a spectrum of .005 microns to .05 microns or using MWCO the range would be from about 6K to 100K. Next, is a unique set of Thin-Film composite UF (TF-UF) membranes that have a range of MWCO values from 500 to 5,000. Next to smallest in pore size and MWCO are Nanofiltration (NF) membranes these membranes have specific MWCO from 150 to 500 molecular weights and have the unique ability to fractionate divalent anions from monovalent ions. Finally, the tightest membranes are Reverse Osmosis (RO) which have specific MWCO ranges from 50 to 150 molecular weights and reject nearly all cations and anions. (Figure 2)

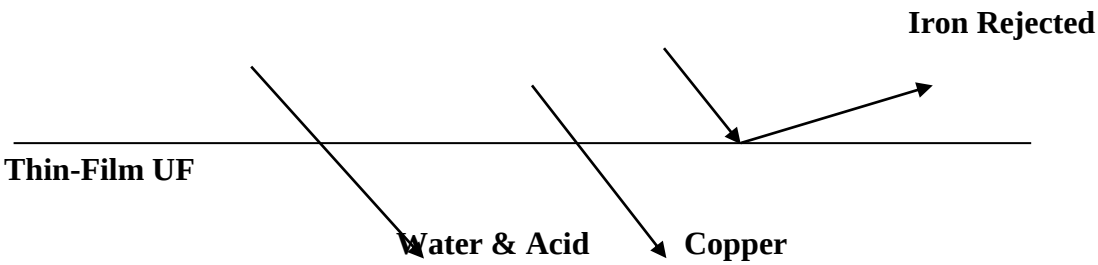


As outlined above membranes reject species on two levels—the absolute size or shape of specific non-charged molecules for all membrane types MF to RO. Or, for the tightest NF and RO membranes, the charge, charge density or degree of hydration of charged inorganic or organic salts would determine the ability of these membranes to reject or permeate a specific charged species. (Figure 2)

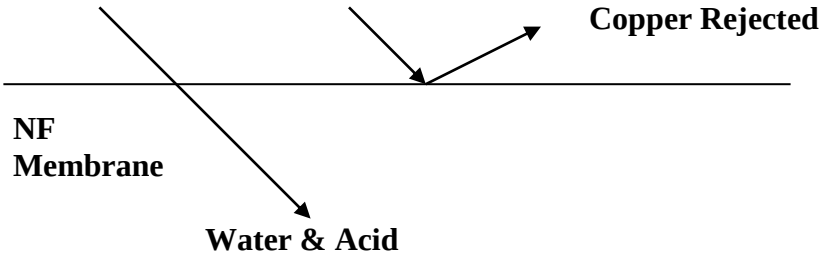


After reviewing the illustrations above and using some creativity, I believe, mining engineers or refinery operators can envision a number of potential applications for membrane technology to enhance current processes or expanded into new and improved copper, nickel, cobalt, gold and silver processing. The technology can be used to add value to these heap leach processes by concentrating or fractionation of metals, but allowing a clean solution to permeate that can be further processed to reclaim another metal or simply to be returned to the heap as a purified solution capable of enhancing metal extraction. Pictorially, I'll place four simplified drawings of the processes referenced above.

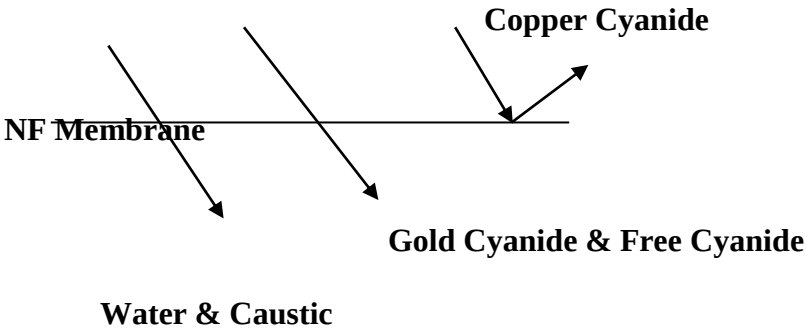
1. **COPPER/IRON FRACTIONATION Thin-Film UF MEMBRANE**



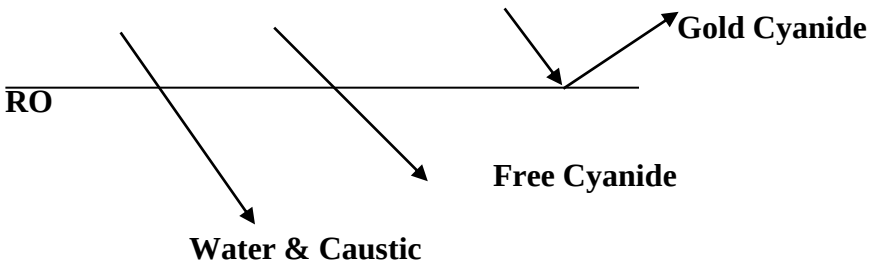
2. **COPPER/ACID FRACTIONATION with NF MEMBRANES**



3. **COPPER/ GOLD FRACTIONATION with NF MEMBRANES**

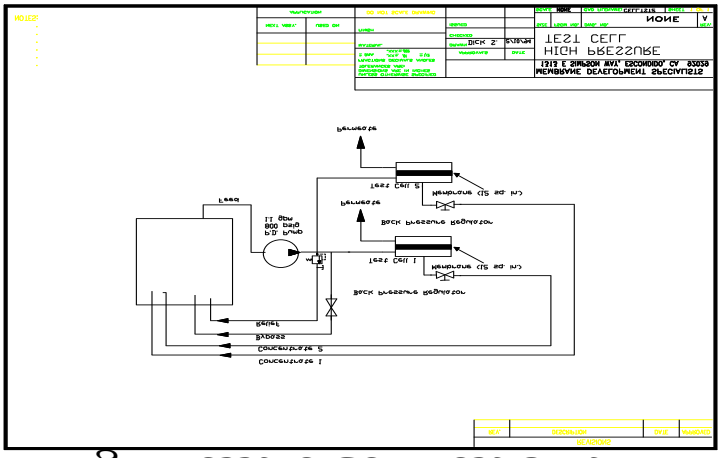


4. **GOLD CONCENTRATION with RO MEMBRANES**



PROCESS DEVELOPMENT

A logical question would be how could one incorporate membrane processing techniques described above into systems that can cost effectively process the volumes of pregnant leach solutions, refinery process streams and mine drainage wastewater? The first step would be to perform a cell test to determine the membrane type and separation factors for specific metals from PLS or electrolyte streams. Such a unit would look as follows and represents a very simple, but effective method to qualify membranes for specific separations.



High Pressure Cell Test Unit

The next step would be to perform an on site pilot study utilizing the specific membrane selected from the bench testing. During this period an entire process is evaluated in real time. Over the years we have discovered the most important considerations for new applications always focuses upon: pretreatment, proper membrane selection, proper element construction, rejection of metals by the membranes, percentage of overall recovery and, most importantly development of an effective and efficient membrane cleaning regime. If we can successfully answer these processing questions, then we can design a membrane system and submit a proposal for a membrane-based system with approximate operating and maintenance costs.

DESAL™
MEMBRANE PRODUCTS

Element Test Unit
Model 4040

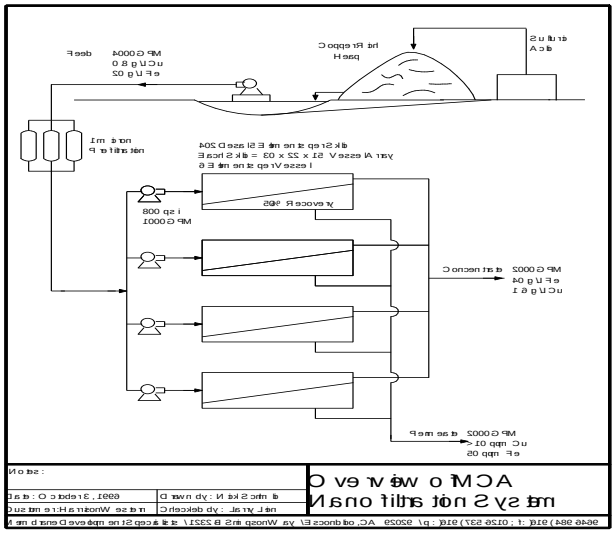
OSMONICS DESAL

OPERATING SYSTEMS USING MEMBRANE TECHNOLOGY

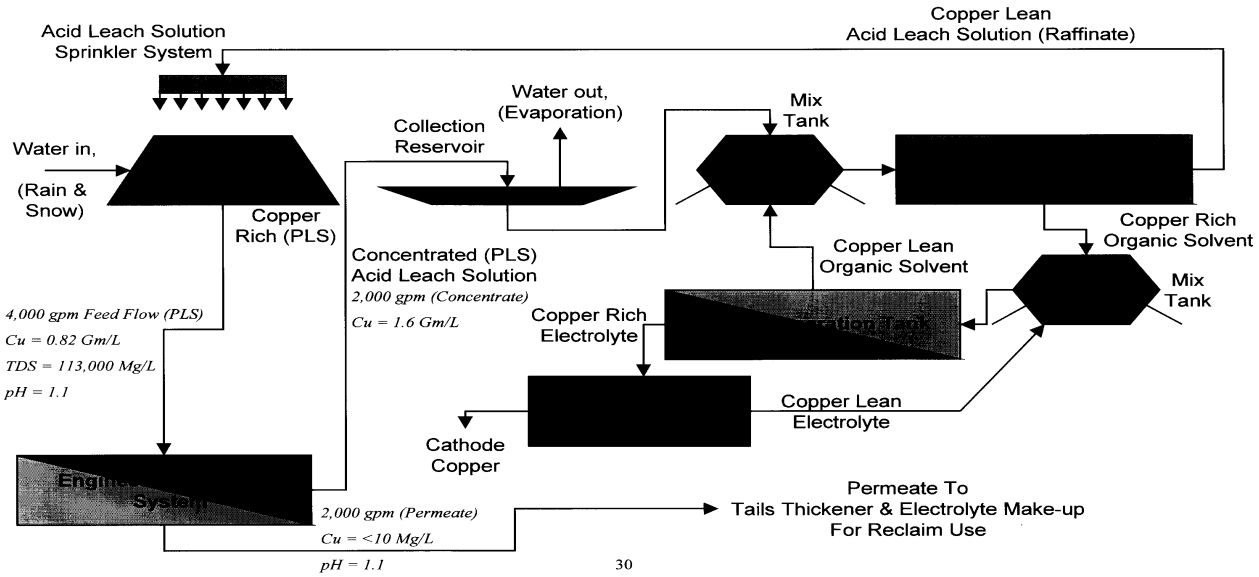
4,000 GPM Copper Heap Leach PLS Concentration system at Cananea, Sonora, Mexico. This system is used to concentrate low pH, 1.0 , copper leach solution at 700 PPM, up to 1,400 PPM. This system uses NF membranes, which reject 99% of the copper, but permeate the acid and water. The 2,000 GPM of permeate, still at pH 1.0, are reused back in the flotation cells. The system has been on line for 2.5 years with a capital investment of about $8M US. If one counts the water and acid recovered, then the pay back was less than one year.

Process Overview of Cananea de Mexicana Copper Heap Leach System

Copper Heap Leach Mine System



WATER BALANCE:
COPPER LEACH & SX/EW CIRCUITS
(With HW Process Technologies, Inc. EMS)



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Concept for Copper-Gold-Cyanide
Fractionation, Concentration and Purification

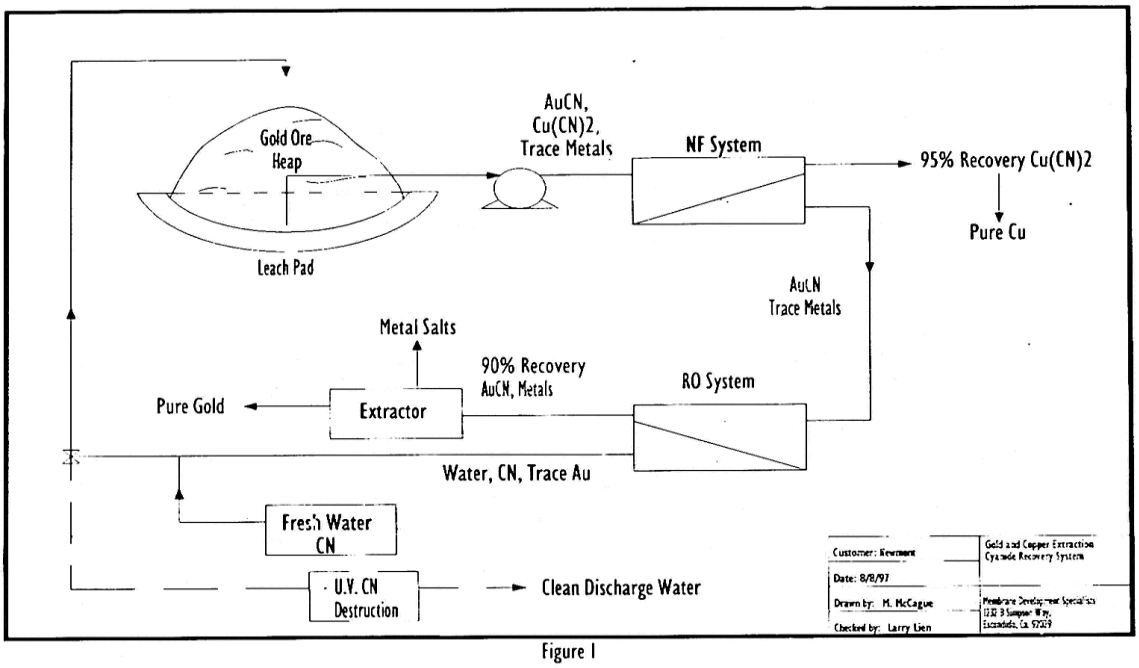
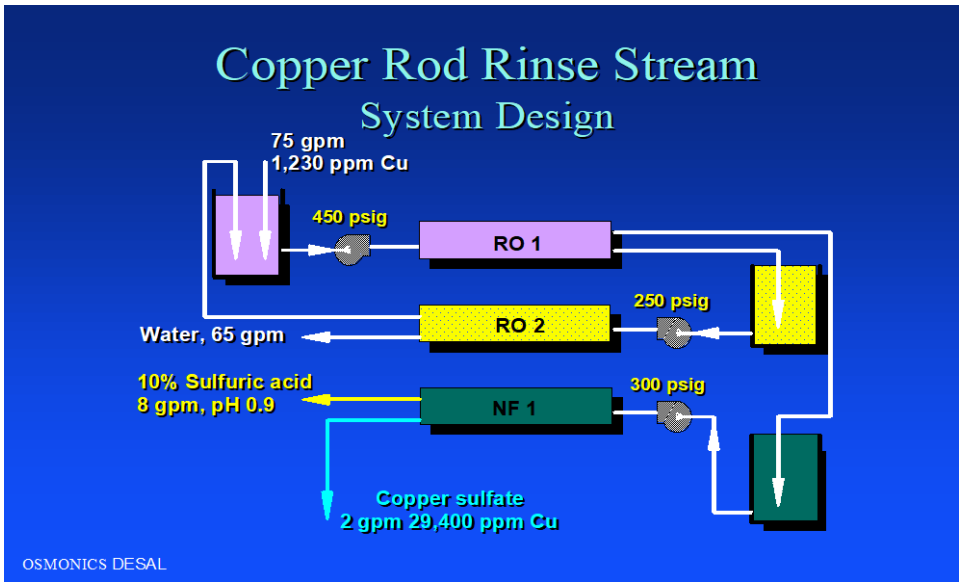


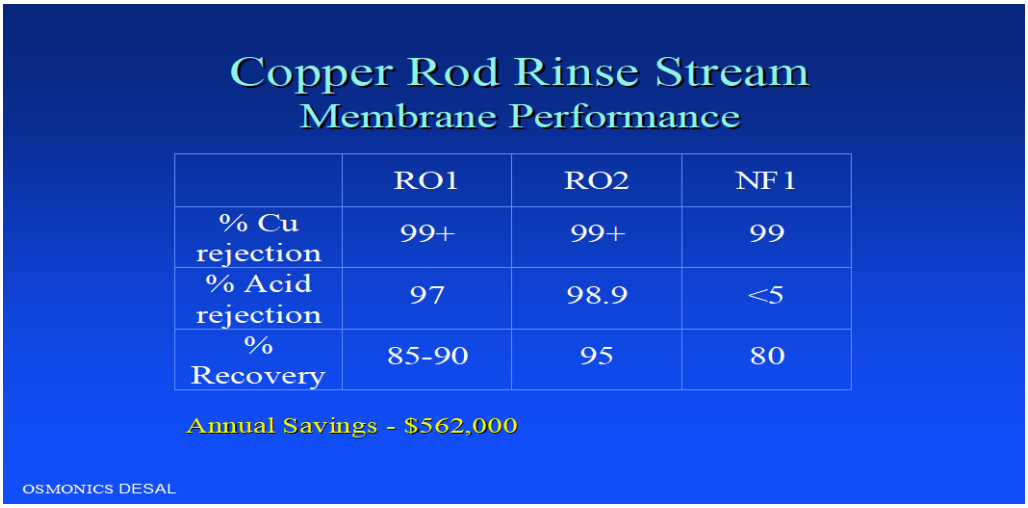
Figure 1

Referencing the process figures 3 and 4 above, one can envision a process whereby membrane technology could be incorporated into heap leach gold mining processing. Utilizing specific membrane types to accomplish unique fractionations one can concentrate dilute gold-cyanide complexes at elevated pH, but transmit (permeate) ion free product water, except for the free cyanide that is not rejected by the membrane. Please review figure 4 to give you an overview of this process.

OPERATING COPPER REFINERY PROCESSS (9 years on line)

Phelps-Dodge Copper Rod Mill Refinery has used RO membrane technology for 9 years to concentrate copper sulfate (.1g/l) and sulfuric acid (1%) from a rinse stream. Special low pH RO membrane technology is applied to recover the concentrated copper sulfate (1 g/l) for resale as copper sulfate crystals and direct reuse the concentrated sulfuric acid (10 g/l).

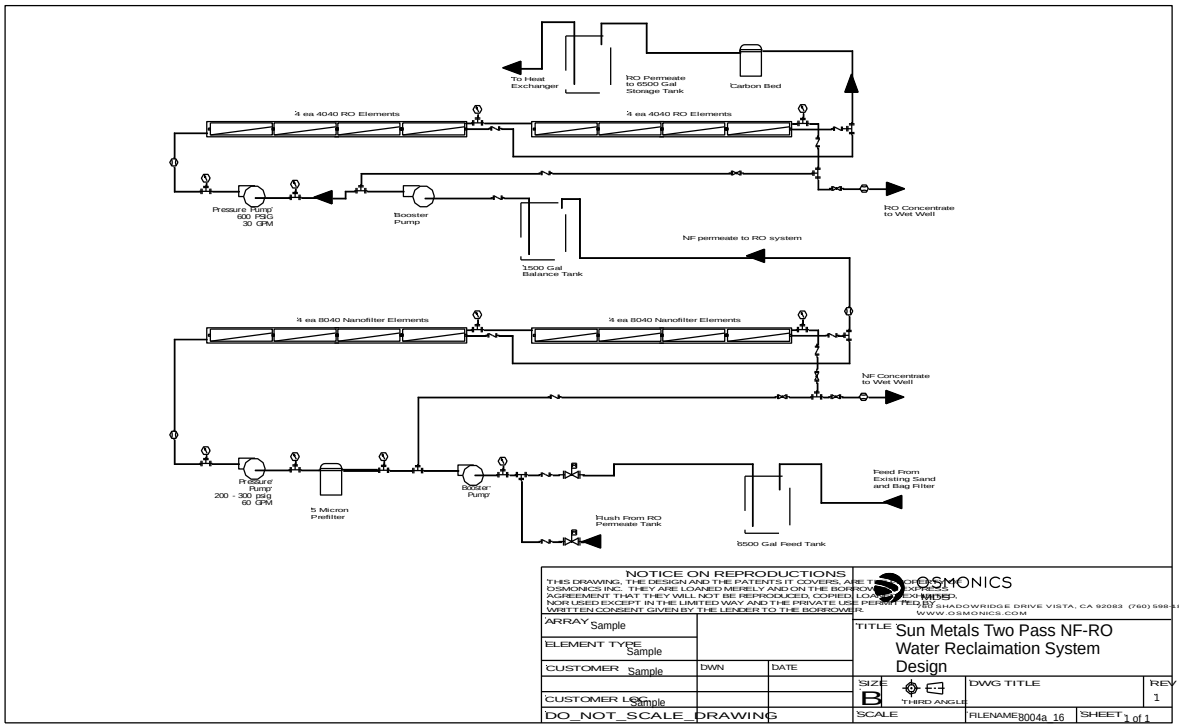




Zinc Refinery Waste Process Water

We recently completed a two-pass membrane system NF followed by RO for a new zinc refinery. The situation is quite unique in that the wastewater from the normal precipitation process is too high in boron to safely be discharged to the surface. So, we tested, designed and built a two- pass membrane process. The first pass uses NF to remove the divalent ions at high recovery from a clarified lime precipitation process. The second pass then uses NF permeate as feed for a RO membrane system to remove the

boron. To achieve high rejection of boron, one must first convert boron to borate by raising the pH of the product of the first NF pass from 8 to 10.3. This converts the feed to the second pass RO from boron to borate that is easily rejected by RO membranes. Again, a diagram of this process may well explain the concept more clearly. See figure 6



This design skid layout was one of three parallel trains. Two systems will be operating and the other will be in reserve, as back up or rotated through the process when cleaning and maintenance become necessary on one of the other skids.

ASARCO REFINERY PROCESS (On line for 6 Years)

Heavy metals from 100 years of refining had contaminated the ground water beneath the Asarco Globe refinery in Denver, Colorado. As a treatment scheme the refinery installed a conventional caustic precipitation system. The system worked OK, but it produced huge amounts of sludge which were hauled by rail to an Asarco refinery in Montana. And the product water from precipitation, which is borderline as far as meeting surface discharge limits for heavy metals. We installed a NF membrane system prior to the existing precipitation system and operate it at 75% recovery, thereby reducing the volume of water to be precipitated by ¾. The permeate water from the membrane system is further polished and as one can see from the water quality data easily meets and exceeds the discharge standards. Furthermore, a huge saving was realized in the volume

of sludge produced and the amount of chemical needed to operate the precipitation system. Please review the three attached documents carefully, because I believe, membrane technology can enhance any existing precipitation process as a pretreatment to precipitation.
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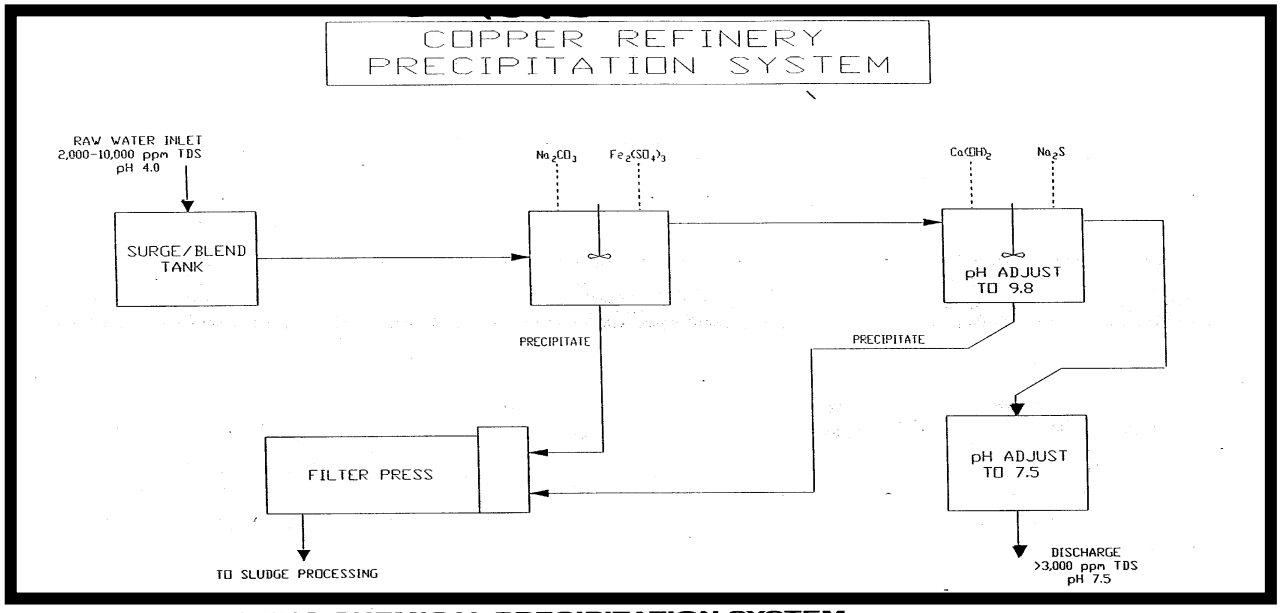

EXISTING CHEMICAL PRECIPITATION SYSTEM

Chemicals Utilized	
Lime	$ 2.81
Celatom	2.82
Sodium Sulfide Flakes	0.10
Ferri Floc	4.02
Acid	0.13
Subtotal Chemical Cost	$ 9.88
Sludge Disposal	
Sludge Generated @ 771.5 lbs/1000 gals treated Disposal at $260/ton	$100.29
Total Cost/1000 Gals Treated	$110.17

MEMBRANE BEAD TREATMENT SYSTEM

Chemicals Utilized	
Anti Scalent	$ 0.27
Membrane Wash	0.35
Heavy Metal Media Regeneration	0.25
Arsenic Media Regeneration	0.11
Subtotal Chemical Cost	$ 0.98
Sludge Disposal & Concentrate Treatment	
Concentrate Treatment with Existing System	$ 0.82
Sludge Generated @ 39.3 lbs/1000 gals treated Disposal @ $260.00/ton	5.11
Total Cost/1000 gals treated	$ 6.91

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CONCLUSIONS

Clearly membrane technology has been successfully and cost effectively applied to mining and refinery process and wastewater streams. We believe the our technology has advanced from a materials and process understanding stand points to where we can unabashedly promote the use of membrane technology to enhance separation processes in a cost effective manner.

At a conference several years ago I was asked what has been the most important new development in membrane technology in the past 20 years. And with out a doubt one can simply state that the advances in

[1]

thin-film membrane technology to reduce the operating pressures from 400 psi to 100 psi while producing higher quality water has been the most significant break-through. In addition the operating and cleaning pH ranges have been extended from 4 to 7 for first generation membrane technology to where we now routinely operate membrane systems at pH's from 0 to 13.

Finally, the worldwide market for membranes is now several billion dollars per year. The shear market size has allowed for efficiencies due to economies of scale that has reduced the price of a standard water element from $1200 to $600 over the past 20 years. Now, these numbers would not phase the computer industry, where the numbers I'm citing occur in an 18 to 24 month time frame, but the increase in performance coupled with a decrease in price is significant.

What Osmonics brings to the table is experience and know-how. And by applying these years of experience we engineer specific membranes, design specific processes and build custom equipment for our industrial clients that are reliable, cost effect and add value to our customers.