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TREATMENT OF WASTEWATER FROM NATURAL GAS WELLS
BY A FILTRATION PROCESS



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สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

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เรือกักเก็บก๊าซธรรมชาติเหลวของบริษัทยูโนแคลมีความจุ 660,000 บาร์เรล ปัจจุบันนอกจากปริมาณก๊าซธรรมชาติเหลวประมาณ 40,000 บาร์เรลต่อวันจากแหล่งผลิตถูกส่งผ่านท่อใต้ทะเลเพื่อกักเก็บบนเรือแล้ว ยังมีปริมาณน้ำจากหลุมผลิตอีกประมาณวันละ 200 บาร์เรลถูกส่งมากับก๊าซธรรมชาติเหลวเช่นกัน น้ำจากหลุมผลิตเหล่านี้ไม่สามารถทิ้งลงทะเลได้โดยตรง หากปราศจากการบำบัดเนื่องจากมีปริมาณสารโลหะหนักเจือปนในปริมาณสูง อาทิ สารปรอท และ สารหนู เพื่อเป็นการแก้ปัญหาปริมาณน้ำบนเรือกักเก็บก๊าซธรรมชาติเหลวมากเกินไป ซึ่งก่อให้เกิดปัญหาในการขนถ่ายก๊าซธรรมชาติเหลวไปยังลูกค้า และ สูญเสียพื้นที่ในการกักเก็บก๊าซธรรมชาติเหลว ทางบริษัทยูโนแคลได้ทำการศึกษาความเป็นไปได้ในการบำบัดน้ำทิ้งจากหลุมก๊าซธรรมชาติโดยกระบวนการกรองบนเรือกักเก็บ อุปกรณ์ที่ใช้ในการกรองเป็นเมมเบรนชนิด Ultrafiltration และ Reverse Osmosis นอกจากนี้ยังมี อุปกรณ์ไฮโดรไซโคลน (Hydrocyclone) ซึ่งใช้ในการกำจัดอนุภาคแขวนลอยในน้ำก่อนส่งเข้าหน่วย บำบัดจากผลการทดลองพบว่าเมมเบรนชนิด Ultrafiltration สามารถลดปริมาณน้ำมันและสารปรอท ในน้ำทิ้งได้มากกว่า 98% เมมเบรนชนิด Reverse Osmosis สามารถลดปริมาณสารหนูใน น้ำทิ้งได้ 90-95% อย่างไรก็ตาม น้ำทิ้งจากการบำบัดยังมีคุณภาพไม่ดีพอตามค่ามาตรฐานของทางบริษัทยูโนแคลที่กำหนด ปริมาณสารหนูไม่เกิน 250 ส่วนในพันล้านส่วน (ppb) การใช้งานของเมมเบรนชนิด Ultrafiltration ถูกจำกัดโดยการสะสมตัวของปริมาณอนุภาคแขวนลอยที่อุดตันเยื่อกรอง เมมเบรน ชนิด Reverse Osmosis มีการเสื่อมสภาพจากการสัมผัสกับอนุภาคน้ำมันในน้ำ นอกจากนี้การทดสอบ ยังพบว่าเมมเบรนชนิด Ultrafiltration สามารถให้ค่า Permeability มากกว่า 98% ของค่าตั้งต้น และ เมมเบรนชนิด Reverse Osmosis ให้ค่า Permeability ประมาณ 50%

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The FSO, Floating Storage and Offloading, is a vessel designed to store 660,000 barrels of condensate in the Gulf of Thailand. Currently, water associated with the condensate shipped to the FSO is being segregated from the condensate and is being stored as free water in dedicated tanks on-board the FSO. This amount of water can not be directly discharged overboard due to the environmental concern. This situation causes major problems, e.g. customers complain due to high water carry-over with condensate, high Arsenic, Mercury and hydrocarbon accumulation, difficulty in Tank balancing, lost space for condensate storage, etc. In order to determine the feasibility of cleaning the ship-retained produced water, Unocal Thailand conducted pilot scale testing of a combined ultra-filtration (UF) and RO membrane system. The ultra-filtration membrane from Osmonics-Desal was pre-treated to render it hydrophilic. As a result, the UF membrane resists fouling by dispersed hydrocarbons in the water being filtered. The spiral-wound UF membrane was prone to plugging by solids in the feed water. However, a 1" desanding hydrocyclone was successful in removing most of the solids from the feed water and a 5-micron cartridge was used as a polishing filter. The UF filter removed over 98% of the dispersed hydrocarbons in its feed stream, along with essentially all of the mercury. Typical UF permeate contained 1 to 4 PPB of mercury. Water-soluble arsenic was not removed by the UF filter. The RO membrane was only partially successful, reducing arsenic by between 90 and 95% from incoming values. Although this rejection rate might be considered good, the RO permeate did not meet the 250 PPB as Unocal Thailand self-imposed limit for arsenic in discharge water. The performance life of the UF filter was limited mainly by the deposition of iron-based solids within the spiral-wound membrane. At the conclusion of testing, it was found that the UF membranes had retained over 98% of their original permeability. Some initial swelling of the RO membrane occurred due to the presence of dissolved aromatics in the produced water. The swelling reduced RO membrane permeability to about 50% of its initial value.

Department Chemical Engineering Student's signature.....
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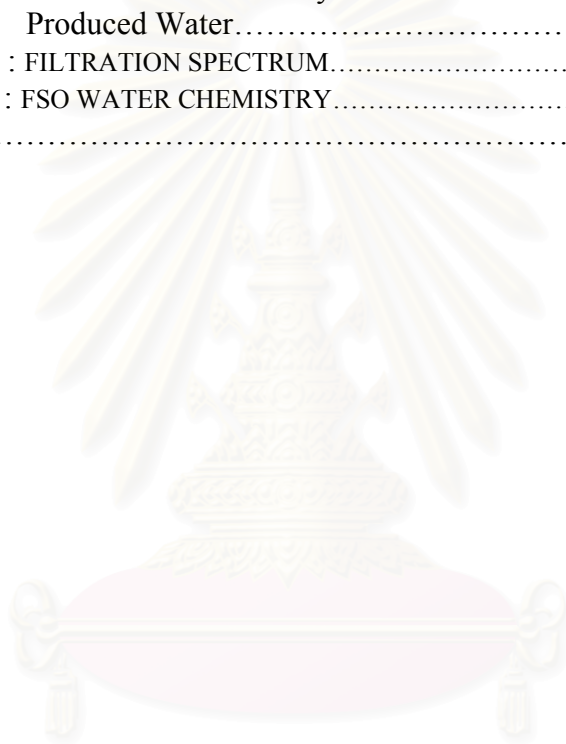
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CHAPTER I

INTRODUCTION

Unocal Thailand's daily production in 2000 averaged around 1 BSCF of gas, over 40,000 barrels of condensate and approximately 75,000 barrels of water. Condensate with between 0.1 to 0.5% BS&W is pumped from five central processing platforms to a floating storage facility before it is transferred to shuttle tankers. Water arriving on the storage tanker is contaminated with hydrocarbons, mercury and arsenic. It remains on the ship and must be cleaned to Unocal Thailand's strict discharge specifications before overboard disposal, or it can be transported to a nearby platform where it can be injected into a disposal well.

The FSO, Floating Storage and Offloading, is a vessel which is designed to store 660,000 barrels of condensate in the Gulf of Thailand. Currently, water associated with the condensate shipped to the FSO is being segregated from the condensate and is being stored as free water in dedicated tanks on-board the FSO. Free water is accumulating on the FSO at a rate of approximately 6,000 barrels per month. Presently approximately 48,000 barrels are stored on-board the FSO. This amount of water can not be directly discharged overboard due to the environmental concern. This situation causes the following major problems:

1. Water carry-over with condensate to customers, approximately 500 barrels per ship
2. High heavy metal and hydrocarbon contamination

Arsenic	16,400 ppb
Mercury	2,200 ppb
TPH	600 ppm
3. Lost space for condensate storage

The existing water removal is done by loading water off the FSO via ship for processing or disposing elsewhere at high cost.

In order to remedy this situation and reduce this amount of water stored on the FSO, a pilot water-treatment unit was installed on the FSO to prove the feasibility of membrane technology. The unit uses non-fouling membrane to filter FSO water to the quality that can be discharged overboard. This project, if successful, could potentially eliminate the need for future FSO water lifting at a one-time investment cost of about US\$300,000.

Although separation of oil and water by Ultrafiltration (UF) is well known, its applications have been limited because of the following three problems:

1. Fouling of membrane from "free oil"
2. Plugging due to particulate entrapment
3. Swelling due to solvent attack (Soluble Hydrocarbons & Polar Organic Compounds)

This study is focused on the new “Ultrafilic” membranes which are neither fouled by free oil or solids nor degraded by soluble hydrocarbons and polar compounds present in oil field produced water.

The Ultrafilic membranes are made of a chemically modified polyacrylonitrine (PAN) polymer. To prevent fouling by free oils, the membranes have been engineered to be highly hydrophilic (water attracting). This property results in consistent rejection of oil and reliable system operation without membrane fouling. The membrane can operate at temperatures to 170 °F and is stable in a broad pH range from 2 to 12. This versatility eliminates the need to neutralize oil field waters.

There is a pilot plant operating for treating produced water from a steam flood. The membrane provided a positive barrier to the incoming oil. The permeate from the pilot unit contained less than 5 ppm oil with varying oil concentrations from 100 to 900 ppm in the feed. Furthermore, another pilot plant has been tested successfully for 2 months on heavy oil in Venezuela without fouling by solids or oil.

The design configuration of this study consists of two pilot plants, one equipped with the Ultrafilic membrane for de-oiling and removing suspended solids, and the other equipped with the Reverse Osmosis membrane for removing Arsenic.

The permeate will be discharged overboard with the following specified quality:

Arsenic	less than	250 ppb
Mercury	less than	10 ppb
Hydrocarbon	less than	40 ppm

The pilot membrane was tested for 6 months. It is proposed to demonstrate a cost effective way of oil and heavy metals removal from produced water from natural gas wells. The definition of a successful test will be the production of overboard quality water continuously with minimal membrane deterioration. If this technology is technically successful, there is another cost-reduction benefit to compare with the existing water disposal on the FSO.

This technology is likely to be economically viable only for higher cost water disposal problems rather than for routine disposal problems. The FSO application is attractive since it is a high cost disposal issue, and it presents the opportunity to find out if clean water can be obtained from this technology at a low enough cost that it can be considered for other applications.

CHAPTER II

LITERATURE REVIEWS

The separation of oil and water by hydrophilic Ultrafiltration(UF) membrane is a proven technology, but there are few numbers of review papers addressing the application and development in oil & gas industry, particularly treating of produced water from natural gas wells. Its widespread utilization for wastewater minimization or recycling applications has the following three common problems:

- (1) Fouling from “free” oil which overflows from upstream pretreatment;
- (2) Fouling from free oil which de-emulsifies as the feed is concentrated;
- (3) Fouling and decomposition of the membrane from accidental contamination of the waste stream by aggressive solvents.

In this chapter, former studies and applications will be provided in other areas of the industries which some of the applications will be related to this thesis.

Crossflow filtration provides unique separation and purification capabilities, particularly in the treatment of small, dissolved impurities normally less than 0.1 micron in size. The crossflow mode of operation continuously "sweeps" the membrane surface, minimizing build-up of rejected impurities. Successful development of an application depends on good membrane selection, machine design, and pretreatment. Feasibility and pilot testing are key steps in making these choices. Working with a vendor experienced in crossflow filtration technology is also very important. The result of good development is a full-scale system that operates simply, reliably, and consistently; and meets application objectives. Crossflow filtration is applicable to plant effluent treatment, water reclamation, or material reclamation. Water with purity suitable for reuse or discharge, or material reclaimed for operations, are benefits to be expected.

A variety of industries are finding that it makes sense to reevaluate the way they treat industrial process water, both to improve the quality of their products and increase the efficiency of their processes. Purification systems utilizing crossflow membrane filtration, such as reverse osmosis (RO), nanofiltration (NF) or ultrafiltration (UF) can be a good alternative to traditional filtration and chemical treatment systems. RO crossflow filtration systems produce water similar in quality to demineralized or distilled water. This makes RO the filtration method of choice for the medical, semiconductor, beverage, pharmaceutical, food and chemical industries where water quality is of paramount importance. Crossflow membrane filtration is generally divided into four groups: RO, NF, UF and microfiltration (MF). The filtration spectrum displays the various filtration groups based upon the size of the particles they can remove. RO membranes have the smallest pore structure, with pore diameter ranging from approximately 5-15 angstroms. The extremely small size of RO pores allows only the smallest organic molecules and uncharged solutes to pass through the semipermeable membrane along with the water. Greater than 95-99% of inorganic salts and charged organics will also be rejected by the

membrane due to charge repulsion established at the membrane surface. Nanofiltration is typically referred to as "loose" RO due to its larger membrane pore structure, which allows more salt passage through the membrane. Because it can operate at much lower pressures, and passes some of the inorganic salts, NF is used in applications where high organic removal and moderate inorganic removal are desired. An advantage of NF over RO is that NF can typically operate at higher recoveries, thereby conserving total water usage due to a lower concentrate stream flow rate. UF operates based upon a "sieving" mechanism that rejects constituents based upon size. The membrane pores are generally too large to effect desalting, so all ionic salts readily pass through the membrane. Ultrafiltration is basically used to remove large organics, colloidal silica and microbiological constituents. Within these broad categories, a system can be engineered to meet most process requirements. The ongoing evolution of membrane technology allows greater flexibility in designing systems that function under a variety of operating conditions. The development of new membranes continues to expand both the range of chemical compatibilities and physical operating conditions (including pressure, temperature and pH) of membrane systems.

Table 2.1 Comparison of Crossflow Membrane Configurations

	Cost	Packing Density	Operating Pressure Capacity	Membrane Types	Fouling Resistance	Cleanability
Traditional Spiral-Wound	Low	High	High	Many	Fair	Fair
Hollow Fiber	Low	UF-High RO-Very High	UF-Low RO-High	Few	UF-Good RO-Poor	UF-Good RO-Poor
Tubular	High	Low	UF-Moderate	Few	Very Good	Very Good
Plate & Frame	High	Moderate	High	Many	Fair	Fair

The proper choice of membrane should be determined by the specific application objective -- particulate or TOC removal, hardness reduction or ultrapure water production for such industries as electronics or pharmaceutical manufacturing (Table 2.2). The most widely used membranes for RO are the cellulosic (CA) and polyamide (PA) types rated at 97%-99+% NaCl rejection. Nanofiltration, also available with CA and PA type membranes, displays characteristic salt rejections from 95% for divalent salts to 40% for monovalent salts and an approximate 300 molecular weight cut-off (MWCO) for organics. The most popular UF membranes are polysulfone (PS), a proprietary fluorinated material (VF), and CA, each generally having a 1000-100,000 MWCO. UF, NF and RO generally operate at 25-100 psig, 135-230 psig, and 250-400 psig (1.7-6.9 bar, 9.3-15.9 bar, and 17.2-27.6 bar). Operating at higher pressures [500-1000 psig (34.5-69.0 bar)], RO and NF membranes must be designed to resist the effects of mechanical

compression, or compaction, which may permanently deform the membrane and diminish performance. The last decade of membrane and module development has lessened the effects of physical compaction and has brought forth spiral membrane modules capable of operating at pressures in excess of 800 psig (55.2 bar). This has led to the widespread use of spiral-wound modules for desalination applications. Process temperature plays an important role in any crossflow membrane system. Flux through a semipermeable membrane will increase with increasing temperature due to lowered viscosity of the process stream. Upper operational temperature limits are established based upon the plastic nature of the membrane itself and the components used in the construction of the membrane module. Spiral-wound RO, NF and UF modules are typically operated near ambient temperatures, 55-90 F (13-320 C), for optimum performance and membrane life. Modules designed for high temperatures can achieve operation up to 202 F (80 C), with shorter membrane life. There are circumstances, however, in which utilizing the thermal energy of a process stream and sacrificing membrane life is more economical than cooling the process stream before treatment. Careful consideration must be given to the combined effects of temperature, pressure and contaminant fouling to ensure successful operation.

Other than operating pressure and temperature limitations, consideration must also be given to the chemical compatibility and membrane stability at a given process stream pH. The large number of membranes commercially available enables a designer to choose among several polymer types to match most pH concerns. The pH of a process stream may become an important operating variable to monitor for RO and NF systems. The solubility levels of dissolved mineral salts, CO₂ and silica are greatly affected by pH. Membrane systems rejecting substantial quantities of dissolved constituents must operate at concentration factors safely below any solubility limits. In general, slightly soluble salts, such as CaCO₃, are more soluble at lower pH values. By lowering the pH a higher concentration factor, or recovery, can be achieved. If a system approaches or exceeds the design recovery, the concentrated salts may precipitate and form a hard scale on the membrane surface. Of course, solubility limits are generally not a concern with membrane systems such as UF where dissolved salts pass through, rather than are rejected by, the membrane. Chemical resistance to oxidizing agents, such as chlorine and iodine, must also be investigated when choosing a membrane. CA membrane, for instance, usually exhibits a higher tolerance for chlorine than PA membrane, making CA an ideal choice for systems requiring the bacteriological benefits of a continuously chlorinated feed stream.

Table 2.2 Crossflow Membrane Processes

Process	Components Retained	Transmembrane Pressure	Process Applications
RO	99% of most ions, most organics over 150 MW	200- 1000 psig (13.8-69.0 bar)	Brackish sea water, Desalting, boiler feed purification, blowdown reclamation, pretreatment to ion exchange, ultrapure water production.
NF	95% divalent ions, 40% monovalent ions, organics greater than 150-300 MW	135-230 psig (9.3-15.9 bar)	Hardness removal, organic and microbiological removal, dye desalting, color removal
UF	Most organics over 1000 MW	25-100 psig (1.7-6.9 bar)	Pre- and post-treatment to ion exchange, beverage clarification, concentration of industrial organics and dilute suspended oils, removal of pyrogens, bacteria, viruses, and colloids.
MF	Small suspended particles greater than 0.1 μ	25 - 50 psig (1.7-3.4 bar)	High volume removal of small suspended solids.

This work is the first of a series of investigations designed to identify key test parameters which need to be controlled to allow objective performance comparisons between different UF membrane products. The current study shows the effect of operating pressure and crossflow velocity on the polydispersed dextran retention of cellulose acetate UF membranes. The operating pressures between 70-280 kPa and crossflow velocities between 0.3-1.5 m/s were investigated in this work. Within the scope of this work (Reynolds numbers between 1500 and 5600), it was demonstrated that the dextran retention was strongly dependent on the test parameters. In general, an increase in transmembrane pressure and/or a decrease in the average crossflow velocity will both decrease the dextran retention. The effect of the pressure and crossflow velocity can be understood based on shear induced deformation of the solute molecule.

The application of membrane technology for the recovery and reuse of water describes the mechanism of membrane effected separation (specifically reverse osmosis, ultrafiltration and microfiltration), membranes commercially available, membrane element configurations, and how complete membrane systems are designed. The paper also discusses case histories of a variety of proven applications, as well as areas of high potential. System design, operating parameters and detailed benefits derived from use of membrane systems are also included. Laboratory, pilot plant and full-scale unit process equipment is presented, as well as the steps required to evaluate feasibility and scale-up to process conditions. Economical evaluation of the process is presented in the case histories. New areas of high potential for payback on water reuse and/or recovery of valuable products, as an added benefit, are also described. For oily waste treatment and water recovery, a die cast manufacturer for automotive parts, Sealed Power Corporation, was discharging their treated end-of-pipe process water to a lagoon. Sulfur compounds and their associated smells created a problem for a small community located nearby. Sealed Power chose to evaluate alternative forms of disposal compared to conventional flocculation and lagoon storage. The location of the nearest mainline for city sanitary sewer (5 miles) made it uneconomical to consider sending the process waste water to the city treatment plant. Estimated cost to tie into the city sanitary sewer was \$1,500,000. The membrane manufacturer, Osmonics, was contacted to evaluate the use of an RO system to concentrate the treated water after flocculation to minimize hauling costs and reuse the permeate in the cooling towers. A feasibility application test was performed on a representative sample to choose the optimum RO membrane. Results from an application test membrane scan showed the membrane of choice was Sepa[®] -92 (CA). Next, a pilot unit was installed on-site to gather long-term operating data. Severe membrane fouling occurred due to the variability of the feed stream in terms of oil content and TDS. The conventional flocculation, functioning as pretreatment to the RO, used both caustic and acid addition, which added considerable TDS to the treated wastewater. Following four months of pilot operation, new RO separators were installed and UF was added as pretreatment to increase overall membrane efficiency. This system was then compared to conventional flocculation as pretreatment ahead of the RO. Testing was performed on the UF/RO system to generate long-term data from which to design full-scale equipment. After evaluating results from both methods, the clear decision was to proceed with UF/RO based on economics and the operating problems associated with flocculation. The annual cost to treat the process wastewater with conventional flocculation was \$60,000/year in materials and 20 man-hours/month for batch operation. In addition to these costs, the plant was severely limited in choice of die lubricants that were compatible with the chemical treatment system. This limitation had an estimated cost of \$15,000/month due to reduced performance and higher lubricant cost. Make-up water to the die cast operation was well water with a TDS of 450 ppm as CaCO₃. The dissolved solids in the well water shortened life and placed an additional load on the high recovery waste treatment RO. The decision was made prior to installation of the waste UF/RO system to install a separate RO system to purify 4 gpm of make-up water to the die cast operation, reducing cost by increasing overall system efficiency. The total installed cost of the UF/RO waste treatment system was \$200,000. Yearly operating cost is \$95,000, which includes replacement membrane, chemicals, electricity, labor and hauling of the concentrated waste. The overall system recovers 5000

gpd of water for reuse, saves \$136,600/year on hauling costs and saves about \$180,000/year materials cost on the flexibility to purchase a wider variety of die lubricants.

Reverse osmosis and ultrafiltration membrane compaction and fouling using ultrafiltration pretreatment on numerous membranes run for a minimum of 1000 hours at temperatures varying from 25°C (77°F) to 50°C (122°F) and pressures from 25 psig (1.7 bar) to 800 psig (55.2 bar) was collected. Comparison of membrane compaction rates indicates that fouling is a much greater cause of flux degradation than has previously been reported. The use of ultrafiltration prior to the membranes on test helped to substantiate the effect of fouling. The system used for these tests is a much-improved method of obtaining compaction results, and it is suggested that all compaction studies use UF pretreatment immediately prior to the membrane being tested. The results of the experiments indicate that membrane flux reduction over time results primarily from fouling with compaction being a minor factor at 25°C (77°F), but a more important factor at 50°C (122°F). There is some evidence to suggest that membrane fouling may also contribute to accelerated membrane compaction. Additional testing on other membrane materials and at even higher temperatures will be undertaken to further identify the true cause for flux decline in RO/UF systems. With UF prefiltration, membrane fouling and hence flux decline can be dramatically reduced. By employing ultrafiltration membranes as prefiltration ahead of RO membrane systems, significant improvements in RO system performance can be expected. As RO membrane becomes more expensive, the use of UF pretreatment should increase significantly to lengthen useful RO membrane life and give more predictable system performance.

The applications of ultrafiltration (UF) and reverse osmosis (RO) membrane technology used to reclaim water, and reduce wastewater discharge costs. The first case history covers oily wastewater treatment at a major aluminum beverage can manufacturing plant. The second case describes treatment of wastewater from a multi-plating bath section of a major wheelchair manufacturing facility. The mechanisms of separation effected by both UF and RO are described at the molecular level and descriptions of the membranes and hardware design employed in this low-energy process are included. Ultrafiltration is discussed as a means of removing oil wastes from the waste stream in the first case study. Reverse Osmosis is presented as a means of removing dissolved inorganic contaminants from the waste stream in both cases to provide water for reuse in the manufacturing processes. Long term successful installations are resulting in rapid acceptance of this emerging technology and virtually all areas of industry which use water for processing are presently, or soon will be utilizing membrane for fluid separations. A brief capsule of two case histories in which reverse osmosis or reverse osmosis/ultrafiltration has been successfully utilized to reclaim water and minimize waste water follows.

Case #1

A major West Coast wheelchair manufacturer generates a nickel and chrome plating rinse waste stream. Their manufacturing facility was located in an industrial area which had waste water discharge limitations on total dissolved solids as well as some of the particular inorganic compounds, most notably boron. Since boron (as boric acid) is a major component in the nickel plating process, its presence in the waste stream caused major concern. The limitations on boron were set due to the fact that the waste water treatment facility was intended for agricultural irrigation, and boron can be detrimental to the growth of plants. Stringent discharge standards had to be met for any effluent streams discharged from the plating process.

A conventional wastewater treatment system was designed to remove nickel, chrome, etc. as a precipitated sludge, leaving a relatively high total dissolved solids stream containing mostly sodium sulfate from the various pH adjustments in the conventional process with NaOH and H₂SO₄. Since this total dissolved solids level was too high for water reuse in the rinses, reverse osmosis was identified as the best approach to reduce the total dissolved solids, recover the water for reuse in the manufacturing process and totally eliminate the discharge.

The RO unit concentrates the dissolved solids by a factor of ten and sends one-tenth of the flow to an evaporation system, greatly reducing energy consumption and operating expense compared to a single large evaporator to handle the total stream.

The RO machine processes the waste stream at 55 gallons per minute (gpm), returning 50 gpm of permeate (pure water) to the plant for reuse and sending 5 gpm to the evaporator for further concentration. The salt concentration in the feed to the RO unit ranges from 2,000 to 6,000 micromhos and the permeate produced for return to the plating rinse tanks ranges from 200 to 500 micromhos. Figure #1 is a schematic illustrating where the RO unit is located in the overall waste treatment system.

Since discharge of this particular waste stream was completely prohibited, the economics of the installed waste water treatment system can only be compared to alternate disposal methods associated with waste water treatment equipment to accomplish the necessary objectives. However, simply taking into consideration the value of the water recovered, the RO system pays for itself. The operational costs of the RO machine are approximately \$3 per thousand gallons of water (3.8 m³) which is quite comparable to the cost of water and water disposal. Discharge of the effluent stream from the conventional waste treatment system would have been banned without the use of RO, evaporation or ion exchange to polish the effluent. The most economical method to produce a closed-loop system was to couple RO with evaporation to produce a sludge for disposal and 50 gpm of water for reuse, saving the company over \$50,000/year in water and sewer cost alone.

The closed-loop system is completely operational and has been performing well for over 12 months.

Case #2

An aluminum can manufacturer has placed a facility in an area, which is in close proximity to their major customer, a national brewer. Since the brewery was located in a relatively remote area, the can manufacturing facility was built on a site which lacks a sewer access, and therefore requires the hauling of all wastes.

The various rinsing stages that the aluminum cans must go through during the manufacturing process are major contributors to the total waste stream. This stream ends up with metal fines, cutting oils and dissolved salts, which must be dealt with as pollutants.

The waste treatment system design includes a bag filter system to remove the metal fines, followed by an ultrafiltration unit to concentrate the oily waste to a point where it can be sent to an oil stripper. Utilizing this method allows the oil to be removed from the system and recovered for use as a fuel source, aiding the overall economics of the waste water treatment system.

The permeate from the ultrafiltration unit, containing the small MW organics and dissolved salts which pass through the larger pore UF membrane, is sent to the reverse osmosis unit for concentration. The permeate from the RO unit is reused in the process as can rinse water while the concentrate is hauled away. Figure #2 is a system schematic showing this process.

Initial testing showed that the Sepa®-CA polymer UF membrane was superior to Sepa-PS polymer (the two most common UF membranes) in that it resisted fouling and therefore maintained its permeate rate (flux) better. A custom manufactured CA membrane with optimum pore size for both flux and the required separation proved to be well suited for the job. After several years of successful operation, a new UF membrane, Sepa-O (VF) was developed and tested in the system. This membrane proved to be superior in both flux maintenance and separation. The membrane in the entire machine was gradually changed over to Sepa-O (VF) and even more efficient operation resulted.

The total system is designed to handle 20 gpm on a 20 hour per day basis. Overall, only 10% of the waste stream must be hauled. Based on the original cost of \$0.075 per gallon hauling charges, the UF/RO system saves over \$400,000/yr. in hauling costs. The system is extremely cost-effective since operating the total RO/UF system costs only \$0.005 per gallon, or less than 10% of the hauling charges. Total installed cost of the waste treatment system was under \$300,000, showing a payback within one year.

CONCLUSION

Large potential savings exist where process disposal problems must be alleviated. Crossflow membrane is a proven technology well suited to not only solve disposal

problems, but reclaim water for reuse in the process. In many cases, membrane technology is much more cost-effective than alternative methods.

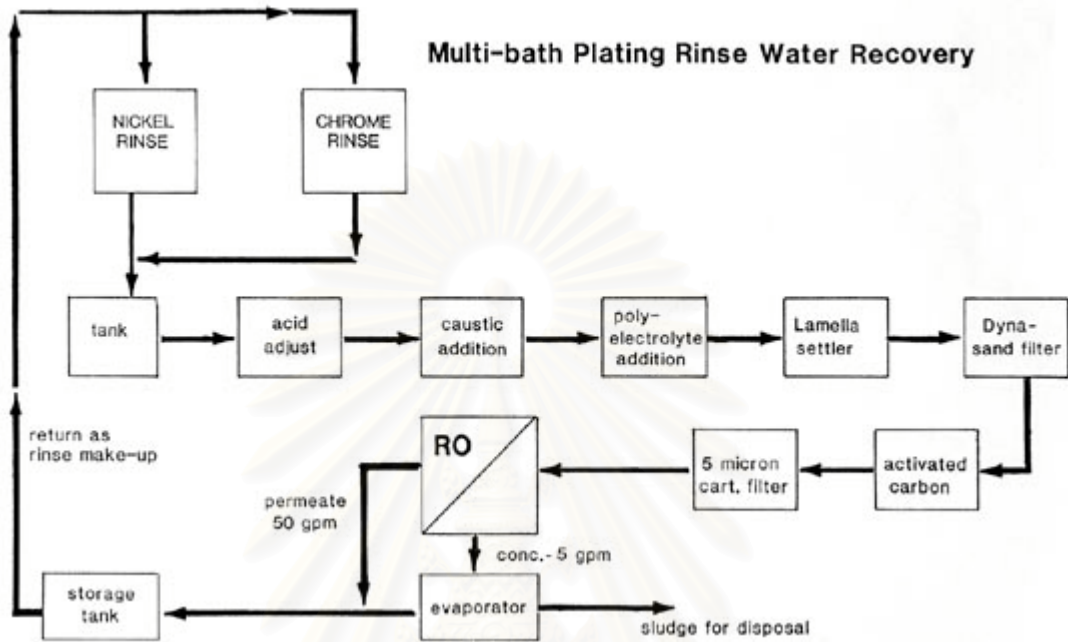


Figure 2.1 : Multi-bath plating rinse water recovery

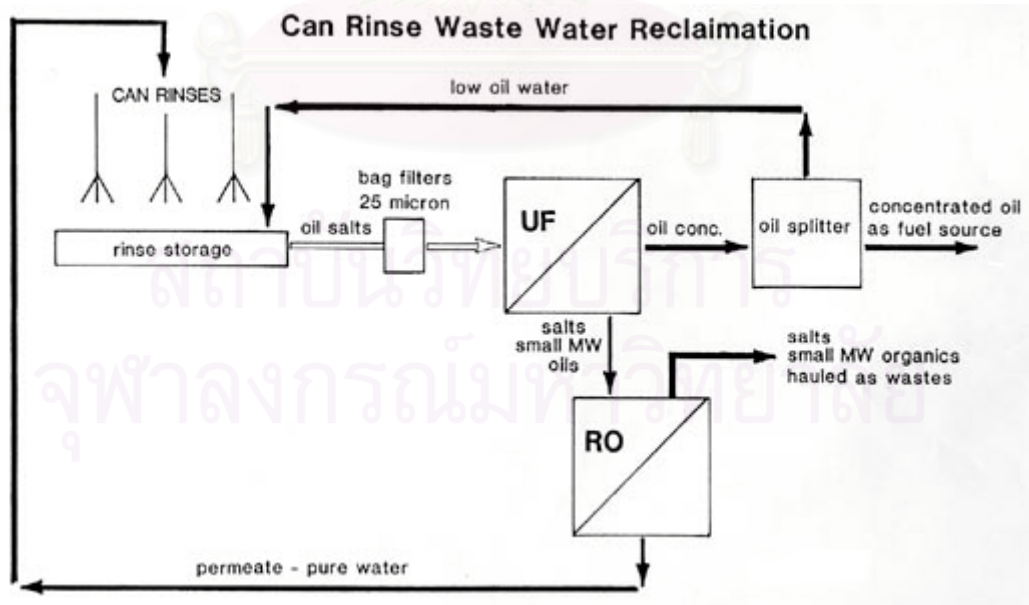


Figure 2.2 : Can rinse waste water reclamation

CHAPTER III

THEORY

3.1 Ultrafiltration

Ultrafiltration is a form of filtration that uses membranes to preferentially separate different fluids or ions. Ultrafiltration is not as fine a filtration process as Nanofiltration, but it also does not require the same energy to perform the separation. Ultrafiltration also uses a membrane that is partially permeable to perform the separation, but the membrane's pores are typically much larger than the membrane pores that are used in nanofiltration.

Ultrafiltration is most commonly used to separate a solution that has a mixture of some desirable components and some that are not desirable. One of the uses that demonstrates the usefulness of ultrafiltration is electrodeposition paint recovery. In this instance the paint, composed of a resin, a pigment and water are separated into two streams that can be reused. The first stream includes the water and a small amount of the paint resin, which can be used to rinse the parts later in the process. The paint pigment is separated from that stream and can be re-used in the paint bath, allowing the bath to be concentrated to a useable level.

Ultrafiltration is capable of concentrating bacteria, some proteins, some dyes, and constituents that have a larger molecular weight of greater than 10,000 daltons. Ultrafiltration is only somewhat dependant upon the charge of the particle, and is much more concerned with the size of the particle. Ultrafiltration is typically not effective at separating organic streams.

3.1.1 Membrane Structure and Fabrication

Figure 3.1 is cross section of a typical asymmetric (anisotropic) UF membrane. The prominent feature of these membranes is the thin skin on the surface-usually 0.1 to 1 μ in thickness. This thin skin permits high hydraulic permeability while the more open/porous substructure (typically 125 μ in thickness) provides good mechanical support. In addition, the pore configuration virtually eliminates internal pore - fouling. Since the minimum pore size is at the membrane surface, once a solute molecule gains entrance into the pore, it easily passes through to the other side of the membrane. The solute molecule sees an ever - widening pore channel with no restrictions or bottlenecks leading to entrapment.

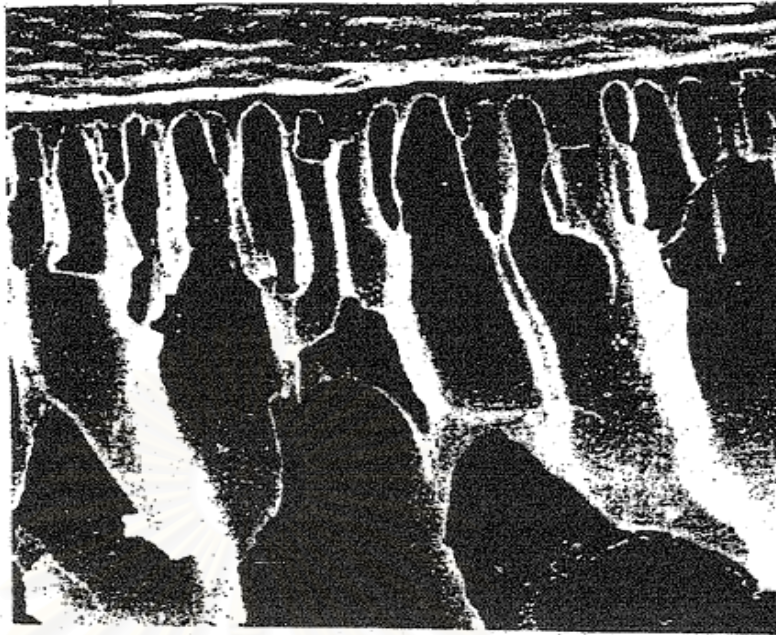


Figure 3.1 : Cross – section photomicrograph of asymmetric UF membrane.

Additional strength is sometimes provided by casting the membrane on a spun – bonded polyethylene or polypropylene backing (see Figure 3.2)

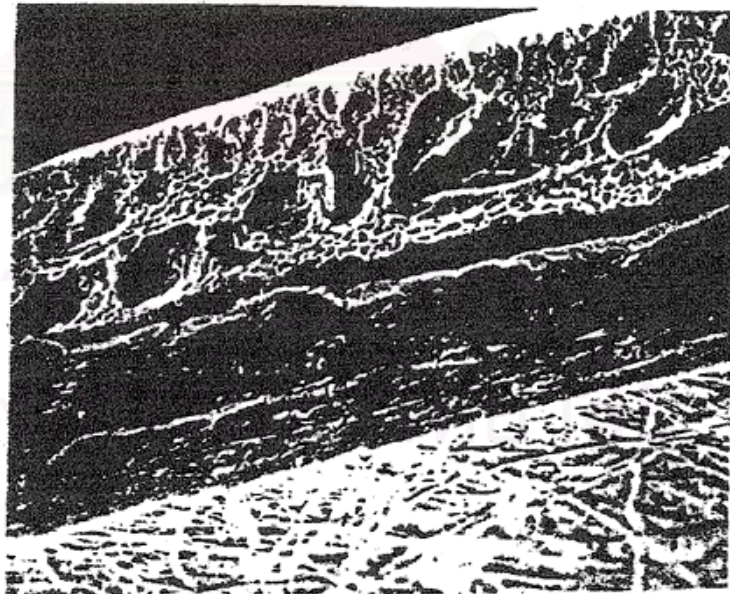


Figure 3.2 : Cross – section of UF membrane cast on spun – bonded polyethylene backing.

As mentioned earlier, the procedure used by Loeb and Sourirajan to make RO membranes from CA produces a very tight UF membrane (only 5% NaCl rejection) prior to annealing. In fact, the line of demarcation between UF and RO usually refers to the tightest UF membranes as those able to pass salts but retain the simple sugars. Cellulose acetate and polyelectrolytes were among the first synthetic polymers to be used for UF membranes. Today, UF membranes are made from a wide variety of chemically and thermally stable synthetic polymers including polyvinyl chloride (PVC), polyacrylonitrile (PAN), polycarbonate (PC), aliphatic, and aromatic polyimides (PA), polyimides (PI), polysulfone (PS), polyarylsulfone (PAS), and polyvinylidene difluoride (PVDF). In addition, there are inorganic UF membranes made from zirconium and aluminum oxides.

With the exception of the inorganic membranes, all of the above are solution cast or spun from a polymer solution. For the more chemically resistant polymers like PS, PAS and PVDF, solvents like dimethylformamide (DMF), dimethylsilfoxide (DMSO), or dimethylacetamide (DMAc) are required.

3.1.2 Effect of Pressure

Figure 3.3 presents rejection data for three different dextrans on the same UF membrane as a function of pressure. Figure 3.4 shows the effect of pressure on the rejection of 0.1 M NaCl by a cellulose acetate RO membrane. It is obvious that the mechanism for solute transport through the membrane is different for UF and RO.

In the case of RO (Figure 3.4), the increase in salt rejection with increasing pressure suggests a “solution – diffusion” model as opposed to a “pore – flow” model for transport of solvent and solute across the membrane. It is known that although the water flux through RO membranes increases with pressure, the salt flux is almost invariant with pressure. The net result is that a higher water flux dilutes the salt concentration in the filtrate resulting in a higher calculated rejection by Equation 2. If “pore – flow” were in effect, leakage of salt through large pores would also be expected to increase with pressure. This suggests that the RO membrane acts as a nonporous diffusion barrier.

$$(1) \quad R = 100 (1 - C_{uf} / C_R)$$

Where C_{uf} = concentration of the solute in the ultrafiltrate

C_R = concentration of the solute in the retentate

In a “solution – diffusion” process, the rate of transport of water and salt is proportional to the chemical potential gradient of each species across the membrane. The chemical potential of each is affected by pressure and concentration. For water, there is little difference in concentration across the membrane, the dominant effect is the difference in pressure. For salt, the ratio of upstream to downstream salt concentration is very large and this dominates over the effect of pressure difference. The water flux is higher than the salt flux because the solubility of water in the membrane and its diffusivity through the membrane is higher than that of salt.

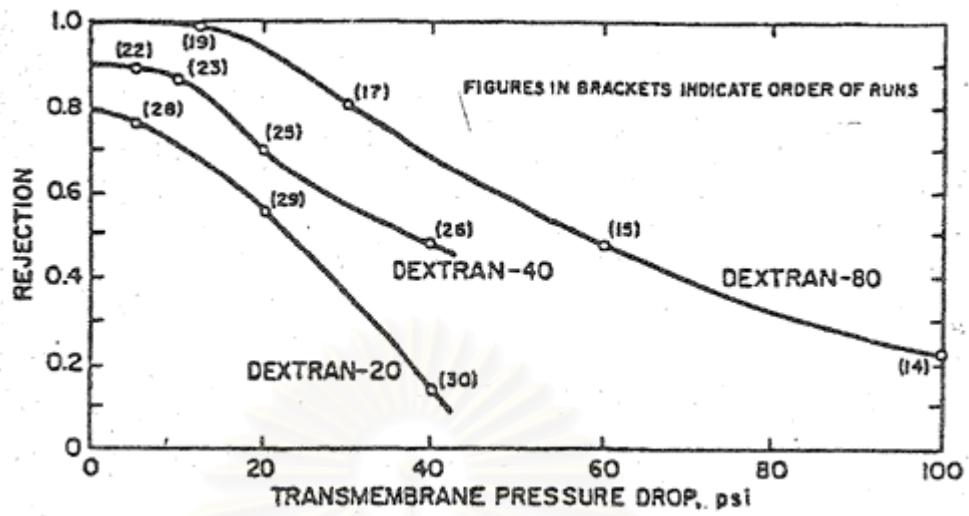


Figure 3.3 : Effect of pressure on UF rejection of dextrans.

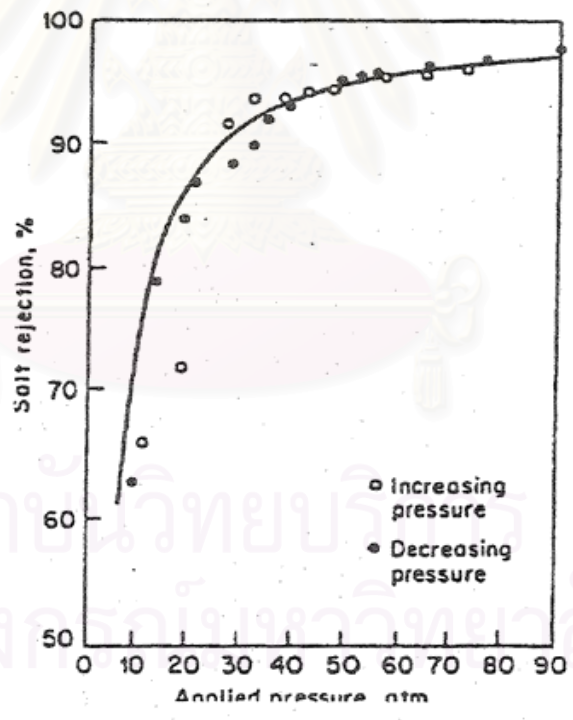


Figure 3.4 : Effect of pressure on RO rejection of 0.1 M NaCl.

The “solution – diffusion” model explains why molecules larger than salt sometimes pass through an RO membrane more readily. For example, cellulose acetate membranes which show a 95 % rejection for NaCl (MW 58) and a 99% rejection for dextrose (MW 180X, show a negative – 34% rejection for 2,4-dichloro-phenol (MW 163). This means the dichlorophenol passes through the membrane more readily than water. This is hard to explain with a “pore-flow” sieving mechanism.

In a “pore-flow process”, the solute flux (J_s) should be proportional to the water flux (J_w) which carries solute to the membrane and through the larger pores.

$$(2) \quad J_s = \sigma J_w C_s$$

Where C_s = concentration of solute at the upstream surface of the membrane

σ = the fraction of the total liquid flowing through pores large enough to pass solute molecules

The retention for solute may be expressed as :

$$(3) \quad R = 1 - (J_s / J_w)$$

or

$$(4) \quad R = 1 - \sigma C_s$$

Thus, in a “pore – flow” model, R would not be expected to increase with pressure since the solute and solvent flux are “coupled”. As the pressure is increase, both fluxes increase.

However, the phenomenon of “concentration polarization” may cause the rejection to *decrease* with increasing pressure as in Figure 3.5. The reason is that the concentration of solute at the surface of the membrane (C_s) has increased over that in the bulk stream (C_b). As the pressure is increased, the solvent flux is increased and the convective transport of solute ($J_w C$) to the membrane is increased (see Figure 3.5). If the solute is retained by the membrane, it accumulates at the surface of the membrane until the back diffusive mass transport, $D_s(dc/dx)$, is equal to the forward convective transport. Even if a steady state is maintained, there must be a concentration gradient (dc/dx) to remove solute from the membrane. Thus, C_s will increase with pressure resulting in a decrease in solute retention by Equation 4 and as shown in Figure 3.3. The pores large enough to pass solute, at higher pressures, pass more solvent, carrying a higher concentration of solute (C_s).

Further increases in pressure will increase the solute concentration at the surface of the membrane (C_s) to a limiting concentration. Proteins begin to form a semisolid gel on the membrane surface with a gel concentration (C_g) between 20 and 50 wt %. Colloidal suspensions form a densely packed layer of close - packed spheres usually between 70 and 80 volume %. Under these conditions (see Figure 3.6), the membrane is to be “gel – polarized”, and further increase in pressure will not increase C_s . Therefore, once the membrane is “gel – polarized”, the retention should be independent of pressure (see

Equation 4). In figure 3.3, the rejection of Dextran – 80 is beginning to level out at the higher pressures as the membrane becomes gel – polarized.

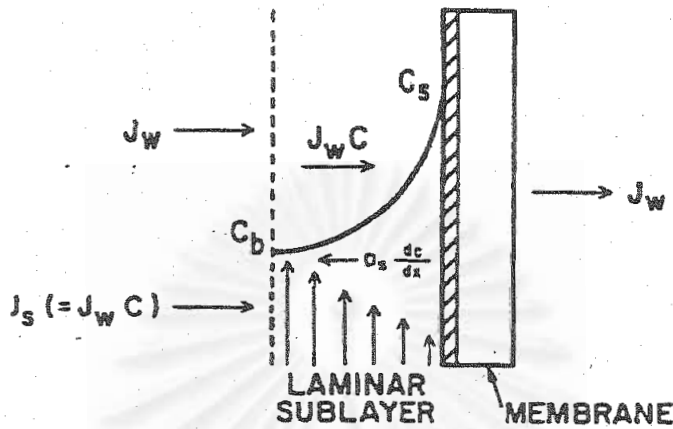


Figure 3.5 : Concentration polarization in UF.

Further increases in pressure will increase the solute concentration at the surface of the membrane (C_s) to a limiting concentration. Proteins begin to form a semisolid gel on the membrane surface with a gel concentration (C_g) between 20 and 50 wt %. Colloidal suspensions form a densely packed layer of close - packed spheres usually between 70 and 80 volume %. Under these conditions (see Figure 3.6), the membrane is to be “gel – polarized”, and further increase in pressure will not increase C_s . Therefore, once the membrane is “gel – polarized”, the retention should be independent of pressure (see Equation 4). In figure 3.3, the rejection of Dextran – 80 is beginning to level out at the higher pressures as the membrane becomes gel – polarized.

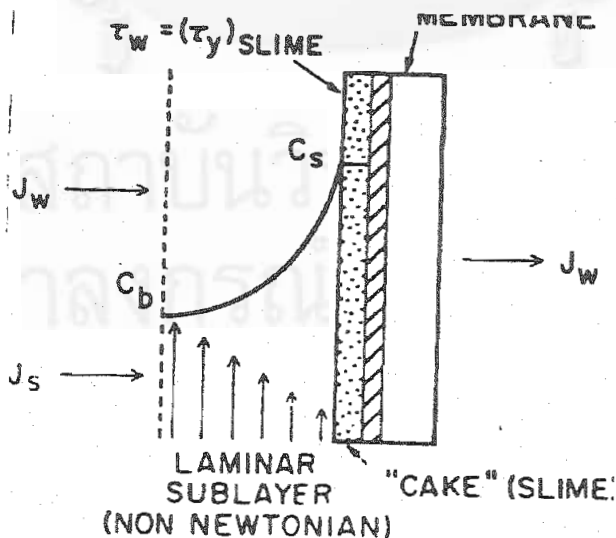


Figure 3.6 : Gel formation due to concentration polarization.

3.1.3 Membrane Flux with Concentration Polarization

The effect of “concentration polarization” on retention was discussed in the previous section. In this section, it will be seen that concentration polarization can severely limit the flux. The control of polarization by proper fluid management techniques is essential to the economic feasibility of the process.

Without the development of an anisotropic UF membrane, UF would not be a commercial process today. The thin skin minimizes the resistance to flow, and the asymmetry of the pores virtually eliminates internal pore fouling. However, the hydraulic permeability of these membranes also increases the convective transport of solutes to the membrane surface. Consequently, the polarization modulus (defined as the ratio of the solute concentration at the membrane surface, C_s , to that in the bulk process stream, C_b) is higher than that experienced with lower permeability RO membranes.

This accumulation of solute at the membrane interface (see Figure 3.5) can severely limit the flux. In the case of RO, the salts retained have a significant osmotic pressure (π) and the effective pressure gradient is reduced by the osmotic pressure difference across the membrane ($\Delta\pi$), thereby reducing the flux. Some researchers have used this “osmotic pressure model” in an attempt to explain the effect of concentration polarization on UF membrane flux. Even though the macromolecules and colloidal suspensions retained by UF membranes are quite large and have negligible osmotic pressures it is argued that the high solute concentrations at the membrane surface can result in an osmotic pressure difference across the membrane which should be taken into account. At present, the “gel-polarization model” appears to do a better job predicting the UF flux for a wider range of process streams than the “osmotic-pressure model”. Therefore, the following treatment will neglect the osmotic pressure.

Gel-Polarization

If the transmembrane pressure drop (Δp) and solute concentration in the bulk process stream (C_b) are high enough, the concentration at the membrane surface (C_s) can rise to the point of incipient gel precipitation forming a dynamic “secondary membrane” on top of the primary structure (see Figure 3.6). This “secondary membrane” can offer the major resistance to flow. In a stagnant “dead-ended” system, the gel layer will grow in thickness until the pressure activated convective transport of solute towards the membrane surface just equals the concentration gradient activated diffusive transport away from the surface. Thus, the flux in stagnant “dead-ended” systems is often so small as to be virtually nonexistent unless the bulk stream concentration is extremely low. Furthermore, by the very nature of the process, increased pressures will not help since the gel layer only grows thicker to offer more resistance to the increased driving force.

$$(5) \quad J_w = \Delta P / (R_c + R_m)$$

where J_w = water flux (volume/time/membrane area)
 ΔP = transmembrane pressure drop

R_c = hydraulic resistance of the membrane
 R_c = hydraulic resistance of the deposited cake

Since R_m is a constant which can be calculated from the *pure* water flux, R_c can be calculated from the experimental flux. Figure 3.7 is a plot of the cake resistance (R_c) as a function of stirrer speed (in a stirred cell), protein concentration, and pressure. As the stirrer speed increases, the boundary layer thickness decreases (see Figure 3.5), thereby increasing the concentration gradient (dc/dx) for removal of the cake. Lower protein concentrations in the bulk (C_b) also increase the concentration gradient; the gel concentration at the membrane surface is fixed (C_g).

Effect of Pressure. One of the curious aspects of data like those in figure 3.7 is that flux does not increase monotonically with pressure. Indeed, when flux is plotted versus pressure, as in Figure 3.8, the flux often becomes independent of pressure in the steady state.

When the pressure is increased, the flux does increase initially. The increase results in a higher rate of convective transport of solute to surface of the membrane. If the system is not “gel-polarized”, the solute concentration at the surface (C_s) increases resulting in an increase in the concentration driven back diffusive transport away from the membrane. In fact, C_s will increase until the backdiffusive transport of solute just equals the forward convective transport.

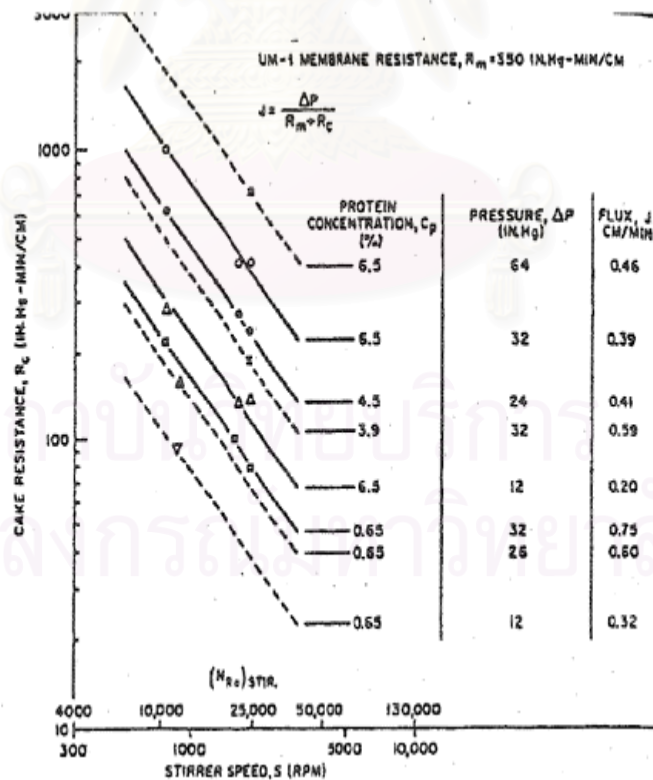


Figure 3.7 : Gel (cake) resistance as a function of stirrer speed, protein concentration and pressure.

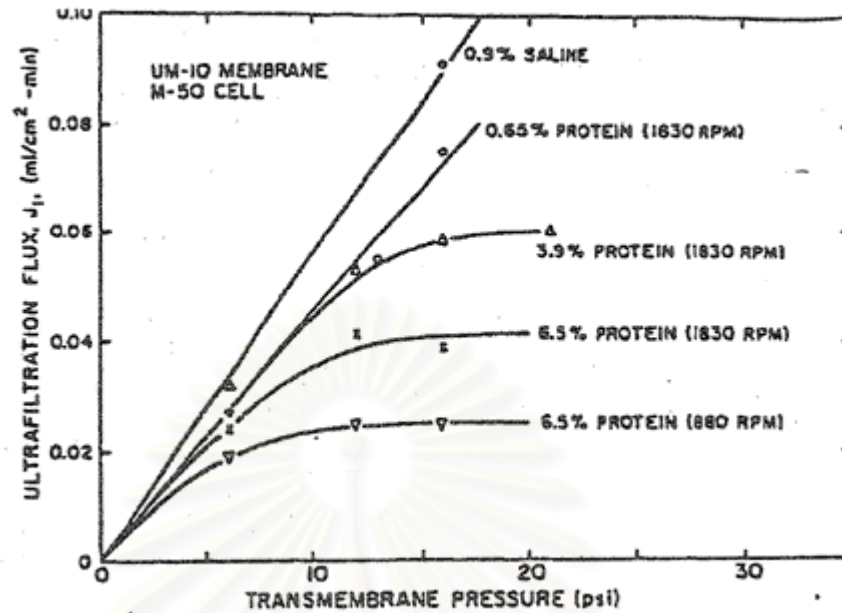


Figure 3.8 : Effect of pressure on flux (flux becomes independent of pressure).

Eventually the concentration at the membrane surface will be high enough for a gel to form ($C_s = C_g$). Further increases in pressure will again temporarily increase the convective transport (J_c) to the membrane surface. However, since the surface concentration is at a maximum, the back diffusive transport will be fixed (assuming no changes in the fluid dynamics in the boundary layer), and solute will accumulate on the membrane. The gel layer will thicken or compact just compensating for the increased driving force (ΔP) by an equal increase in the resistance of the cake (R_c). The net result is that the flux will decrease to its original value in the steady state. Therefore, in the “gel-polarized regime”, flux is independent of pressure and is solely determined by the back-diffusive transport.

In the steady state, the convective transport to the membrane must equal the back-diffusive transport away from the membrane.

$$(6) \quad Jc = -D \left(\frac{dc}{dx} \right)$$

where

- J = solvent flux through the membrane
- C = concentration of membrane retained solutes or colloids
- D = solute diffusivity
- X = distance from the membrane surface

In the gel-polarized regime, the boundary conditions are fixed:

- C = C_b at large distances away from the membrane
- C = C_g at the membrane surface.

Integrating Equation 6 assuming that the diffusivity (D) is constant

$$(7) \quad J = K \ln (C_g / C_b)$$

where K is the mass transfer coefficient:

$$(8) \quad K = D / \delta$$

and δ is the boundary layer thickness.

It is recognized that the diffusivity (D) is really a function of the concentration profile near the membrane surface. If one accepts an exponential mode of the diffusivity

$$(9) \quad D = D_o \exp (-\alpha C)$$

where D_o = diffusivity at infinite dilution
 α = constant

If one integrates Equation 6 taking into account Equation 9, the final equation is considerably more cumbersome than Equation 7 without much gain in accuracy. Suffice it to say that the calculation of flux from Equation 7 will overestimate the flux slightly because the diffusivity in the boundary layer is lower than that at infinite dilution (D_o).

Equation 7 shows that the flux is independent of pressure in the gel polarized regime. Figure 3.8 shows that below some “threshold pressure” (P_t), flux still increases with pressure. Lower solute concentrations (C_b) have higher threshold pressures (P_t). Lower solute concentrations favor a high back-diffusive transport is higher.

Likewise, at the same concentration, higher stirrer speeds result in a higher asymptotic flux, because the boundary layer thickness (δ) has been reduced – increasing the mass transport coefficient (K) (see Equation 7 and 8). This also means that the threshold pressure (P_t) will be higher for higher stirrer speeds. The higher removal rate of solute from the membrane requires higher pressures and flux to carry enough solute to the membrane to form a gel.

Once the gel – layer is formed, it is often the limiting resistance to flow. Figure 3.9 shows two membranes with widely difference membrane resistance (R_m). The pure water flux differs by a factor of 3.75; yet in the presence of protein (retained by both), the water flux differs by a factor of only 1.11, for pressures over the threshold pressure of 20 psi. It will be noted that the higher hydraulic permeability of PM 30 membrane results in a much lower threshold pressure (7 psi).

Of course, Equation 7 applies to all forms of fluid management-cross-flow as well as stirred cells. For large scale systems, cross-flow techniques are preferred-where the feed stream flows tangential to the membrane surface (see figure 3.10). There is a

pressure drop down the channel or tube which means that the first part of the channel may be gel - polarized; while the exit region may not be. (Usually, a restrictor is placed on the exit retentate stream to keep the exit pressure high so as to maximize flux throughout the channel length.) For laminar flow, the entrance region of the channel may not be gel - polarized either, because the boundary layer is not well developed at this point.

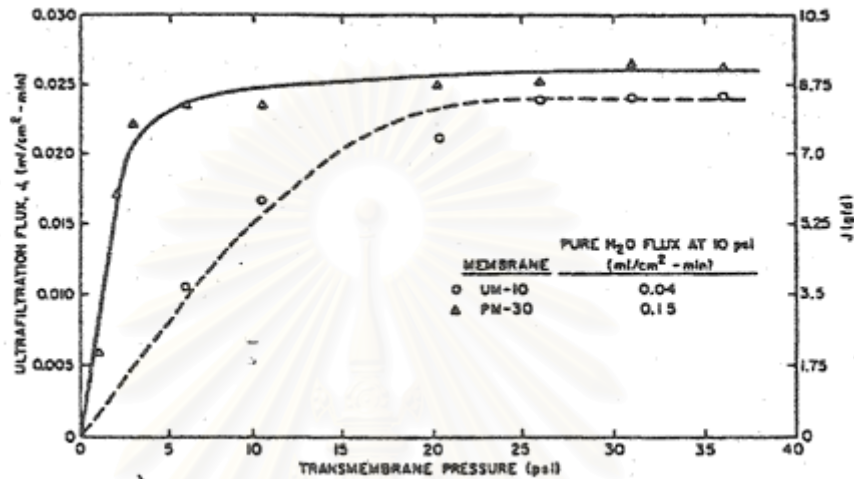


Figure 3.9 : Limiting resistance of gel layer (vs membrane resistance).

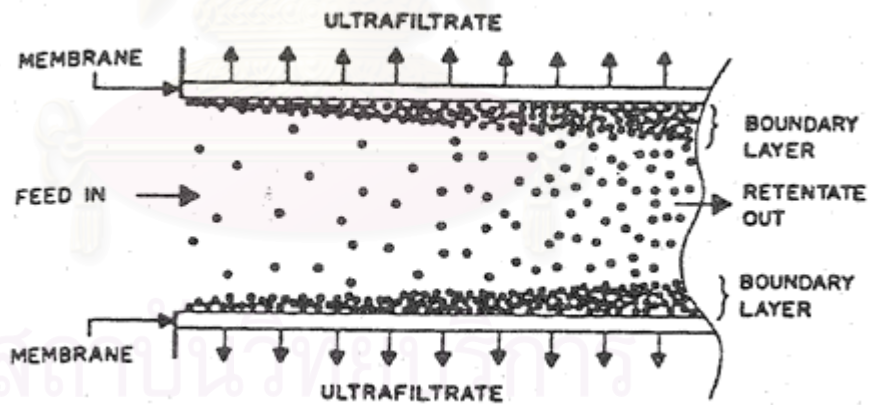


Figure 3.10 : Cross - flow UF system.

Effect of Concentration. If Equation 7 applies, it be possible to plot the solvent flux versus the logarithm of the concentration (C_b) and get a straight line with a negative slope equal to the mass transfer coefficient (K) :

$$(10) \quad J = K \ln (C_g) - K \ln (C_b)$$

The form of Equation 10 has been demonstrated for a large number of macromolecular solutions and colloidal suspensions. The data of Figure 3.11 show the semilogarithmic variation of flux with concentration for two proteins and two colloidal suspensions. According to Equation 10, the intercept with the abscissa should occur when $C_b = C_g$. This provides a way of experimentally determining the gel concentration. The values obtained from Figure 3.11 are entirely reasonable. Many protein solutions reach their solubility limit between 25 and 35%. Likewise, for colloidal suspensions, the equivalent of a gel layer should be a layer of close packed spheres having a packing density between 60 and 75 %.

The negative slope of each of the straight line in Figure 3.11 is equal to the mass transfer coefficient which is a strong function of the stirrer speed or the tangential velocity across the membrane. Figure 3.12 shows increasing slopes with increasing recirculation rate (the volumetric flow rate of retentate recirculated back as feed to the channel, which is proportional to the tangential velocity across the membrane). All lines converge at zero flux where the concentration equals the gel concentration ($C_g = 28\%$). Experimentally, it is difficult to carry out a concentration at constant cross-flow velocity (recirculation rate); the viscosity increases with concentration requiring constant adjustment of the pump. Some data in the literature show flux vs. log concentration *curves*. Often the reason for the curvature is the inconstancy of the recirculation rate; as the process stream is concentrated, the recirculation rate decreases, and the flux drops to lower operating lines (see Figure 3.12). When the data are extrapolated to zero flux, the inconstancy of recirculation rate can lead to inaccurate estimates of the gel concentration (C_g).

In addition, if the data are not gel-polarized, Equation 10 will not plot as a straight line on semilog paper. The concentration at the surface of the membrane (C_s) is less than C_g and not constant. Therefore, at low pressures or low concentration, some curvature is expected. In Figure 3.13, protein concentrations below 1% at high recirculation rates are not fully gel-polarized; the back diffusive mass transport removes protein from the membrane surface at a high rate. Low recirculation rates (<2.5 GPM) have lower back – diffusive transport and are gel – polarized. All data on Figure 3.13 could be gel – polarized if the average transmembrane pressure were raised sufficiently. However, at extremely low solute concentrations, there is a ceiling on solvent flux due to the limiting hydraulic resistance of the membrane; eventually, the flux will reach an asymptotic value equal to the pure solvent flux of the membrane.

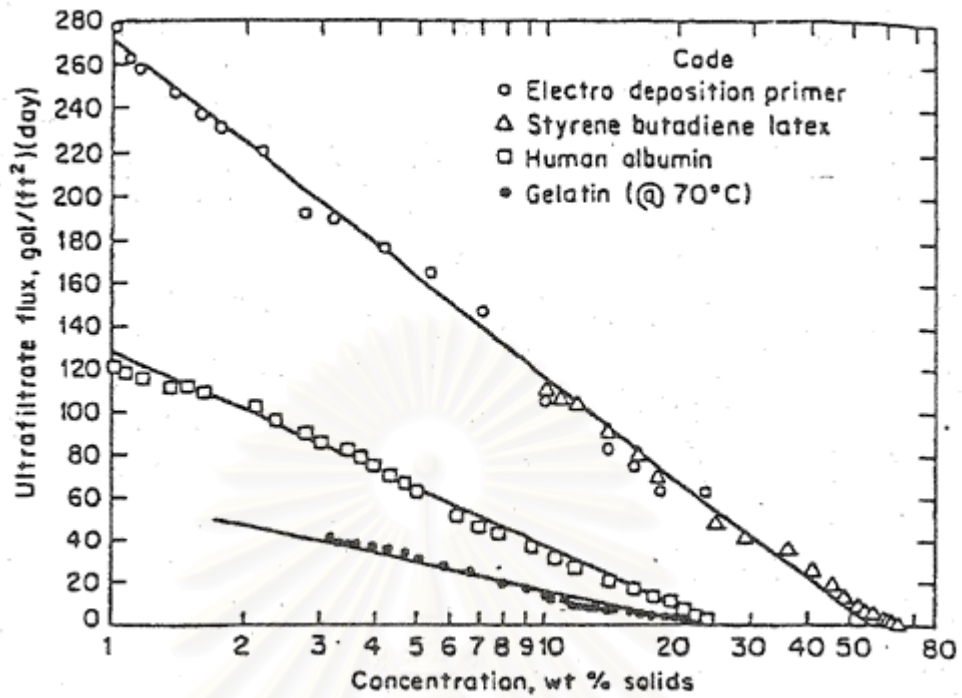


Figure 3.11 : Semilogarithmic variation of flux with solute concentration.

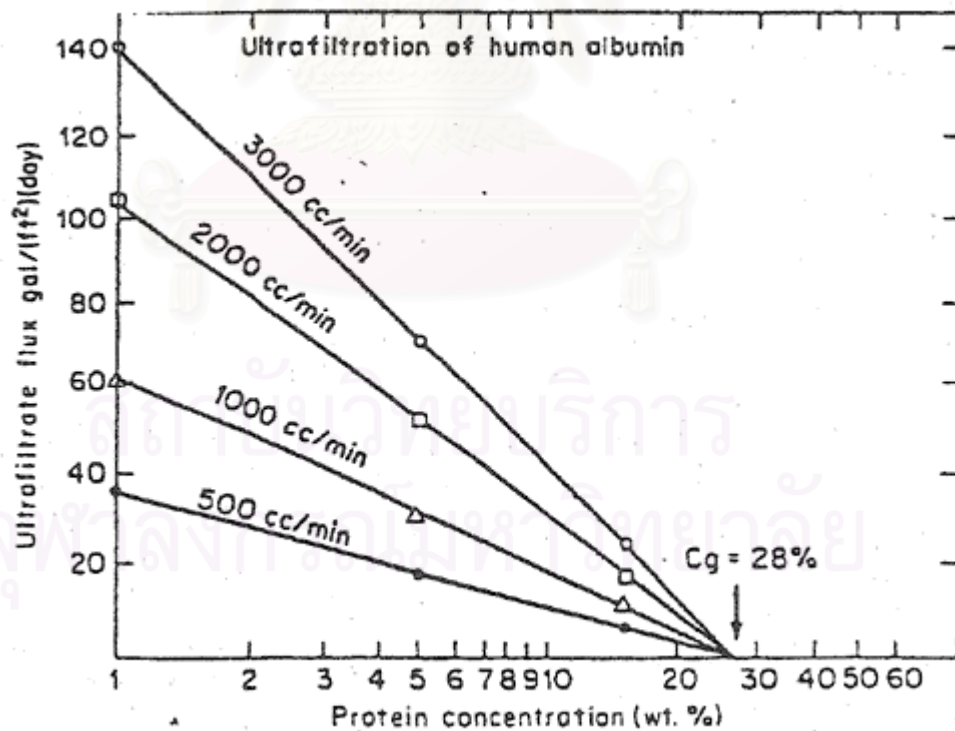


Figure 3.12 : Effect of recirculation rate (cross-flow velocity) on flux variation with concentration

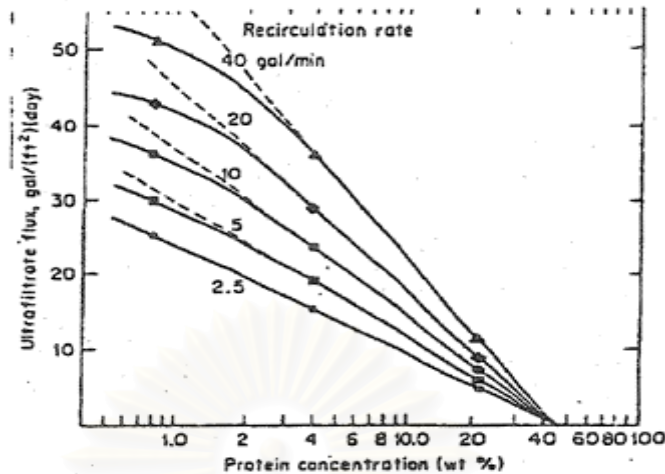


Figure 3.13 : Variation from semi – log dependence in non gel – polarized regime.

Effect of pH. Comparing Figures 3.12 and 3.13, both showing flux data on human albumin solutions, it will be seen that the gel concentration is 28% in one case and 45% in the other. This reflects the difference in solubility of proteins for different conditions such as pH.

Since the isoelectric point of most proteins is between a pH of 4 and 5, it would be expected that operation in this pH range would result in the lowest gel concentration. Further, since changes in pH are not expected to change the mass transfer coefficient (K), the operating lines in Figures 3.12 and 3.13 do not change in slope but are simply to the left or right depending on the gel concentration (C_g). Thus, for a given concentration, there can be dramatic change in flux with pH.

Figure 3.14 shows the variation in the UF flux from cheese whey with pH. Notice the minimum at the isoelectric point.

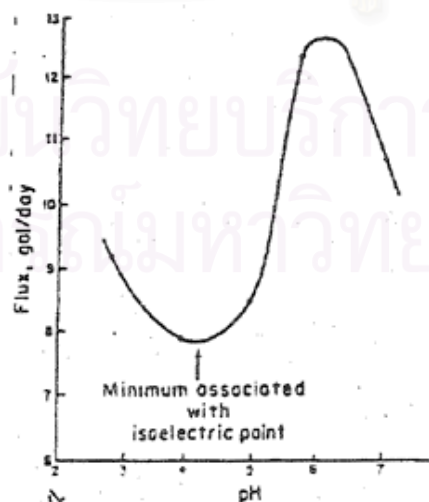


Figure 3.14 : Effect of pH on flux (Cheshire cheese whey).

3.1.4 Membrane Fouling; Flux Decay and Restoration

With some process streams the flux can be stable for months or even years without cleaning or membrane replacement. For most applications, however, there is a gradual flux decay with time as in Figure 3.15. This is not due to internal pore fouling (as in symmetrical MF membranes). Rather it is the result of the accumulation of materials on the membrane which no longer participate in the mass – transport to or away from the membrane. In effect, they “blind” small sections of the membrane, thereby reducing the effective area and the flux through the membrane.

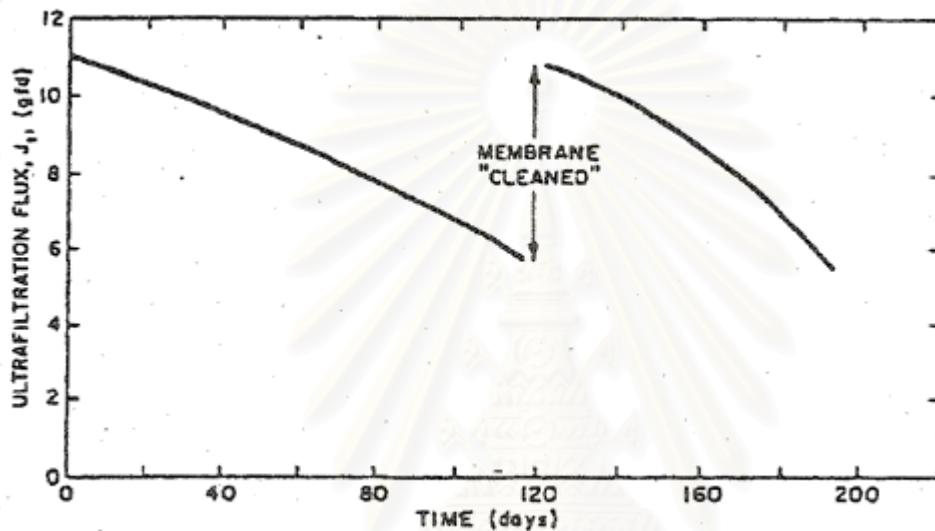


Figure 3.15 : Long term flux decay and restoration by cleaning.

Often preventive measures may be taken to avoid fouling the membrane. Prefilters or screens can be used to remove large particles which block thin channels or accumulate in stagnant areas of the module. High cross – flow velocities tend to sweep deposits away. Low pressures avoid compaction of gels on the membrane. Some polymers have a higher susceptibility to fouling and chemical modification of the membrane surface can have a profound effect on the propensity to foul.

If fouling does occur, the membrane deposits can some times be removed by aggressive cleaning agents, such as detergents, acids, bases, or even organic solvents. The advantage of a chemically – resistant membrane is that severe cleaning agents may be used. However, even with periodic cleaning, the flux cannot always be restored to the initial value. This results in an overall long – term decay.

Effect of Cross – Flow Velocity

High cross – flow velocities tend to prevent fouling and also aid in the cleaning process. Figure 3.16 shows the flux decay on a log – log plot for low, medium and high recirculation rates (Q_L , Q_M and Q_H). Plotting the data in this way often permits a

reasonable good extrapolation of the flux for much longer times – up to 2 or 3 years. The flux decay data usually plots on a straight line, and because of the cyclical nature of the log – log plot. 10 days of data often permits extrapolation to 100 or even 1,000 days.

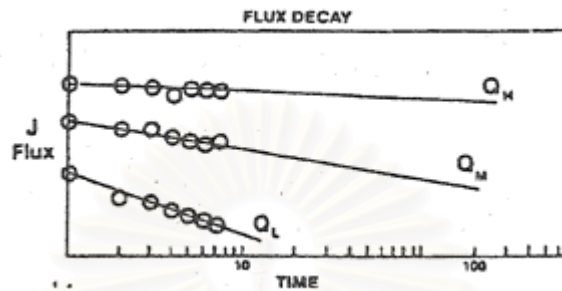


Figure 3.16 : Effect of cross – flow velocity on long term flux decay.

High cross – flow velocities also facilitate cleaning. Figure 3.17 shows that the flux is restored more rapidly and to a higher level with high velocities.

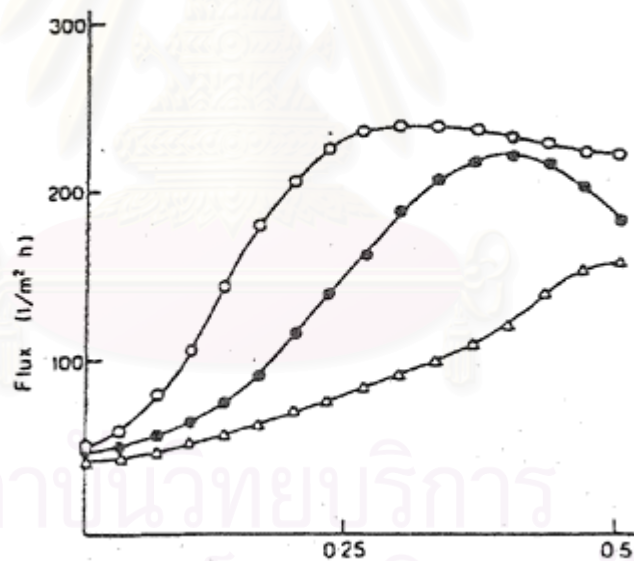


Figure 3.17 : Effect of recirculation rate on detergent cleaning.

Effect of Pressure

If no fouling occurs, the maximum flux will be obtained in the gel-polarized regime above the threshold pressure (P_T). However, for solutes which form semigels on the membrane, pressures (P_H) higher than the threshold pressure may compact the gel layer resulting in greater fouling. Flux decay data like that of figure 3.18 may show greater flux stability at pressures (P_L) lower than the threshold pressure. Even though the initial flux at P_L is lower (since not gel polarized), the long-term flux at this pressure may be higher.

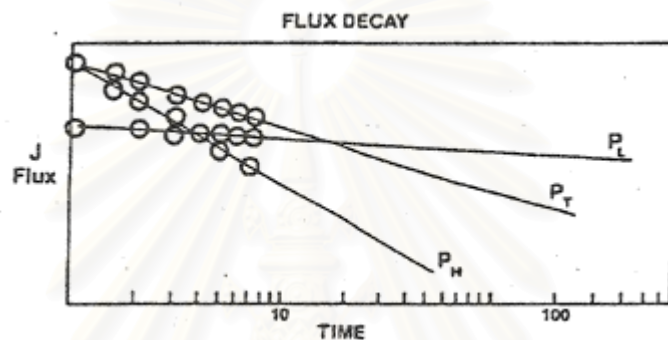


Figure 3.18 : Effect of pressure on long term flux decay.

Effect of Membrane Surface Treatments

Changes in cross-flow velocity or transmembrane pressure cannot always alleviate fouling. Membranes made from hydrophilic polymers like cellulose acetate are generally less prone to fouling than the hydrophobic polymers. However, cellulose acetate is limited in its tolerance to high or low pH, organic solvents and elevated temperature. In some cases, surface modification of the more chemically-resistant polymers has rendered them less susceptible to fouling.

For example, a vinyl copolymer membrane (Romicon's XM-50) was used for years with anodic paint. The slight electronegativity of this membrane repelled the negatively charged anodic paint producing stable flux over a long period of time. When the electropaint users switched to cathodic paints, the XM-50 membrane experienced catastrophic flux decline-presumably because of the electrostatic interaction with the positively charged paint particles. Cellulose acetate membranes provided a stable flux but could not be cleaned with the solvents used in paint makeup (e.g., butyl cellosolve). Therefore, a "charged" XM-50 membrane (designated CXM) was developed for cathodic paints. Figure 3.19 compares the performance of the "charged" membranes with the uncharged.

Various functional groups may be applied to a membrane by techniques such as chemical grafting, plasma polymerization, and sputtering. Figure 3.20 shows an

increasing resistance of the protein gel-layer (R_g) (decreasing flux) with time for three samples of the same membrane, two which have been coated with carbon and a polysiloxane. In this case, the inorganic coatings tend to resist fouling producing a more stable flux.

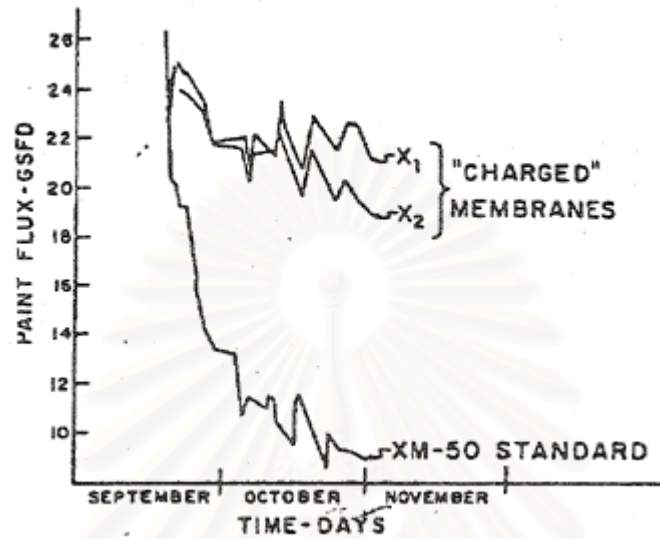


Figure 3.19 : Effect of “charged” membrane on long term flux decay with cathodic paint.

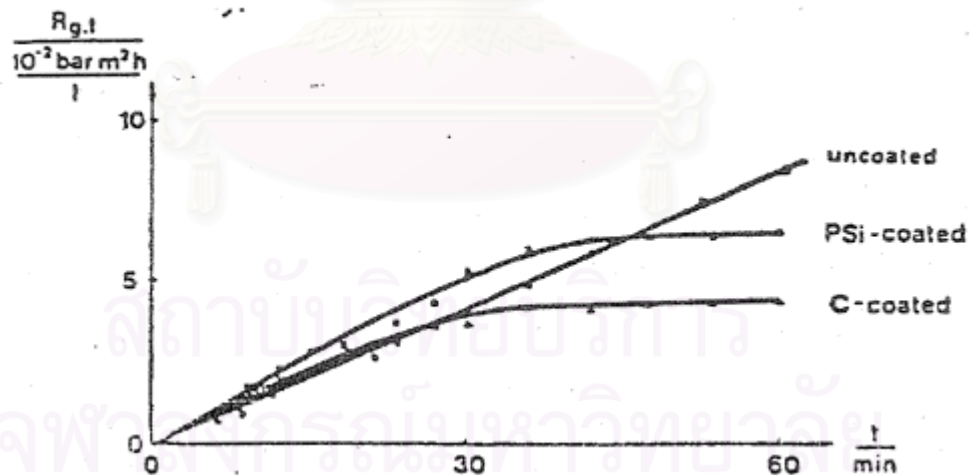


Figure 3.20 : Effect of inorganic coatings on flux decay.

Howell and Velicangil have developed a “self-cleaning” membrane by attaching food-grade proteases onto UF membranes. The enzyme protease hydrolyzed fouling proteins, thereby increasing the permeability of the gel layer.

This resulted in a 25 to 75% improvement in the permeate yield during a 22-hour run concentrating 0.5% albumin or hemoglobin. Figure 3.21 shows the effect of papain and fungal proteinase in decreasing the rate of flux decline over a 20.5-hour run concentrating BSA from 0.5 to 5.0%. The net protein loss through the membrane due to cleavage of albumin by the active enzyme was found to be only 4% of the total. The enzyme may be crosslinked and immobilized on the membrane surface with 0.125% glutaraldehyde in a phosphate buffer (pH 6.5).

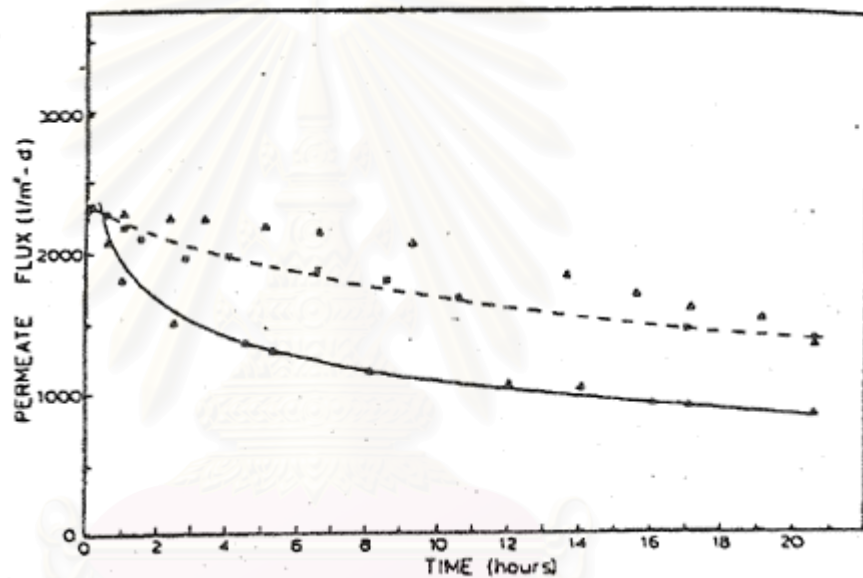
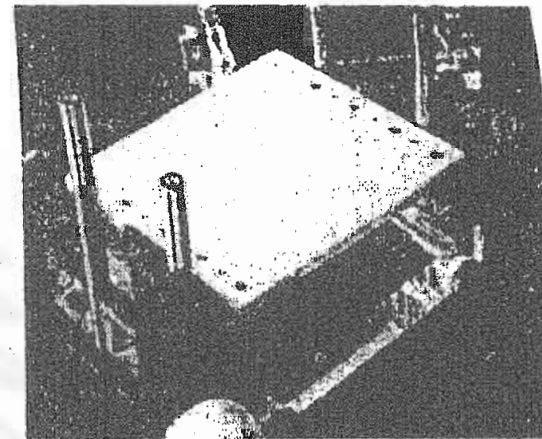
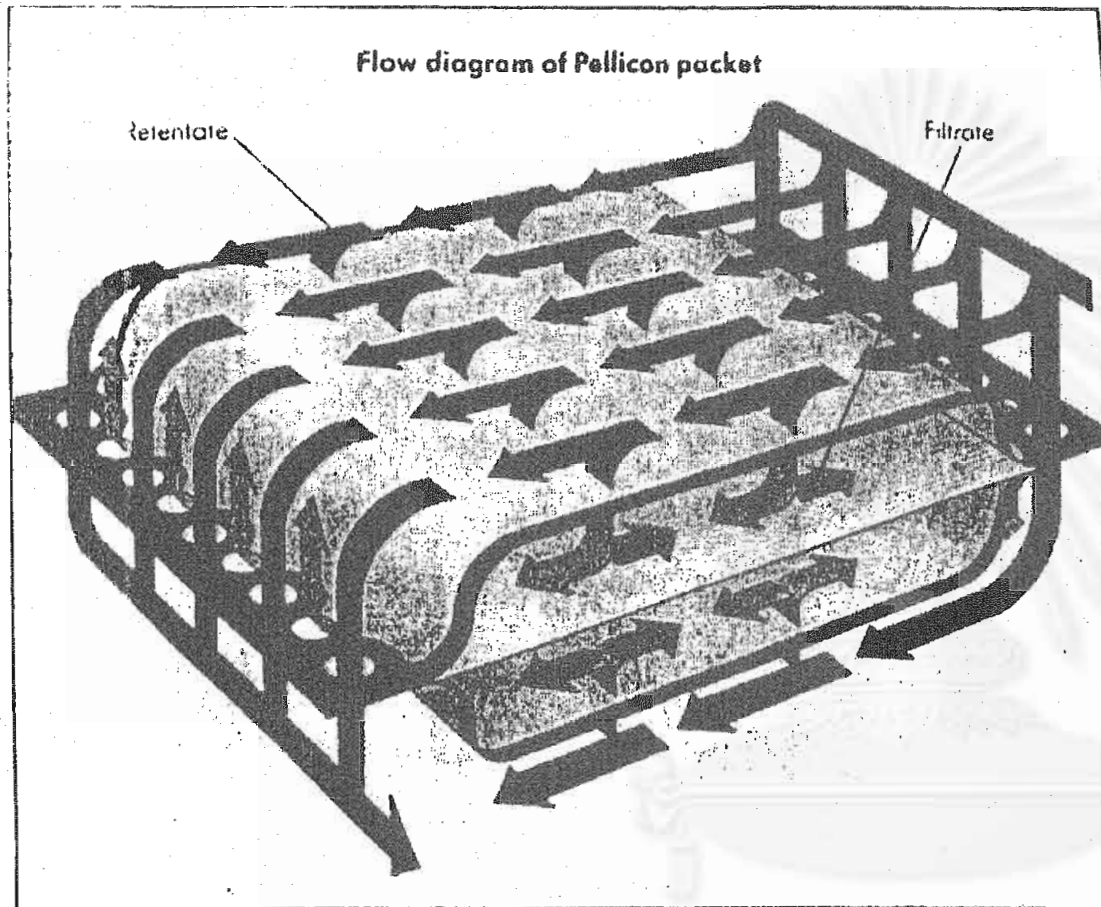


Figure 3.21 : Effect of immobilized protease on UF of BSA (a self-cleaning membrane).

3.1.5 Spiral Wound Modules

Spiral wound modules were originally developed for RO but are capturing an ever increasing share of the UF market. They currently provide one of the least expensive UF modules available in terms of cost per unit of membrane area.

A spiral wound module is essentially the cassette of Figure 3.22 rolled up in a “jelly-roll” configuration. An envelope of two membranes enclosing a filtrate carrier is sealed around three edges and the fourth edge is connected to a perforated tube which carries the permeate (product water) (see Figure 3.23). As the module is rolled up, the



Installation of the Pellicon cassette filter. To change from one procedure to another requires only a simple five-minute filter change.

Figure 3.22 : Millipore cassette and flame design.

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membrane layers are separated by a screen or corrugated spacer where the feed solution flows parallel to the tube axis (see Figure 3.24). Again, the corrugated spacers are preferable for cellular suspension processing. The whole module is inserted in a pressure vessel; sometimes several modules are placed in one long pressure vessel. Often a chevron seal is used to seal the outer surface of the module to the inside of the pressure vessel; this insures that all of the feed stream is forced between the membrane layers. However, for sanitary applications, a screen (controlled bypass spacer) is used to permit flow in the annular region between the module and the pressure vessel; this eliminates the stagnant area and facilitates in-place cleaning and sterilization.

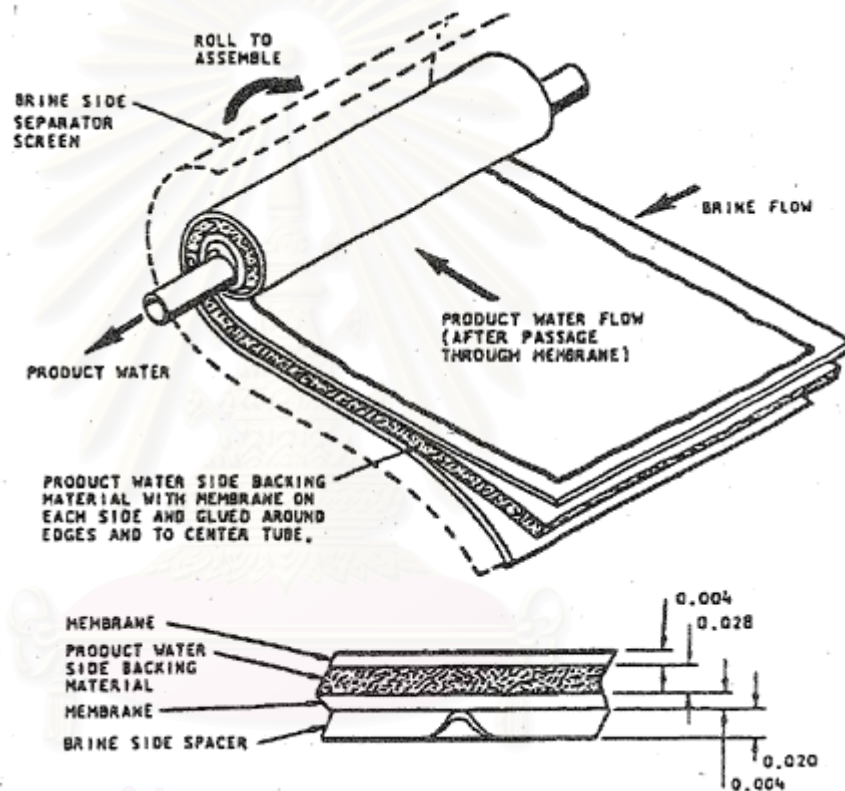


Figure 3.23 : Spiral wound module unrolled.

Spiral-wound modules cannot be unwrapped for cleaning lest the glue line seal rupture; and most cannot be autoclaved. They are more prone to fouling than tubes and some plate and frame units (depending on the type of feed channel spacer), but they are more resistant to fouling than hollow fibers.

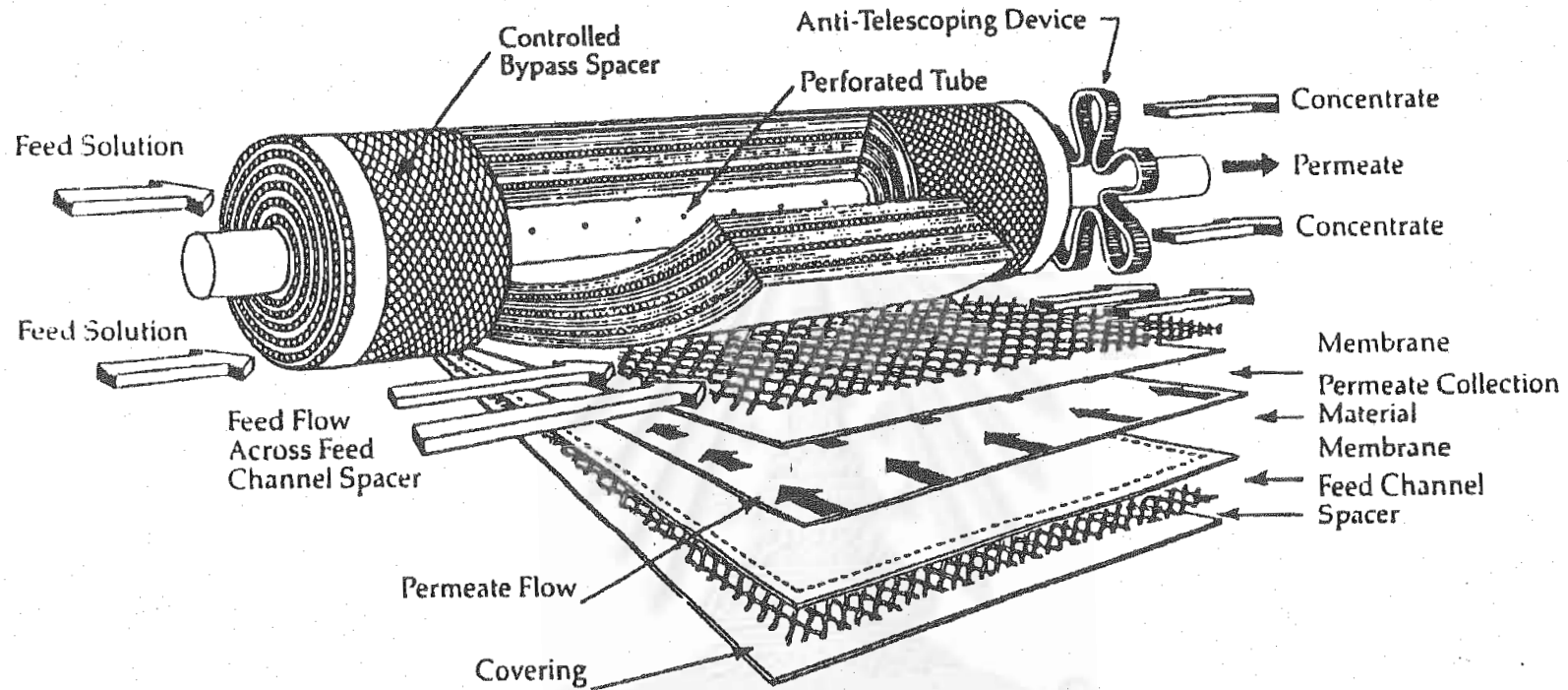


Figure 3.24 : Spiral wound module showing screen spacer.

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3.2 Hydrophilicity Property

Membranes in an aqueous environment have an attractive or repulsive response to water. The material composition of the membrane and its corresponding surface chemistry determine the interaction with water. This phenomena is termed hydrophilicity and hydrophobicity.

Hydrophilicity

Also called hydrophilic, is a characteristic of materials exhibiting an affinity for water. Hydrophilic literally means "water-loving" and such materials readily adsorb water. The surface chemistry allows these materials to be wetted forming a water film or coating on their surface. Hydrophilic materials also possess a high surface tension value and have the ability to form "hydrogen-bonds" with water.

Hydrophobicity

Also termed hydrophobic, materials possessing this characteristic have the opposite response to water interaction compared to hydrophilic materials. Hydrophobic materials ("water hating") have little or no tendency to adsorb water and water tends to "bead" on their surfaces (i.e., discrete droplets). Hydrophobic materials possess low surface tension values and lack active groups in their surface chemistry for formation of "hydrogen-bonds" with water.

Wettability

A surface property characteristic for all materials which yields a unique value for each compound. The surface tension value of a material can be utilized to determine wettability of a material by specific liquids. Through the measurement of the contact angle between a solid surface and a droplet of liquid on the surface, the surface tension for the solid material can be calculated.

Surface Tension

This is an internal force, due to an unbalance in molecular forces that occurs when two different materials (e.g., a liquid droplet on a solid surface) are brought into contact with each other forming an interface or boundary. The force is due to the tendency for all materials to reduce their surface area in response to the unbalance in molecular forces that occurs at their points of contact.

The result of this force will vary for different systems of liquids and solids, which dictates the wettability and contact angle between the drop and surface.

Contact Angle

For a given droplet on a solid surface: The contact angle is a measurement of the angle formed between the surface of a solid and the line tangent to the droplet radius from the point of contact with the solid. The contact angle is related to the surface tension by the Young's equation through which the behavior of specific liquid-solid interactions can be calculated.

A contact angle of zero results in wetting, while an angle between 0 and 90 results in spreading of the drop (due to molecular attraction). Angles greater than 90° indicate the liquid tends to bead or shrink away from the solid surface (see Figure 3.25).

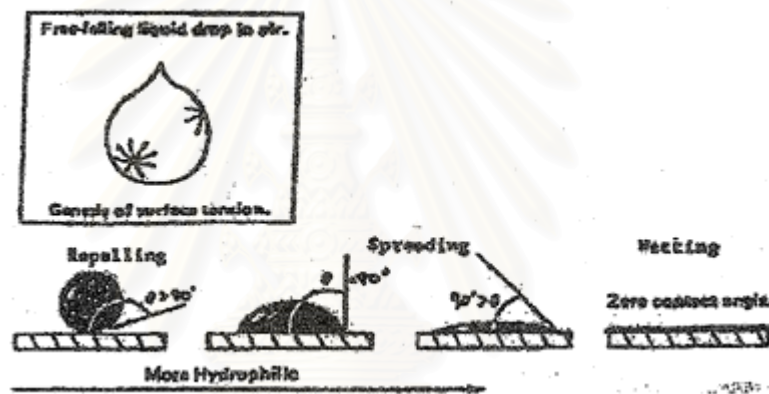


Figure 3.25 : Wetting of solids surfaces: contact angle

For RO and UF, the degree of hydrophilicity/hydrophobicity is determined by the membrane surface chemistry. This effects the formation of the pure water layer (thickness varies with increased hydrophilic character) and dictates the required pore size requirements for a specific level of solute rejection (see Figure 3.26).

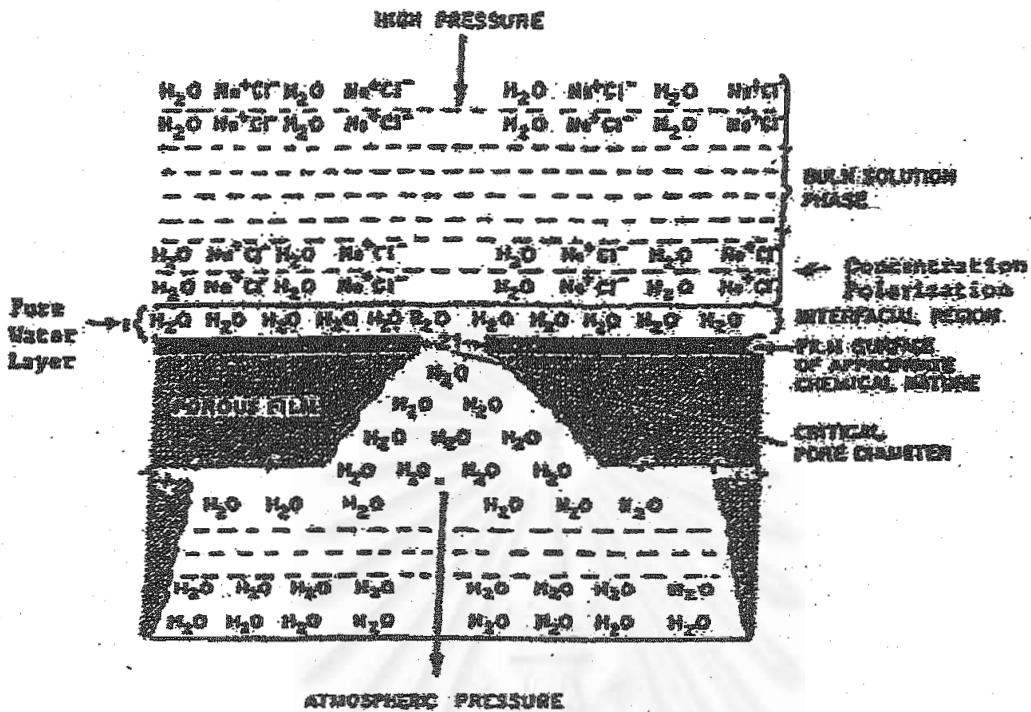


Figure 3.26 : Schematic of preferential sorption-capillary flow mechanism for reverse osmosis Separations of sodium chloride from aqueous solutions.

3.3 Reverse Osmosis

Reverse Osmosis, also known as hyperfiltration, is the finest filtration known. This process will allow the removal of particles as small as ions from a solution. Reverse osmosis is used to purify water and remove salts and other impurities in order to improve the color, taste or properties of the fluid. It can be used to purify fluids such as ethanol and glycol, which will pass through the reverse osmosis membrane, while rejecting other ions and contaminants from passing. The most common use for reverse osmosis is in purifying water. It is used to produce water that meets the most demanding specifications that are currently in place.

Reverse osmosis uses a membrane that is semi-permeable, allowing the fluid that is being purified to pass through it, while rejecting the contaminants that remain. Most reverse osmosis technology uses a process known as crossflow to allow the membrane to continually clean itself. As some of the fluid passes through the membrane the rest continues downstream, sweeping the rejected species away from the membrane. The process of reverse osmosis requires a driving force to push the fluid through the membrane, and the most common force is pressure from a pump. The higher the pressure, the larger the driving force. As the concentration of the fluid being rejected increases, the driving force required to continue concentrating the fluid increases.

Reverse osmosis is capable of rejecting bacteria, salts, sugars, proteins, particles, dyes, and other constituents that have a molecular weight of greater than 150- 250 daltons. The separation of ions with reverse osmosis is aided by charged particles. This means that dissolved ions that carry a charge, such as salts, are more likely to be rejected by the membrane than those that are not charged, such as organics. The larger the charge and the larger the particle, the more likely it will be rejected.

3.3.1 Basic Process Consideration

An industrial reverse osmosis plant usually will consist of three separate sections which are shown in figure 3.27. The first section is the pretreatment section in which the feedwater is treated to meet the requirements of reverse osmosis element manufacturers and the dictates of good engineering practice. Following pretreatment, the feedwater is introduced into the reverse osmosis section where the feedwater is pressurized and routed to the reverse osmosis elements which are in pressure vessels. The feedwater flows across the membrane surface where product water permeates through the membrane and a predetermined amount remains behind as reject. The reject is discharged to waste while the product water is routed to the posttreatment section. The third or post-treatment section treats the product water to remove carbon dioxide and adds chemicals as required for industrial use of the product water.

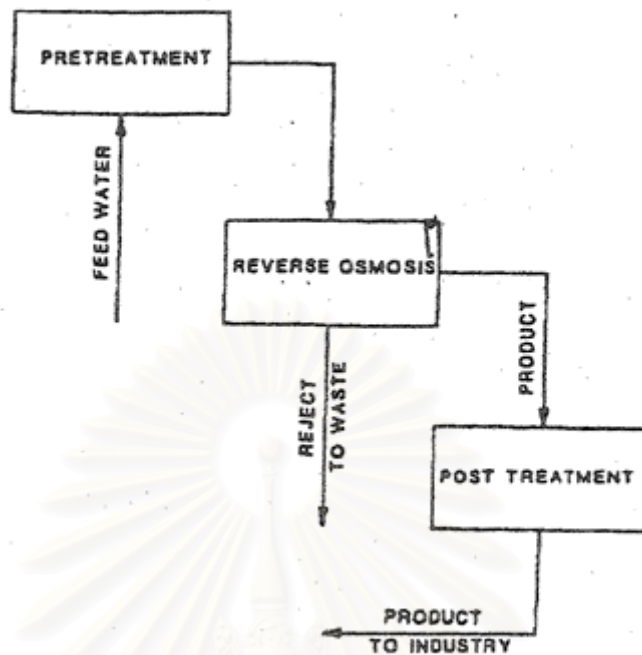


Figure 3.27 : Industrial reverse osmosis.

The sieve mechanism is the simplest and easiest model to understand. This model proposes that salt and water are separated due to physical size differences by a membrane with a pore size that lies between the sizes of salt and water. While most laymen prefer this concept, it is unfortunate that for solutions, such as sodium chloride in water, the sizes of the salt and water molecules are almost the same. This fact would seem to rule out the sieve mechanism model.

Another model proposed is the wetted surface mechanism or the water clustering concept of transport. It is generally recognized that reverse osmosis membrane material is wettable and that water tends to be absorbed on the membrane by hydrogen bonding. In this concept, it is theorized that the water film at the surface of the membrane obstructs the pores and prevents salt from entering the pores. The water passes through the membrane by passing from one absorbed site to the next until it reaches the other side of the membrane barrier layer. The energy requirements for solvent migration are much less than the energy requirements for salt migration and, thus, the separation of salt from water takes place.

Another concept of water and salt transport in reverse osmosis is the preferential sorption-capillary flow mechanism. In this model, the surface of a membrane is microporous and heterogeneous at all levels of solute separation. It is hypothesized that, due to the chemical nature of the membrane skin layer in contact with the aqueous

solution, a preferential sorption for the water causes a sorbed water layer to be formed at the skin. This layer of purified water is then forced through the capillary pores by pressure.

The solution-diffusion model of transport assumes a nonporous, homogeneous membrane surface layer. Each component in a pressurized solution dissolves in the membrane and then diffuses through the membrane. The flow of water and salt through the membrane is uncoupled, i.e., they are independent of each other, and the water transports through the membrane at a more rapid rate than the salt.

The product water flow through the membrane is defined as follows:

$$F_w = A * (\Delta P - \Delta \pi)$$

where F_w = water flux through the membrane
 A = water transport coefficient
 ΔP = pressure differential across the membrane
 $\Delta \pi$ = osmotic pressure differential across the membrane

The flow of water through a reverse osmosis membrane is primarily dependent on the applied pressure differential and the osmotic pressure differential across the membrane. The osmotic pressure is directly dependent on the salt concentration of the process stream. As a rule of thumb, each 100 mg/l of dissolved solids is roughly equivalent to one psi of osmotic pressure. Since the product stream usually has a very low salt content, the osmotic pressure of that stream is negligible. In addition, the product stream normally leaves the reverse osmosis pressure vessels at near atmospheric pressure so that the applied pressure differential is the feed pressure. Consequently, the term “net applied pressure” has come to mean the applied pressure minus the feed osmotic pressure.

The flow of salt or dissolved solids across the membrane is dependent on the following equation:

$$F_s = B * \Delta C$$

where F_s = salt flux
 B = salt transport coefficient
 ΔC = salt concentration gradient across the membrane

The salt transport is primarily dependent upon the concentration of dissolved solids on each side of the membrane.

The solution-diffusion model seems to represent the performance of a reverse osmosis membrane. Figure 3.28 shows the salt rejection and flux of a low pressure polyamide membrane as a function of applied pressure. The membrane was operated on a 5,000 mg/l aqueous solution of sodium chloride at 25°C. As can be seen, there was no product water flow until the applied pressure exceeded the osmotic pressure (50 psi).

After this, the flux increased linearly as would be predicted by the above water flux equation. Rejection is poor at lower pressures and increases rapidly until it reaches an asymptote at an applied pressure of about 150 psig. This can be attributed to a near constant flow of salt with a rapidly increasing product water flow which results in a more dilute product or in increased rejection. These data tend to substantiate the assertion of the solution-diffusion model that flow is uncoupled.

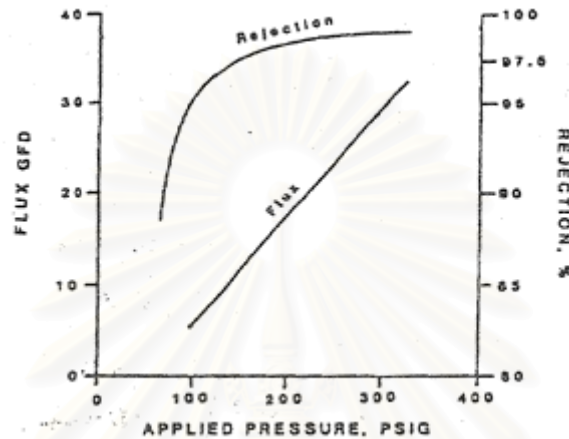


Figure 3.28 : Membrane flux and rejection vs. applied pressure.

It is noted that the data shown in Figure 3.28 was derived in membrane test cells with near perfect small areas of membrane. In a practical system, there would be a number of imperfections in the membrane and the salt flow through these capillaries would contribute to the total salt flow. Therefore, a practical salt transport model must also take into account the contribution of the membrane imperfections to salt flow.

The water transport coefficient (A) is not a constant in that it varies with temperature. The product flow as a function of temperature may be estimated⁶ by using the following equation:

$$Q_{25}/Q_t = e^x$$

- where
- Q₂₅ = flow at 25°C or 77°F
 - Q_t = flow at temperature T, °C
 - E = 2.71828
 - X = U [1/(T + 273) – 1/298]
 - T = Temperature in °C
 - U = 2723 (for cellulose acetate membranes).

Figure 3.29 graphically shows the ratio of water flux at 25 °C to water flux at other temperature.

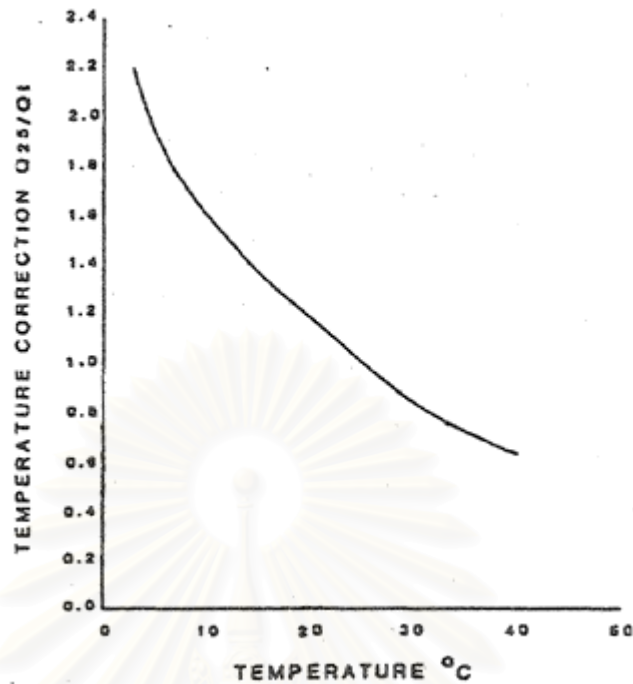


Figure 3.29 : Temperature correction factor.

As a rule of thumb, the product water flow with constant net applied pressure will increase about 3% for each degree centigrade increase in feedwater temperature. Salt flux through the membrane is also directly proportional to temperature and the ratio of salt flux to water flux is essentially constant at different temperatures. This results in little or no change in rejection as a function of temperature. For some of the newer composite membranes, the water and salt permeation coefficients also vary as a function of pH.

Reverse osmosis is a cross-flow membrane separation process which separates a feed stream into a product stream and a reject stream. The recovery of a reverse osmosis plant is defined as a percentage of feedwater that is recovered as product water. As all of the feedwater must be pretreated and pressurized, it is economically prudent to maximize the recovery in order to minimize power consumption and the size of the pretreatment equipment. Since most of the salts remain in the reject stream, the concentration of salts increases in that stream with increased recovery. For instance, at 50% recovery, the salt concentration in the reject is about double that of the feed and at 90% recovery, the salt concentration in the reject is nearly 10 times that of the feed. In cases of sparingly soluble salts, such as calcium sulfate, the solubility limits may be exceeded at a high recovery. This could result in precipitation of the salt on the membrane surface resulting in decreased flux and/or increased salt passage. In addition, an increase in recovery will increase the average salt concentration in the feed/reject stream and this produces a product water with increased salt content. Consequently, the recovery of a reverse osmosis plant is established after careful consideration of the desired product quality, the

solubility limits of the feed constituents, feedwater availability and reject disposal requirements.

While the above equations are helpful in describing the reverse osmosis process, the water and salt transport coefficients seldom are used to describe membrane performance. Most manufacturers test reverse osmosis membrane with standard solutions as described below.

- (1) Brackish Water Membrane- The flux and rejection of the membrane is determined when the membrane is tested on a feedwater of an aqueous sodium chloride solution with a concentration of 2,000 mg/l at an applied pressure of 420 psig (net applied pressure = 400 psig) with a temperature of 25°C and a feed pH of from 5.0 to 6.0 for 30 minutes prior to data collection.
- (2) Seawater Membrane – The seawater test is similar to the brackish water test except that the feedwater is an aqueous sodium chloride solution with a concentration of 35,000 mg/l and the test pressure is 800 psig.

The results are reported as gallons per day per square foot of membrane area (membrane flux) and as rejection of sodium chloride. Rejection is calculated as follows:

$$R = (1 - CP/CF) 100$$

where R = Rejection, percent
CP = Product water concentration
CF = Feedwater concentration

The sodium chloride rejection differs from that of other inorganic and organic dissolved solids, and membrane manufacturers will provide information and rejection data that are available for their specific membrane. Table 3.1 shows typical results for a composite membrane when tested on a multicomponent solution. The rejection of the divalent ions such as calcium and sulfate is much better than the rejection of the monovalent ions such as sodium and chloride. If salt passage is defined as product concentration divided by the feed concentration, or one minus rejection, then it can be seen that the salt passage for the divalent ions is about one-fifth of the salt passage for the monovalent ions.

The above described tests are conducted at a low recovery rate to minimize the effects of concentration polarization which is described below. For example, membrane Tests above are conducted at less than 1% recovery and tests with spiral wound elements are conducted at recoveries from 5 to 10%.

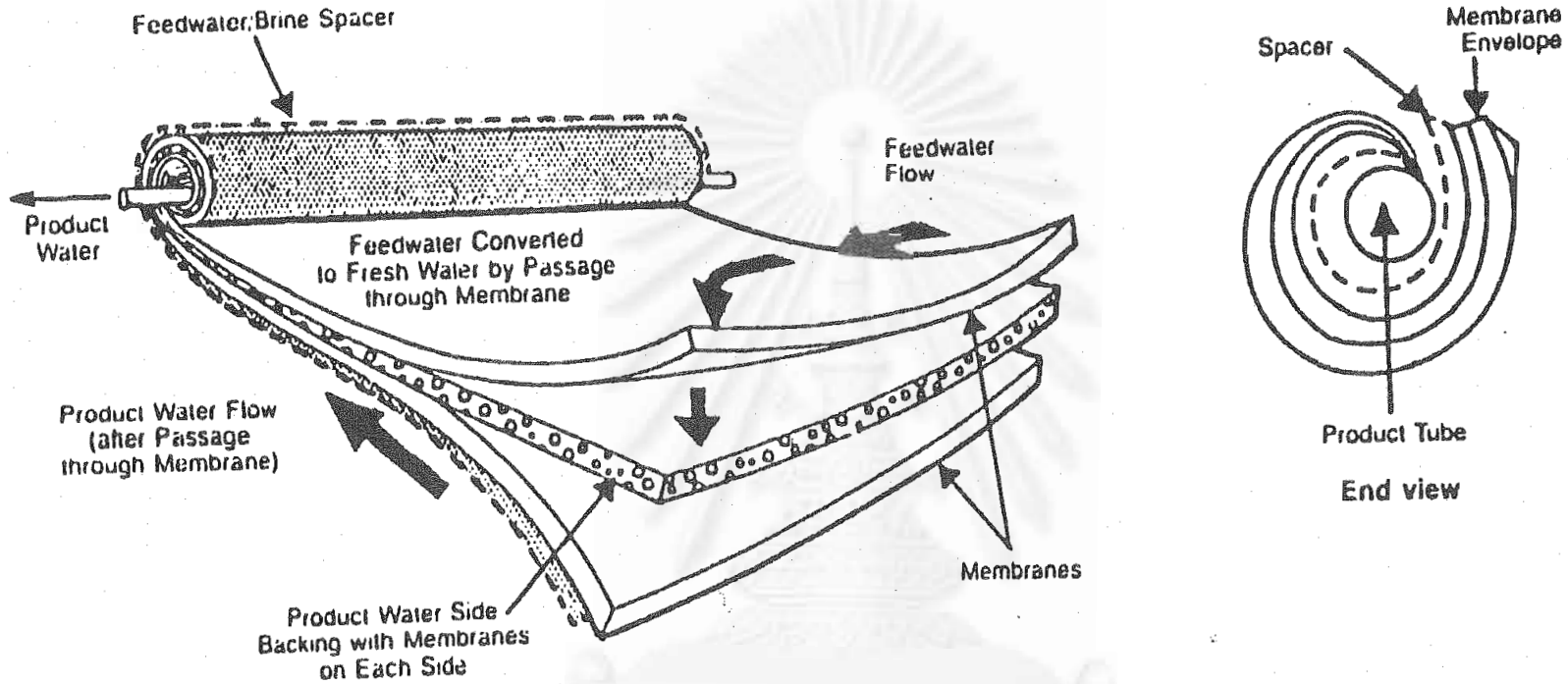


Figure 3.30 : Spiral wound packaging

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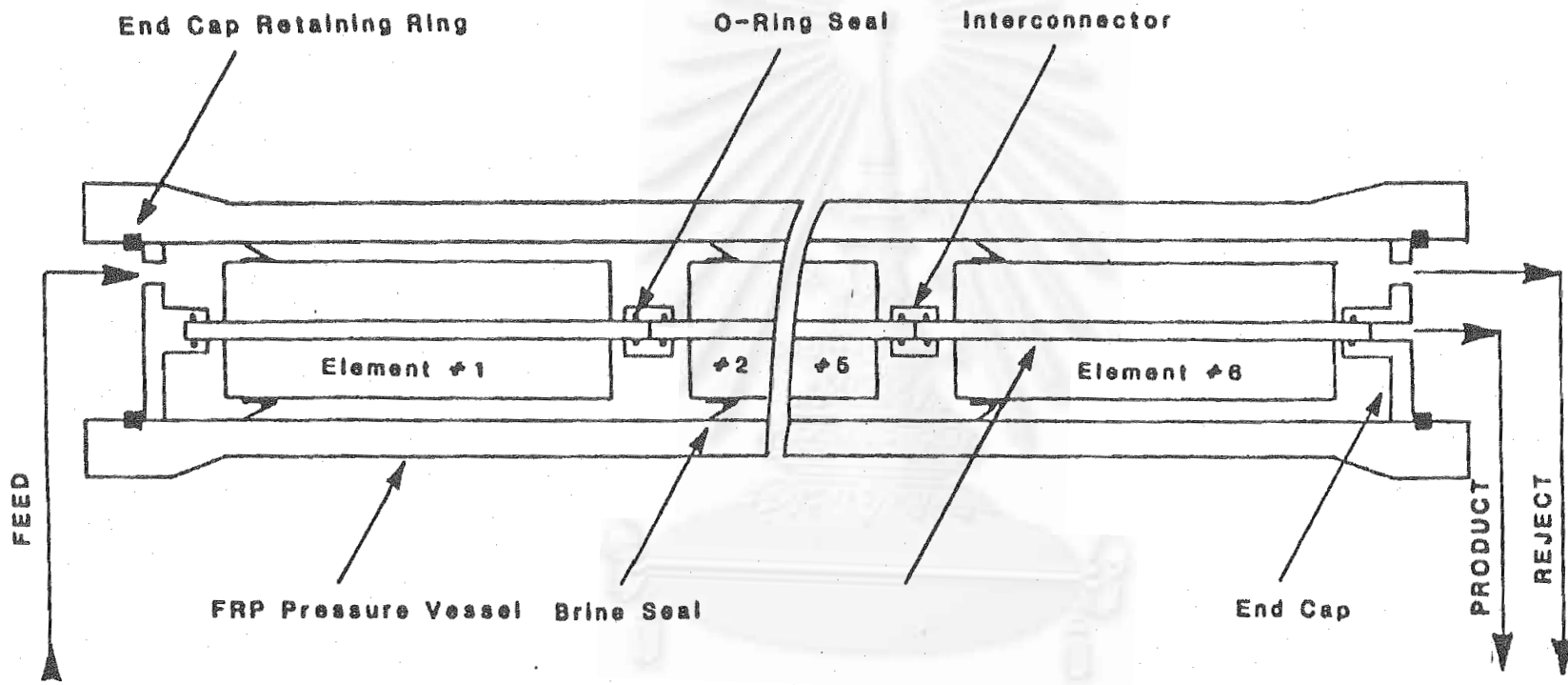


Figure 3.31 : Spiral wound element pressure vessel assembly

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Table 3.1 : Ionic Rejections

<u>Ion</u>	<u>Feed, mg/l</u>	<u>Product, mg/l</u>	<u>Rejection, %</u>
Calcium	61	0.2	99.6
Sodium	150	3.0	98.0
Potassium	12	0.3	97.4
Bicarbonate	19	0.7	96.2
Sulfate	189	0.4	99.8
Chloride	162	2.9	98.2
Nitrate	97	3.5	96.4
TDS	693	11.0	98.4

Reverse osmosis is a cross-flow process and, as in any dynamic hydraulic process, the fluid adjacent to the membrane moves slower than the main stream. While the main stream flow may be turbulent, the layer next to the membrane surface is laminar. This thin, laminar flow film is called the boundary layer. When water permeates through the membrane, nearly all of the salt remains behind in the boundary layer next to the membrane. The salt must then diffuse across the boundary layer and back into the bulk stream. This result in a boundary layer with a salt concentration which is more concentrated than the bulk stream. The effect has been termed concentration polarization, and it is defined by the following equation:

$$\beta = CB/CM$$

where β = Concentration polarization
 CM = Concentration in the main stream
 CB = Concentration in the boundary layer

Concentration polarization increases the salt concentration at the membrane surface, and this results in an increased osmotic pressure at that surface. The increased osmotic pressure causes a drop in water flow as shown in the following equation:

$$F_w = A*(P - \beta\pi)$$

where F_w = the water flow
 A = the water transport coefficient
 P = applied pressure
 β = concentration polariaztion

π = osmotic pressure of main stream

The increased salt concentration at the membrane surface will also increase the tendency of sparingly soluble salts to precipitate on the membrane.

The flow of salt also increases and this can be simply shown in the following equation:

$$F_s + B * (\beta C_1 - C_2)$$

where F_s = salt flux
 B = salt transport coefficient
 β = concentration polarization
 C_1 = main stream salt concentration
 C_2 = product water salt concentration

In the imperfect membrane with a small number of pores, the increased salt concentration at the membrane surface would also result in increased salt passage through the pores which would be directly proportional to concentration polarization.

The information shown in Table in Table 3.2 below assumes a membrane operating on various feedwaters with a total dissolved solids (TDS) content of 2,000, 5,000 and 25,000 mg/l. It is assumed that the membrane will deliver 20 gallons per square foot per day at a 400 psi “net applied pressure” and have a rejection of 99% when there is no concentration polarization, i.e., $\beta = 1.0$.

Table 3.2 : Effects of Concentration Polarization

<u>Feed TDS, mg/l</u>	<u>2,000</u>	<u>5,000</u>	<u>35,000</u>
Flux, gfd			
$\beta = 1.0$	20.0	20.0	20.0
$\beta = 1.1$	19.9	19.8	18.3
$\beta = 1.5$	19.5	18.8	11.3
$\beta = 2.0$	19.0	17.5	2.5
Rejection, %			
$\beta = 1.0$	99.0	99.0	99.0
$\beta = 1.1$	98.9	98.9	98.8
$\beta = 1.5$	98.5	98.4	97.3
$\beta = 2.0$	97.9	97.7	84.0

The penalty of a high concentration polarization is not as severe with a low TDS feedwater as it is with a high TDS feedwater. The recommendations as to minimum flows or maximum recoveries which are specified by the reverse osmosis element manufacturer should be followed at all times, especially when the application is the desalination of high TDS waters.

Concentration polarization cannot be eliminated, but it can be minimized by decreasing boundary layer thickness. This is done by increasing the flow rate across the membrane surface or introducing turbulence promoters into the feed/reject stream. In order to achieve optimum performance, most membrane manufacturers will recommend a minimum feed rate to or from their elements and a maximum recovery in order to minimize the effects of concentration polarization.

3.3.3 Spiral Wound

The spiral wound membrane packaging configuration is shown in Figure 3.30. Basically, the spiral wound element consists of two sheets of membrane separated by a grooved, polymer reinforced fabric material. This fabric both supports the membrane against the operating pressure and provides a flow path for egress of product water. The membrane envelope is sealed with an adhesive on three sides to prevent contamination of the product water. The fourth side is attached to a product water carrier material. The membrane envelope is rolled up around central product water tube, with a plastic mesh spacer between the facing membrane surfaces, in a spiral. The mesh spacer not only serves to separate membrane surfaces but it provides a flow path for and turbulence in the feed/reject stream of each element. The elements have an outer wrap to contain the feed/reject stream in the mesh passageway and brine seal to insure that the feed/reject stream goes through the element and not around it. Spiral wound elements are available in lengths from 12 to 60 inches and diameters from 2 to 12 inches. Packaging densities of up to 300 square feet of membrane to 1 cubic foot of pressure vessel have been attained. Reverse osmosis plants with a capacity from 100,000 to 5,000,000 gpd of product water normally use elements with an 8-inch diameter by a 40-inch or 60-inch length.

Spiral wound elements are installed in a pressure vessel which is usually fabricated from fiberglass reinforced plastic. The pressure vessel inside diameter is sized to match the outside diameter of the element brine seal. The pressure vessels are designed and fabricated to accommodate from 1 to 6 elements and operating pressures from 50 to 1,000 psig. Figure 3.31 shows a pressure vessel with 6 elements installed. Feedwater enters one end of the pressure vessel and flows through the first element in which about 10% of the feed permeates through the membranes and flows through the product water carrier material into the product water tube. The reject from the first element flows to and through the second element and the reject from this element becomes the feed to the next element, etc. The reject from the last element is routed from the pressure vessel to the high pressure reject manifold. The first and sixth element product water tubes are sealed to the pressure vessel end caps by O-ring devices to prevent contamination by the high

pressure feed or reject to the purified product water stream. The element product water tubes in the pressure vessel are connected to each other with interconnectors which again are O-ring devices whose seals prevent product water contamination. The product water can exit the pressure vessel, usually at near ambient pressure, from either end of the pressure vessel. In a single pressure vessel with six elements, between 40 and 60% of the feedwater to the pressure vessel is recovered as product water from a brackish water feed and from 25 to 35% is recovered from a seawater feed.

The advantages of the spiral wound elements are the high packing density and high flux which makes it one of the most cost effective elements. The disadvantage of the element is that a moderate amount of pretreatment is required for some feedwaters to prevent fouling of the mesh brine spacers.



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3.3.3 Thin Film Composite Reverse Osmosis Membranes

A thin film composite reverse osmosis membrane can be defined as a multilayer membrane in which an ultrathin semipermeable membrane layer is deposited on a performed, finely microporous support structure. This contrasts with asymmetric reverse osmosis membranes in which both the barrier layer and the porous substructure are formed in a single-step phase inversion process and are integrally bonded.

Fabrication of a thin film composite membrane is typically a more expensive route to reverse osmosis membranes because it involves a two-step process versus the one-step nature of the phase inversion film casting method. However, it offers the possibility of each individual layer being tailor-made for maximum performance. The semipermeable coating can be optimized for water flux and solute rejection characteristics. The microporous sublayer can be optimized for porosity, compression resistance and strength. Both layers can be optimized for chemical resistance. In nearly all thin film composite reverse osmosis membranes, the chemical composition of the surface barrier layer is radically different from the chemical composition of the microporous sublayer. This is a common result of the thin film composite approach.

The term “thin film composite” has the connotation that the barrier layer is extremely thin, and hence quite fragile. Indeed, the barrier layer may be quite thin, varying to as low as 200 angstroms depending on the nature of the particular reverse osmosis membrane and its method of manufacture. But this does not necessarily result in fragility. Some of these membranes may be considerably more rugged and chemically resistant than the typical asymmetric cellulose acetate membrane in field service. It should be noted that the barrier layer in asymmetric cellulose acetate membranes is itself only about 2000 angstroms thick. Therefore, it may be more correct to refer to such membranes simply as “composite” reverse osmosis membranes.

There are several potential routes to the preparation of composite reverse osmosis membranes, whereby the ultrathin semipermeable film is formed or deposited on the microporous sublayer.^{1,2} The film can be formed elsewhere, then laminated to the microporous support, as was done in the earliest work on this membrane approach. Or it can be formed in place by plasma polymerization techniques. Alternatively, membrane polymer solution or polymer-forming reactants can be applied in a dipcoating process, then dried or cured in place. The most attractive approach from a commercial standpoint, however, has been the formation of the semipermeable layer in situ by a classic “nonstirred” interfacial reaction method. Several examples of membranes made by this last approach have reached commercial status.

3.3.4 Cellulose Acetate Membranes

The first composite reverse osmosis membrane to be developed and described consisted of an ultrathin film of secondary cellulose acetate deposited onto a porous Joeb-Sourirajan membrane. The ultrathin film of cellulose acetate was fabricated by a water surface float-casting technique. This has been described to some extent in the published technical literature, and inconsiderable detail in several reports on government-funded research projects.

In float-casting, a polymer such as cellulose acetate is dissolved in an aqueous solvent, usually cyclohexanone, to a level of about 5% by weight. A solvent is preferred which has a slight solubility in water and a specific gravity of less than 1.0g/cc. When a casting dope of this type is allowed to flow down an inclined plane onto a quiet water surface, it shows a pronounced tendency to spread over the water surface. Migration of the solvent into the water surface (as well as some loss by air evaporation) occurs, leaving behind a floating solidified polymer film. Continuous addition of the casting dope with mechanical drawing off of the solidified film, can be used to control the thickness of the ultrathin film. For reverse osmosis membranes of 200 to 5000 angstroms have been achieved. In a related application involving float-cast thin cellulosic membranes for hemodialysis, thicknesses of up to 2.5 μm (25000angstroms) were developed and used.

The free floating film is transferred to a microporous support by bringing a sheet of the support into contact with the underside of the ultrathin film, lifting it from the water surface. Also, two layers can be simultaneously cast and laminated to a carrier web. Numerous patents have appeared in recent years on the fabrication of gas separation membranes by float-casting, even including the double layer membrane technique.

Ultrathin float-cast films exhibit visible light interference colors. These can be used as a general guide for thickness, blue being about 2000 angstroms in the case of cellulose acetate, gold being thinner, green and red being thicker. Actual measurements have been made by interferometric methods on films deposited and air-dried on glass plates.

An alternate route to ultrathin cellulose acetate membranes exists via the carnell-Cassidy technique. In this method, a glass plate is mechanically withdrawn at a slow, careful rate from a dilute solution of the polymer. A thin, airdried film is obtained, which could be released from the glass plate by immersion in water. The result can be achieved on a large scale by the meniscus coating approach. A commercial adaptation of this process was developed by Lonsdale and Riley. A microporous sheet of a cellulose acetate/cellulose nitrate blend was first coated with a thin film of polyacrylic acid. This coating was temporary in nature, intended to protect the microporous sheet from solvent attack during overcoating with the semipermeable barrier film. The polyacrylic acid would dissolve in water

and wash out during subsequent usage under reverse osmosis conditions. An ultrathin coating of cellulose triacetate dissolved in chloroform was meniscus-coated onto the polyacrylic acid surface, and dried. These membranes exhibited salt rejections of as high as 99%

During the period of 1965 to 1972, the best data on flux and salt rejection for cellulose acetate membranes were exhibited by the composite membranes. However, these membranes never reached commercial viability; efforts on them died out completely by 1975. Reasons for this appear to be threefold. First, composite cellulose acetate membranes were technically difficult to scale up. Second, the advent of noncellulosic composite membranes in 1972 (the NS-100 membrane) offered much more promise for high performance (salt rejection and water flux), especially for seawater desalination. Third, continual improvements in asymmetric cellulose acetate membrane casting technology (such as the development of swelling agents and of blend membranes) brought the performance of asymmetric membranes to full equality with composite cellulose acetate membranes.

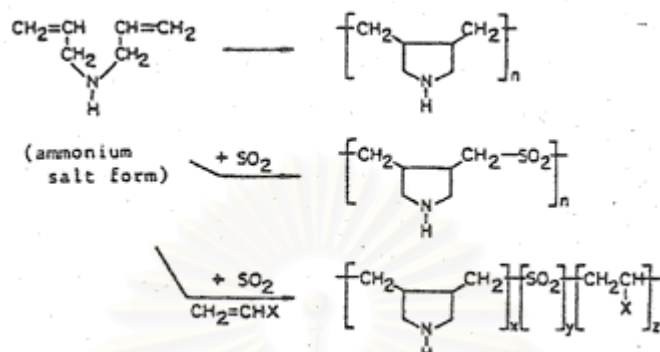
3.3.5 Other Interfacial Membranes Based on Polymeric Amines

Various polyamines have been synthesized and evaluated in the fabrication of the NS-100 type of membrane. These various compositions are described in the patent literature. Some of these efforts have involved polymeric amines containing only secondary amino groups to reach a goal of improved chlorine resistance. Whether any of them have reached commercial status cannot be determined because of the current trend to avoid publication of the compositions of new commercial reverse osmosis membranes.

Kurihara and coworkers at Toray industries prepared several aminated derivatives of polyepichlorohydrin, then formed composite polyamide membranes by interfacial reaction with isophthaloyl chloride. Polyepichlorohydrin was converted to polyepiodohydrin, then reacted with either 4-(aminomethyl) piperidine, 3-(methylamino) hexahydroazepine, or 3-(amino) hexahydroazepine. Also, polyepiaminohydrin was prepared by reduction of the azide derivative of polyepiaminohydrin. Best salt rejections were obtained if the polymeric amines as coreactants in the interfacial reaction. In tests on 3.5% sodium chloride at 800 psi and 25°C, salt rejections of 99.5% at fluxes of 8 to 9 gfd were characteristic. A three-zone barrier layer was produced, consisting of a heat-crosslinked polyamine gel (as in NS-100), a polyamide layer incorporating both the polymeric and monomeric amine reactants, and an additional surface polyamide layer comprised almost solely of the monomeric amine reactant combined with the acyl halide. Toray has recently announced the commercial introduction of a new, high rejection polyamide composite membrane, which may or may not correspond to this patented composition.

Kawaguchi and coworkers at Teijin have prepared a series of polymers based on poly(diallyl amine), its copolymer with sulfur dioxide, and various terpolymers.³⁹ The chemistry of this polymer synthesis is shown below. The patent description shows the diallylamine polymers to be polypiperidine (six-membered ring) derivatives, but there are

a number of publications that show this monomer to produce preferably polypyrrolidine (five-membered ring) structures:



These polymers were then interfacially reacted with di- and trifunctional aromatic acyl halides to give polyamides. Because the only reactive amine groups in these polymers were of the secondary amine type, such polymers should be chlorine-resistant. Dynamic chlorine tests (5 ppm, pH 6.0 to 6.5, 0.5% NaCl, 600 psi, 25°C) of 40 to 80 hours duration appeared to uphold this inference.

Interestingly, the best salt rejections were observed for the polyurea analogs, formed by crosslinking the polymers with isocyanates instead of acyl halides. For instance, poly(diallyl amine) reacted with 2,4-toluenediisocyanate gave membranes with 96.9 and 99.7% salt rejection (50 and 20 gfd flux respectively) under the above test conditions. Salt rejections for the polyamide examples rarely exceeded 95% in the patent examples. The polyurea analogs would not be resistant to chlorine.

Several other systems of polymeric amine-based interfacial polyamide membranes have appeared in patents by Kawaguchi and coworkers. One patent describes the use amine-terminated oligomers prepared by reaction of polyepoxides with polyfunctional amines. Another patent describes the attachment of polyfunctional amines as side groups onto linear soluble polymers via carboxamide or sulfonamide linkages. A third patent covers the use of additives to the polymeric amine phase, these additives bringing about additional crosslinking of the residual amino groups through heat-curing after interfacial formation of the barrier layer. Examples of such additives include esters, chlorohydrins, imidazoamides and carbamates. Finally, one patent describes the preparation of amphoteric polyamide barrier layers containing both free carboxylate groups and ammonium groups. Such membranes show high rejection levels towards sucrose (92 to 99%) while freely passing sodium chloride (15 to 25% rejection).

Yaginuma patented interfacial membranes made by condensation of polyalicyclic diisocyanates and diacyl halides with polyethylenimine or polyepiamine. This approach was claimed to provide high organic rejections simultaneously with low salt rejections, whereas comparative data for typical aromatic diisocyanates or diacyl halides showed high rejections for both types of solutes. However, only a wastewater product, naphthalenesulfonic acid/formaldehyde condensate, was used in the testing of such membranes.

No commercially available membranes corresponding to any of the above series of patents have as yet been reported, with the possible exception of the Toray patent.



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CHAPTER IV

EXPERIMENTAL SECTION

4.1 Process Description

Produced water along with contaminant solids settle to the bottom of the ship's tanks. Tank levels are varied to permit gravity drainage of the water and fluidized solids into one of two smaller tanks that are dedicated to waste holding service. Water along with settled solids from the waste tanks was used as feed to the membrane pilot plant.

Figure 4.1 illustrates the FSO, Floating Storage and Offloading. A process flow diagram for the membrane pilot plant is shown in Figure 4.2. A photograph of the pilot skid mounted on the FSO is shown in Figure 4.3. Contaminated water was pumped to the 1000-liter process feed tank through a 1" FloChamp desanding hydrocyclone. The purpose of the hydrocyclone was to remove as many of the particulate solids as possible and to pre-coalesce condensate in the water going to the feed tank. To maximize hydrocyclone efficiency, about 5% of the feed was continuously bled off from the bottom of the hydrocyclone. The feed pressure to the hydrocyclone varied between about 20 and 40 PSIG. Despite the relatively low pressure drop, the hydrocyclone effectively rejected solids and coalesced condensate droplets in the feed water. In order to prevent the build up of a condensate layer in the feed tank, a continuous skimming was maintained.

From the process feed tank, water was pumped through a 50-micron bag filter and then through two spiral wound UF cartridges in series. Each cartridge had 150 ft² of surface area. UF filter permeate went to the RO feed tank while concentrate (non-permeated feed water) was recycled either to the inlet of the UF membrane or returned to the process feed tank. It was observed that as the condensate became more concentrated in the recycle water, there was a tendency for the liquid hydrocarbons to coalesce and separate out in the process feed tank.

Flow to the UF membrane was varied from about 6 to 15 GPM. 11 to 15% of the UF feed was recovered in the RO feed tank as permeate.

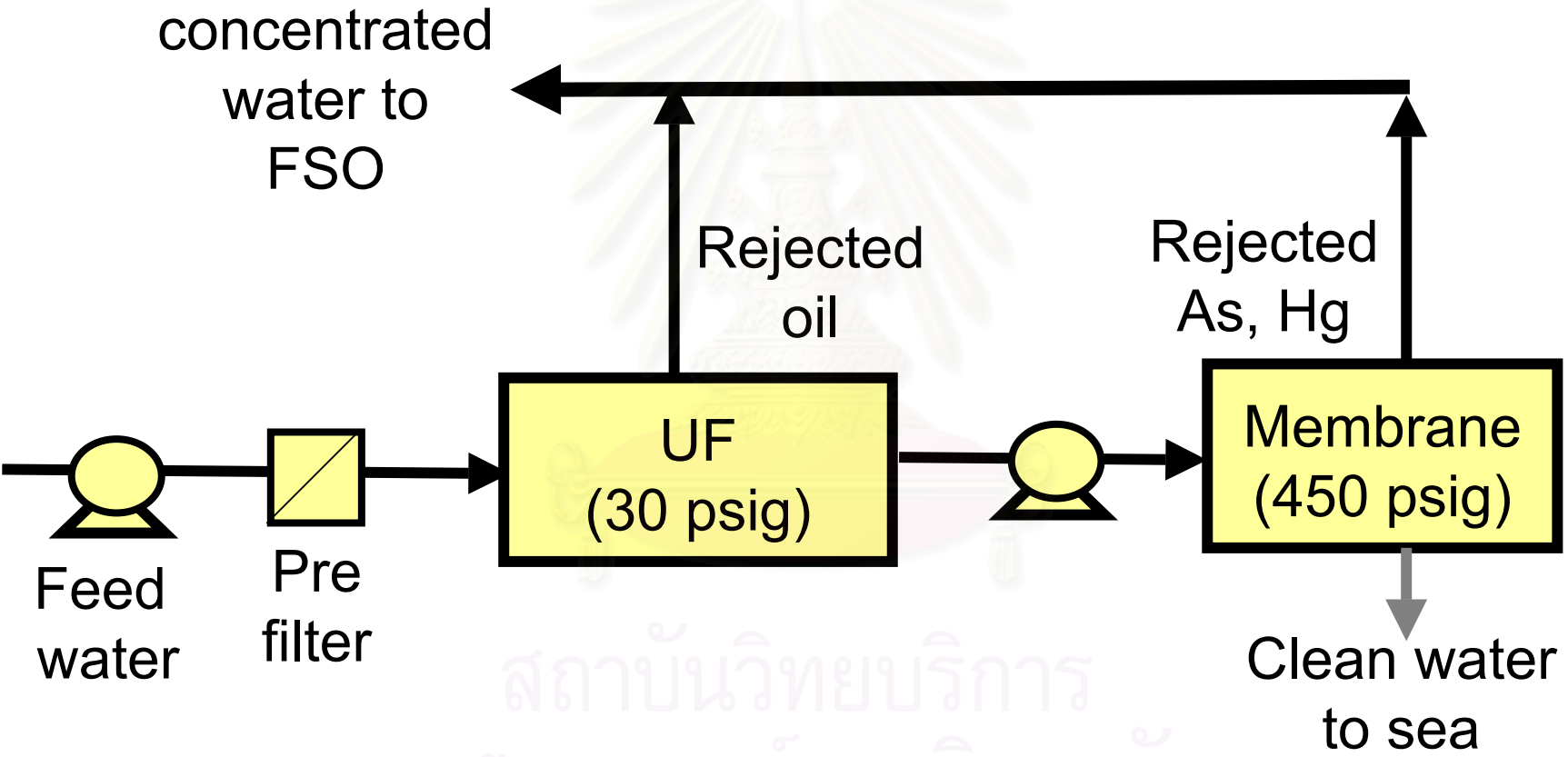
Because the RO feed tank was open to the atmosphere, it was necessary to inject small amounts of citric acid into this water to prevent iron hydroxide precipitation. Water from the RO feed tank was pumped through a single spiral wound RO membrane. RO permeate was either discharged overboard or returned to the ship's tanks while RO concentrate (non-permeated water) was recycled back to the RO feed tank.

Feed water chemistry is summarized in Table 4.1. Note the relatively high iron content and the high alkalinity of the feed water, making scale mineral precipitation a significant risk for this water. The concentration of solids and condensate in the water entering the process feed tank varied significantly. Suspended solids varied from 175 to over 10,000

Figure 4.1 : FSO - Floating Storage and Offloading

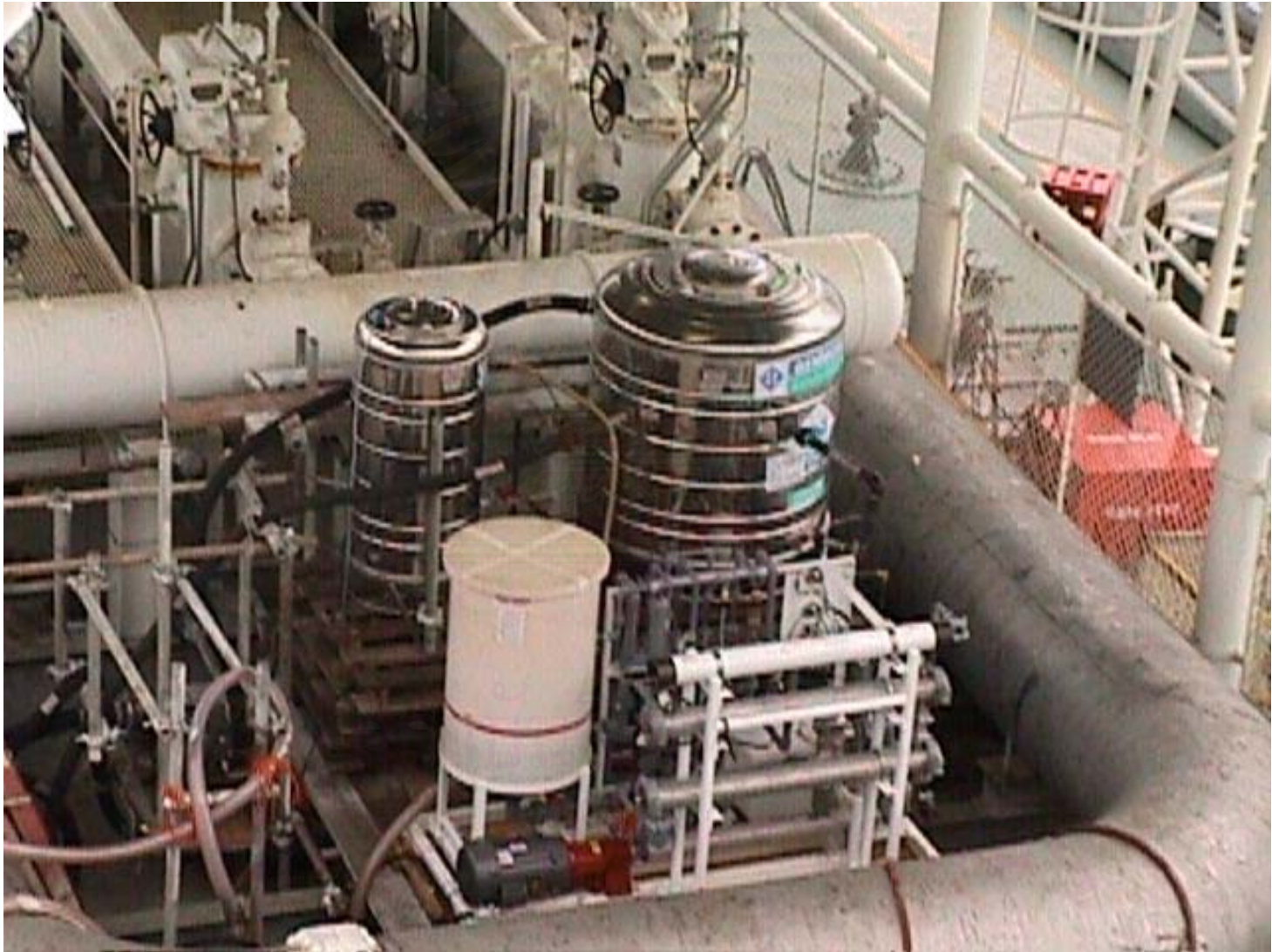


Figure 4.2 : PFD for FSO Membrane Water Treatment Pilot Plant



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Figure 4.3 : Photo of FSO Membrane Pilot Skid



mg/liter ahead of the desanding hydrocyclone. The particle size distribution for the solids is shown in Figure 4.4. XRD analysis indicated that the bulk of the solids were precipitated carbonate minerals. Condensate in the water entering the process feed tank varied from circa 0.1 to 100%. Most of the condensate was removed as feed tank skimming, however, so the actual UF membrane feed water typically contained only 100 to 900 mg/liter of condensate.

Table 4.1 The composition of feed water to the FSO Membrane Pilot Plant is summarized

Calcium	85	mg/liter
Magnesium	60	
Sodium	2400	
Iron	37	
Chloride	1690	mg/liter
Sulfate	21	
Bicarbonate	3900	
Total Alkalinity as CaCO ₃	3200	
Arsenic	15 – 28	mg/liter
Mercury	0.4 – 9.2	
Total Suspended Solids	175 – 10,000	

The UF membranes used for the pilot test program were polyacrylonitrile that had been specially treated by Osmonics-Desal to be rendered hydrophilic. The UF membrane pore size is 0.01 microns. Two types of materials were tested for the RO. The first set of RO membranes was polyamide and the second set was Cellulose Acetate. Both membranes have a pore size rating of 0.0005 microns.

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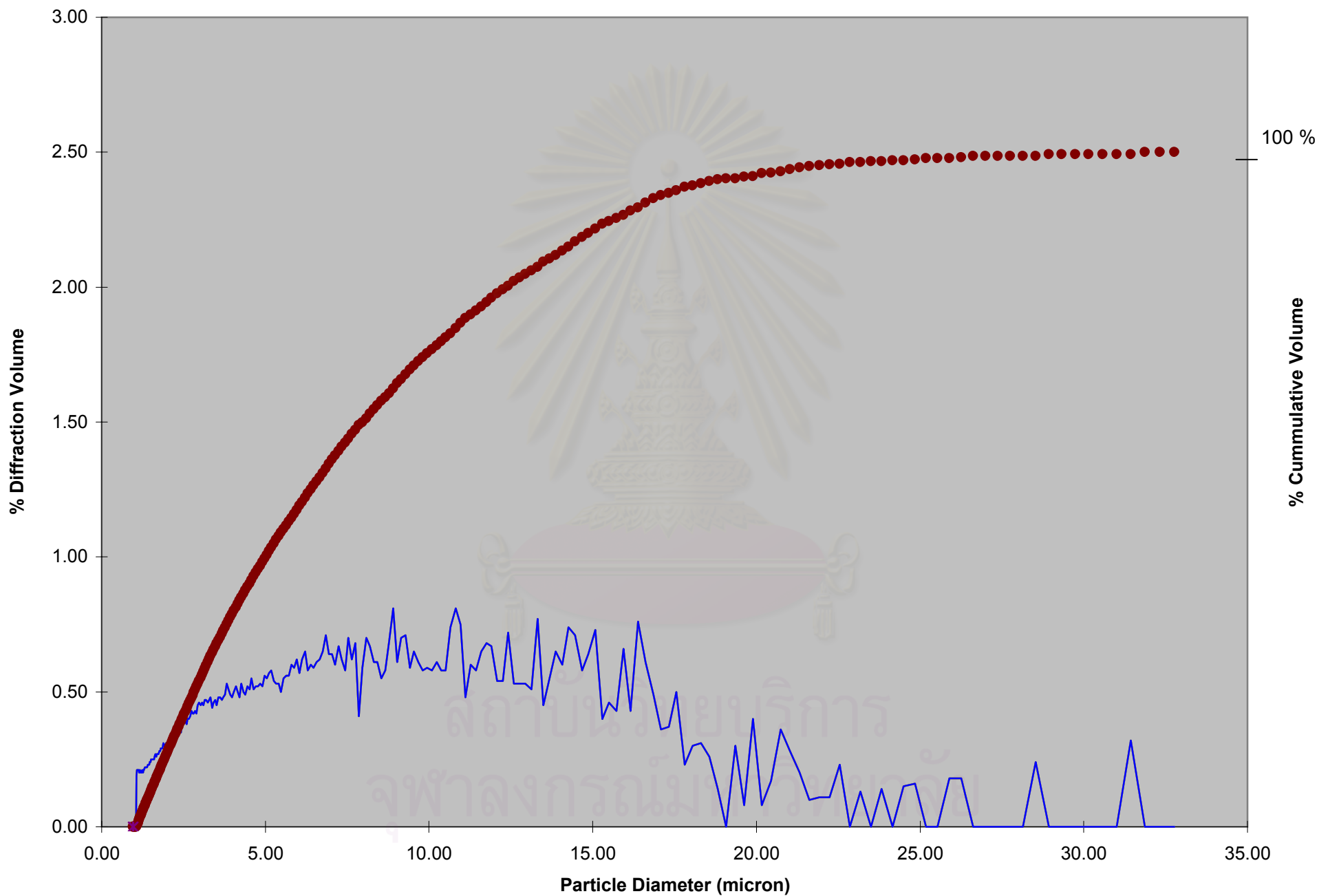


Figure 4.4 : Particle Size Analysis Sample: Solids From FSO Water, 18 Jul 99

4.2 Operating Procedure

4.2.1 Startup Procedure – UF System

Refer to UF P&ID

1. Make sure Tank (T-1 the stainless steel 1100 liters from FSO) is full and overflowing, then open valves V-300, V-301, V-302 (a needle valve which controls the pressure on the system), V-304 and V-305.
2. Close valve V-303, the internal recirculation valve, which returns flow to the suction side of the air driven feed pump, P-3.
3. Open valve from air supply, then activate P-3, large air pump for UF system, by twisting the pressure regulator cap, and then activate the small air pump P-7 which adds anti-scalant to the UF permeate as it enters Tank, T-2, on the membrane skid.
4. Establish that water is flowing through the system denoted by Concentrate Flow Indicator (FI-101 which should be 15 to 20 GPM) and Permeate Flow Indicator (FI-102 which should be 1-3 GPM).
5. Flowrate 2 GPM is required, so if the permeate flow is low, then adjust by tightening the Valve 302 (Concentrate Valve) to produce 2 GPM. However, if the system is producing more than 2, GPM adjust, by tightening Valve 305 (Permeate Back-Pressure Valve) to maintain a constant permeate flow rate.
6. The 2 GPM permeate flow rate is maintained by letting the pressure increase on the system. All the pressures in the UF system are read from a multi-port pressure gage on the skid panel. UF feed pressure, UF inter-stage pressure, UF concentrate pressures are read from this gauge. For instance, when the membranes are clean, the system may start out at 20 PSI, but as the membranes foul with oil and debris, the feed pressure will increase to maintain the targeted permeate flow rate of 2 GPM.
7. Make sure the other small air pump P-7 is operating, pumping anti-scalant into the UF permeate as it enters Tank T-2.

4.2.2 Starting Procedures - RO System

Refer to RO P&ID

Be sure tank T-2 (50-gallon plastic tank on skid) is always full.

1. Open the following valves: V-309, V-313 (needle valve on discharge of centrifugal high pressure pump), but once this has been established, it is not necessary to change the position of this valve frequently. Needle Valves V-314 (Concentrate Recirculation) and V-323 (Concentrate Back-Pressure) must be open. This is very important, so make sure the valves listed above are indeed open. Because this is the

high-pressure side of the system, we want to start out with as low a pressure as possible before we increase the system pressure.

2. Ball Valve V-310 is closed.
3. Permeate ball valves V-320 and V-321 are both open. One or both of these valves must be open at all times. After 5 minutes, close Valve V-320, the return line to FSO. But Valve V-321 remains open and will send RO permeate to Tank T-3 (stainless steel 100 liters) for testing prior to being returned to FSO or sent overboard.
4. Activate high-pressure pump by throwing breaker, then turning on the pump in the electrical control room. This should be a two-person operation. All operators must know where this room is located. You can turn the pump off by yourself, but to activate the high pressure system, it must be a two-person operation.
5. By adjusting the Concentrate Valve, V-323, and Recirculation Valve, V-314, you can increase RO feed pressure, so that you are producing 1-2 GPM as noted on the RO permeate Flow Indicator FI-106. This will be at an initial pressure of about 250 psi. The pressure is read from the multi-port RO feed and RO concentrate pressure gauge on the system's face panel. The Concentrate Flow Indicator FI-108, directly above V-323, should read about 2-3 GPM. While the Recirculation Flow Indicator FI-104, directly above V-314, will have 6-10 GPM.
6. The concentrate flow, V-323 and V-314, has to be open. By adjusting one or both of these, one increases or decreases the feed pressure and, at higher pressure, produces more permeate and less permeate at lower pressure. This is a balancing act, so carefully adjust the appropriate valves until the system is operating at its initial pressure of about 250 psi. Again, like the UF operation, we will maintain constant permeate flow and let the pressure increase as the membranes foul or as the osmotic pressure of the soluble salts in the feed increases.

4.2.3 Systems Operation and Troubleshooting – UF System

While the system is running, the summary of the most important aspects of operating the system to reinforce and interpret the important operating parameters is as follows:

1. As stated above, it is intended to operate the system by controlling the permeate flow to about 2 GPM, and we will let the pressure increase to maintain this goal.
2. The UF feed pressure is measured with a multiple tap pressure gauge, including the UF feed pressure, inter-stage pressure and concentrate pressure to determine the pressure drop and subsequent net driving pressure to produce 2 GPM of UF permeate.

3. In addition, this same multiple tap gauge measures the back pressure of the permeate with a permeate back pressure valve, V-305. When these UF membranes are new and clean, the permeate flux can be very high, in fact too high, so the permeate is required back pressure to maintain a constant permeate flux.
4. Also, as stated above, increase the pressure until it is needed to flush and clean the UF membranes. So, if a feed pressure is started at 20 PSI, when it reaches 40 PSI, membrane cleaning is required.
5. The system contains a bag filter BF-4 to catch debris from the FSO feed tank. This filter will need to be changed periodically. When the gauge on the prefilter (located on the side of the bag filter housing) reads 15 PSI higher than the UF feed pressure (read from the multiple port pressure gauge), then the bag filter must be replaced. Do not discard the bags as they can be cleaned and reused.
6. There are two UF membrane modules MX-50 4040CJL in operation and one element on the tanker as a spare, in the event that one element is defective or the membrane can not be clean properly.

4.2.4 Systems Operation and Troubleshooting - RO System

1. Maintaining permeate flow at 1-2 GPM at modest pressures indicate the membranes are clean.
2. Check conductivity with hand-held meter, as measured in ppm, of RO feed in Tank T-1, and check RO permeate quality at the sample port on permeate Flow Indicator FI-106. When operating properly, there should be about 98% rejection of soluble salts with the membranes.
3. If this changes dramatically, then either we have a mechanical leak, O-rings, or the membrane has been somehow compromised. A spare vessel with new element must be installed.

4.2.5 Flushing the Systems - UF System

Upon any extended shutdown of the equipment, it is required to flush the FSO feed from the UF membrane system with clean pure water from the tanker's storage.

1. Turn off the air to pump P-3 and small anti-scalant pump P-7.

2. Close valve V-300 and open the valve from fresh water supply, which contains clean, pressurized water, and open completely the Concentrate Valve V-302.
3. Turn on the air to pump P-3. Flush system for 2-3 minutes, then turn off the air pump P-3 and close the valve from fresh water supply.

The membranes can sit in this clean water for up to one week with no problems.

4.2.6 Flushing the Systems - RO System

1. Turn off the pressure pump P-10 in the electrical control room.
2. Close valve V-309 from the feed tank.
3. Open needle valves V-323 on the concentrate line and V-314 on the recirculation line.
4. Open valve from the fresh water line connected to pressurized water system.
5. No need to turn on the high-pressure pump, as the pressurized clean water will flow through the system. Operate in this manner for 2-3 minutes.
6. Close the valve from the tanker's clean water supply and let the membrane sit in this clean water for up to one week without any problems.

4.2.7 Cleaning Procedures for FSO Membrane Systems – UF System

1. System has been properly flushed per instruction listed above.
2. Fill about 50% of the RO permeate Tank T-3, if possible, with hot ship-board water, but if hot water is not available, then normal ship water is sufficient.
3. Add laundry detergent. A supply will be near the skid, but when it runs out, it can be obtained at the laundry. One cup of detergent should be sufficient.
4. Connect hose from T-3 to valve next to V-304, and connect concentrate line with flexible hose to return to T-3.
5. Turn on Pump P-3 and recirculate back to Tank T-3 for about 5 minutes. Let the system soak for 5 minutes, then turn on the air pump and recirculate for another 5 minutes. Do this procedure for about 30-40 minutes.
6. Then drain Tank T-3.

7. Connect Flush lines to the system and flush the residual soap from the UF membranes.
8. Return to UF start-up procedures to restart the system after cleaning.

4.2.8 Cleaning Procedures for FSO Membrane Systems – RO System

1. Flush System per instruction above.
2. Fill Tank T-2 with hot water.
3. Open Valve 309.
4. Add citric acid and mix it until it is entirely dissolved Tank T-3 and until the pH is about 2.
5. Turn on high-pressure pump, but operate it at as low a pressure as possible, meaning both Valve V-323 and V314 are completely open.
6. Recirculate and soak for 30-40 minutes. Check the pH. If it has risen above pH 2, then add more citric acid to reduce it back to pH 2. After 40 minutes, flush the system per flushing instructions, and then proceed to start the system per the start-up instructions listed above.

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CHAPTER V

RESULTS AND DISCUSSION

The water treatment system onboard the FSO consists of two separate systems. The first is Ultrafiltration System (referred to as UF) and the other is a Reverse Osmosis System (referred to as RO). These two units are linked by a common tank mounted on the water treatment skid. The UF and RO systems are independent and can be operated or cleaned independently.

The UF system receives the FSO water and its purpose is to remove all free all entrained oils and suspended solids. Hydrophilic membranes are used. As a result, oils will be rejected efficiently. The pore size of the membrane is about .01 microns. The UF system operates at relatively low pressures, 20 to 40 psig, and will produce from 1 to 2 Gallons Per Minute (GPM) which goes to the small 50 Gallon tank mounted on the skid.

This tank containing the UF product (called permeate) becomes the feed to the RO system. The RO system will produce about 1 Gallon per Minute (GPM). The RO membrane is a thin-film composite of polyamide polymer and has pore sizes about .0005 microns. Under modest pressure it will remove from water-soluble salts such as: arsenic, mercury, sodium, chloride and sulfates. The RO system will operate at much higher pressures than UF membranes, i.e. 250 to 550 psig, depending upon the amount of salt in the feed (UF Permeate).

The purpose of this thesis is to study the performance, the reliability, and the feasibility of the membrane technology for water treatment in oil and gas operations, additionally to treat produced water from natural gas wells to the specified discharge quality so that the permeate can be disposed overboard. The work scope is to design, fabricate and install the pilot plant onboard the FSO, study the feasibility of using membrane technology in the water treatment process in oil and gas operations, study and analyze the effects of the operating conditions on the permeability of the membranes and design a process for the full scale operation.

A membrane pilot plant was tested with 2 sets of the different RO membrane elements during July - December 1999. The first set was utilized a polyamide (PA) RO membrane and the second set was utilized a cellulose acetate (CA) RO membrane while UF elements were used the same type of polyacrylonitrine (PAN) polymer. The first and the second sets were operated approximately 140 hours and 180 hours, respectively.

5.1 Pilot Scale Evaluation

Figure 5.1 visually illustrates the quality of water being fed to and recovered from the membrane treatment pilot plant. Much of the black color in the feed water is from

Figure 5.1 : Photo of Membrane Pilot Plant Feed and Product Water



suspended solids that were removed by the desanding hydrocyclone ahead of the process feed tank. The UF permeate typically retained a very light haze while the RO permeate was crystal clear. The samples shown in Figure 5.1 were analyzed with the following results

	<u>TPH</u>	<u>Mercury</u>	<u>Arsenic</u>
Pilot Plant Feed	530 PPM	6,017 PPB	22,020 PPB
UF Permeate	174	5	4,540
RO Permeate	34	1	1,450

The successful removal of mercury and arsenic at this point in the test (42 hrs of run time on the membrane) suggests that both the UF and RO membranes are mechanically intact. Later in the test program this was not the case as RO permeate tube collapse and possible mechanical failure of UF membrane adhesive bonds was observed. However, given the mechanical integrity of the membranes at this point, the high permeation rate through the UF membrane for hydrocarbons, in contrast with the visual clarity of the sample and the lack of sheen on the sample's surface, suggests that the concentration of dissolved hydrocarbons in the process water is quite high. High levels of BTEX hydrocarbons in the produced water would not be surprising since the Thai condensate is relatively rich in aromatics.

Tables 5.1 – 5.4 summarize additional data on the performance of the pilot plant membranes during the course of the test program.

5.1.1 Hydrocarbon Reduction

Hydrocarbon removal efficiency by the UF membrane is somewhat difficult to interpret. Under some run conditions, e.g., relative clean membranes, low ΔP across the UF membrane, and/or low percent of recycle water, TPH removal by the UF membrane ranged from 86 to 98%. At other times, the measured removal efficiency was far lower.

Several considerations suggest that the high concentration of hydrocarbons passing through the UF membrane are dissolved rather than dispersed. First, the UF permeate was visually clear. Second, the Unocal Thailand condensate is reasonably aromatic in nature with a substantial BTEX content. Third, the water arriving on the FSO is known to be contaminated with water-soluble corrosion inhibitors and water treatment polymer. Also, water treatment experience in nearby platforms has demonstrated that high levels of dispersed condensate in the produced water are associated with high levels of residual mercury. As will be discussed below, the concentration of mercury in the permeate water was very low, quite independent of the residual hydrocarbon levels. Finally, attempts to measure the TPH of the UF permeate using UV-fluorescence was not successful. Typical UV-fluorescence signals were 10 – 100 X the expected values based upon IR analysis of the same produced water sample. This suggests the presence of excess aromatics in the produced water compared to the aromatics content of the bulk condensate.

It should be noted that when a high fraction of recycle water is being fed to the membranes, the timing of sampling could be critical as most of the dissolved hydrocarbons would permeate the membrane early in the day's run, leaving fewer dissolved hydrocarbons to be detected in later samples.

Hydrocarbon removal by the tandem UF-RO membrane system was excellent, generally exceeding 95%. The RO membranes showed no evidence of fouling from exposure to hydrocarbon liquid, further suggesting that dissolved rather than dispersed hydrocarbons were passing through the UF membrane.

5.1.2 Mercury Reduction

Overall, the removal of mercury from the feed water was highly efficient, exceeding 99%. This result is consistent with water treatment tests that were conducted in 1996 (see OTC Paper 8712, May 1998) wherein it was determined that mercury present in the Gulf of Thailand produced water was elemental and tended to be present in particulate form. Both colloidal mercury droplets and mercury chemisorbed onto carbonate solids were found on the test filters. The data showed that mercury could be removed from the produced water by filtration at less than 1.2 microns.

Operational experience in the Gulf of Thailand on the Funan, Satun, and Platong platforms confirmed that efficient removal of hydrocarbons from the produced water was associated with high levels of mercury removal. Generally speaking, when the produced water TPH meets the Unocal Thailand self-imposed discharge limit of 40 PPM, the mercury levels fall below the self-imposed discharge limit of 10 PPB. However, at higher TPH levels, e.g., >100 PPM, the mercury in the produced water tends to exceed 10 PPB.

5.1.3 Arsenic Reduction

Arsenic is present in the condensate as As^{+3} that is extracted into the water phase. The equilibrium between arsenic in the condensate and in the water appears to be pH dependent. In the water, the thermodynamically favored form for arsenic is arsenite, AsO_3^{-3} . The equilibrium between As^{+3} and Arsenite is also pH dependent. Two reasons can be proffered for the unexpected success of the UF membrane in rejection of arsenic. First, some arsenic probably remains associated with the condensate and may thus be rejected when the UF membrane separates dispersed hydrocarbons.

Alternatively, the formation of Ferric Arsenite solid ($FeAsO_3$) may be responsible for limiting the passage of arsenic through the UF membrane. It is interesting to note that data in Table 5.3 show the ability of the UF membrane to reject arsenic was lowest early in the testing of UF membrane Set #1, when it would have had the fewest solids deposited within the canister. The use of the 1" hydrocyclone and the cartridge filters during the testing of UF membrane Set #2 limited the deposition of iron-based solids in

the membrane canister and the ability of the UF membrane to reject arsenic was found to be correspondingly lower.

Until mechanical problems with the RO membranes were encountered late in the pilot plant campaign (collapsed inner collection tube), arsenic rejection by the UF and RO membranes in series average a respectable 92%. Unfortunately, the arsenic in the produced water feed to the pilot plant was sufficiently high that the discharge specification of <250 PPB could not be met by this system.

Table 5.1 Hydrocarbon removal data are summarized for the FSO Membrane Water Treatment Pilot Plant

	Membrane Run Time (Hours)	Hydrocarbons in Feed (PPM)	TPH of UF Permeate (PPM)	TPH Reduction (%)	TPH of RO Permeate (PPM)	Total TPH Reduction (%)
Membrane Set #1	4	122	17	86	4	97
	23	361	7	98	3	99
	32	910	240	74	10	99
	42	530	174	67	34	94
	52	420	256	39	40	90
	62	328	130	60	10	97
	75	176	70	60	6	97
	89	102	81	20	10	90
	99	312	115	63	58	81
	122	1895	27	99	2	>99
128	2240	22	99	--	--	
Membrane Set #2	5	975	18	98	7	99
	24	486	387	20	35	93
	37	614	435	29	19	97
	42	449	395	12	10	98
	54	492	376	30	32	94
	67	444	38	91	22	95
	72	314	34	89	15	95
	131	228	102	55	21	91
	165	500	370	26	40	92

Table 5.2 Mercury removal data are summarized for the FSO Membrane Water Treatment Pilot Plant

	Membrane Run Time (Hours)	Mercury in Feed (PPB)	Hg in UF Permeate (PPB)	Hg Reduction (%)	Hg in RO Permeate (PPB)
Membrane Set #1	4	588	0.7	99.9	0.3
	23	7139	4	99.9	0.2
	32	9170	2	>99.9	0.3
	42	6017	5	99.9	0.9
	52	6943	2	>99.9	0.6
	62	3144	3	99.9	0.6
	75	539	2	99.6	0.4
	89	1700	5	99.7	4.2
	99	1763	3	99.8	2.1
	122	988	0.6	99.9	0.5
	128	--	--	--	--
Membrane Set #2	5	261	1.3	99.5	0.5
	10	--	--	--	--
	37	105	0.9	99.1	0.2
	42	--	--	--	--
	54	--	--	--	--
	67	44	1.9	95.7	0.2
	72	49	2.9	94.1	0.5
	131	433	--	--	0.6
	148	67	0.9	98.7	0.6

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Table 5.3 Arsenic removal data are summarized for the FSO Membrane Water Treatment Pilot Plant

	Membrane Run Time (Hours)	Arsenic in Feed (PPB)	As in UF Permeate (PPB)	UF As Reduction (%)	As in RO Permeate (PPB)	Total As Reduction (%)
Membrane Set #1	4	13120	12670	3	1856	86
	23	17980	7260	60	807	95
	32	22640	14600	36	1616	93
	42	22020	4540	79	1448	93
	52	28700	4060	86	1058	96
	62	16920	3320	80	1768	90
	75	13800	4080	70	876	94
	89	8220	635	92	142	98
	99	11180	1695	85	602	95
	122	6590	1145	83	684	90
	128	--	--	--	--	--
Membrane Set #2	5	28680	11670	59	1476	95
	10	21060	10290	51	2544	88
	37	14790	10080	32	1193	92
	42	--	--	--	--	--
	54	--	--	--	--	--
	67	19760	19720	1	2296	88
	72	18540	15910	<1	2004	89
	131	12980	6950	47	--	--
	148	16480	14670	11	8920	46

Table 5.4 Contaminants removal data are summarized for the FSO Membrane Water Treatment Pilot Plant

Contaminants	Feed	Product # 1	Product # 2	Disposal Standard	Unit
Arsenic	16,800	2,500	4	250	PPB
Mercury	1,700	0.7	<0.2	10	PPB
TPH	620	64	-	40	PPM

5.1.4 Operations

The major problems encountered during the course of the pilot test campaign were related to solids and to the accidental introduction of high concentrations (up to 100%) of condensate to the UF membrane. Figure 4.4 shows the particle size for solids in the FSO water. These solids were determined by XRD to be mainly precipitated carbonate minerals. Figure 5.2 shows how the normalized permeation rate varied over time for the UF membranes. Despite regular attempts to clean the membrane, it became progressively fouled by the very fine solids over time.

After about 140 hours on-line, the UF membranes were removed for inspection by Osmonics-Desal and a new set of membranes installed. The disassembly and inspection confirmed the presence of substantial solids that blocked over 50% of the membrane surface from the cross-flow of produced water. To control solids, a 2" desanding hydrocyclone was installed on the inlet to the process feed tank. This was then replaced with a 1" FloChamp desanding hydrocyclone with an improved ability to capture solids in the 5 to 10 micron particle size range.

Cartridge guard filters were later installed on the inlet to the UF filters. However, few solids deposited on the cartridges. With better solids control, the second set of UF membranes retained a higher and relatively constant permeation rate until they were fouled by the introduction of 100% condensate. Based upon Figure 5.2 data, the design for a full scale treatment system for this produced water system would be based upon a normalized permeation rate of 15 ± 5 GPM/(ft²-day).

Figures 5.3 – 5.4 illustrate how the pressure drop across the first and second set of UF canisters and through the UF membranes varied with run time. Data in Figure 5.4 illustrate the impact of the 1" desanding hydrocyclone on the system's performance. The steep pressure drop immediately following the installation of the FloChamp resulted from a detergent flushing of the membrane. However, contrary to earlier experience, no pressure increase was observed subsequent to the washing.

Normalized permeation rates (gallons of permeate per ft² of membrane surface per day) are shown in Figure 5.5 for both of the RO membranes used in the test program. Note the loss of permeation that occurred early in the life of each membrane. This loss was most likely due either to swelling resulting from exposure to dissolved aromatics, or to membrane compression at the relatively high pressures being employed in the test campaign. In this system, the cellulose acetate membrane's relative permeability exceeded that of the polyamide membrane. However, selectivity and rate of arsenic rejection was better for polyamide. Figures 5.6 – 5.7 illustrate how the pressure drop across the first and second set of RO canisters and through the RO membranes varied with run time.

Based upon Figure 5.5 data, the design for a full scale treatment system for this produced water system would be based upon an RO membrane normalized permeation rate of 8 ± 3 GPM/(ft²-day).

**Fig. 5.2 Normalized Permeation Rate vs Time for Ultra-Filtration Membrane
(Trend Line is 10 pt. Moving Average)**

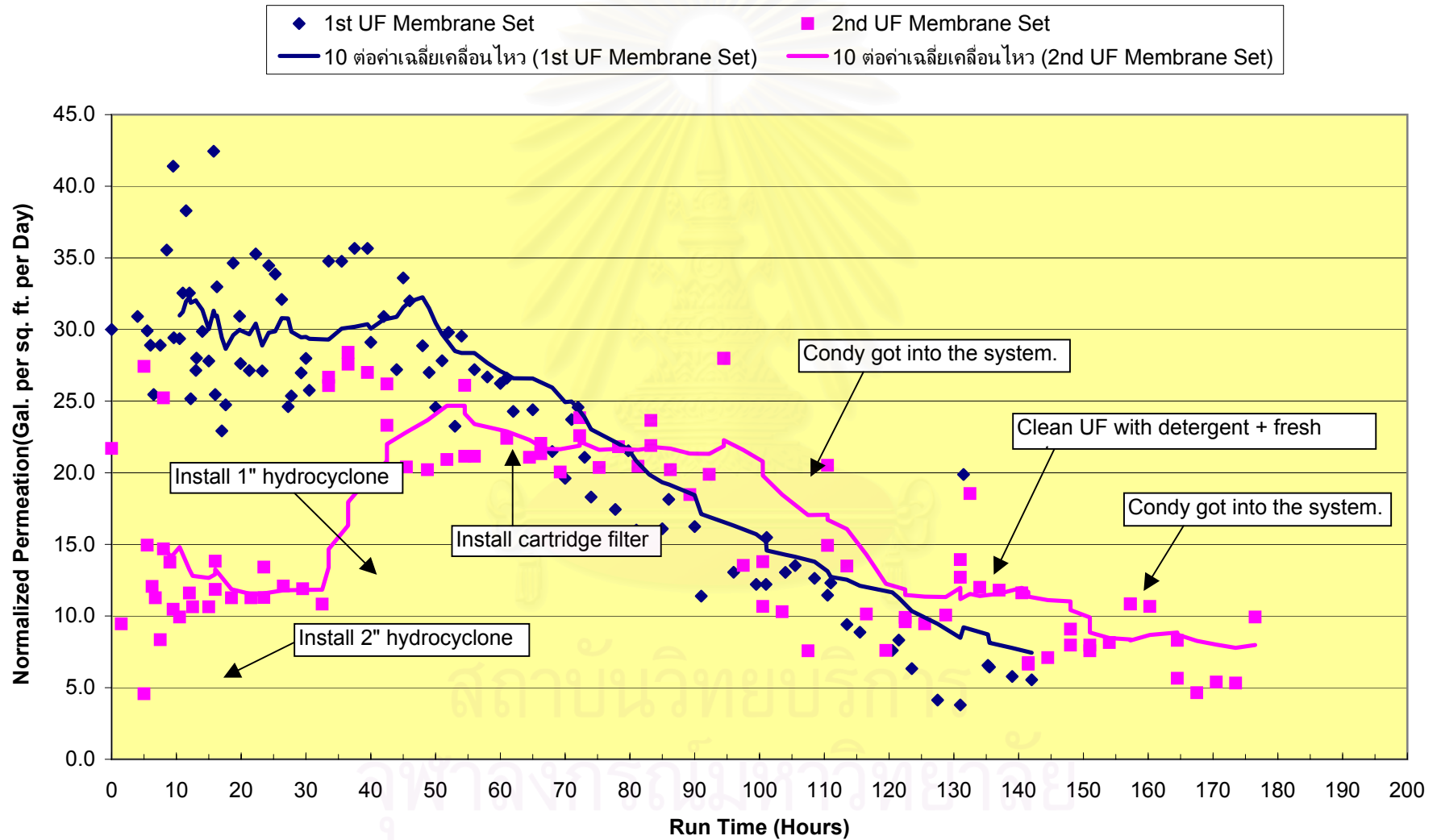


Fig. 5.3 Pressure Drop Across UF Membrane vs. Time (1st Set)

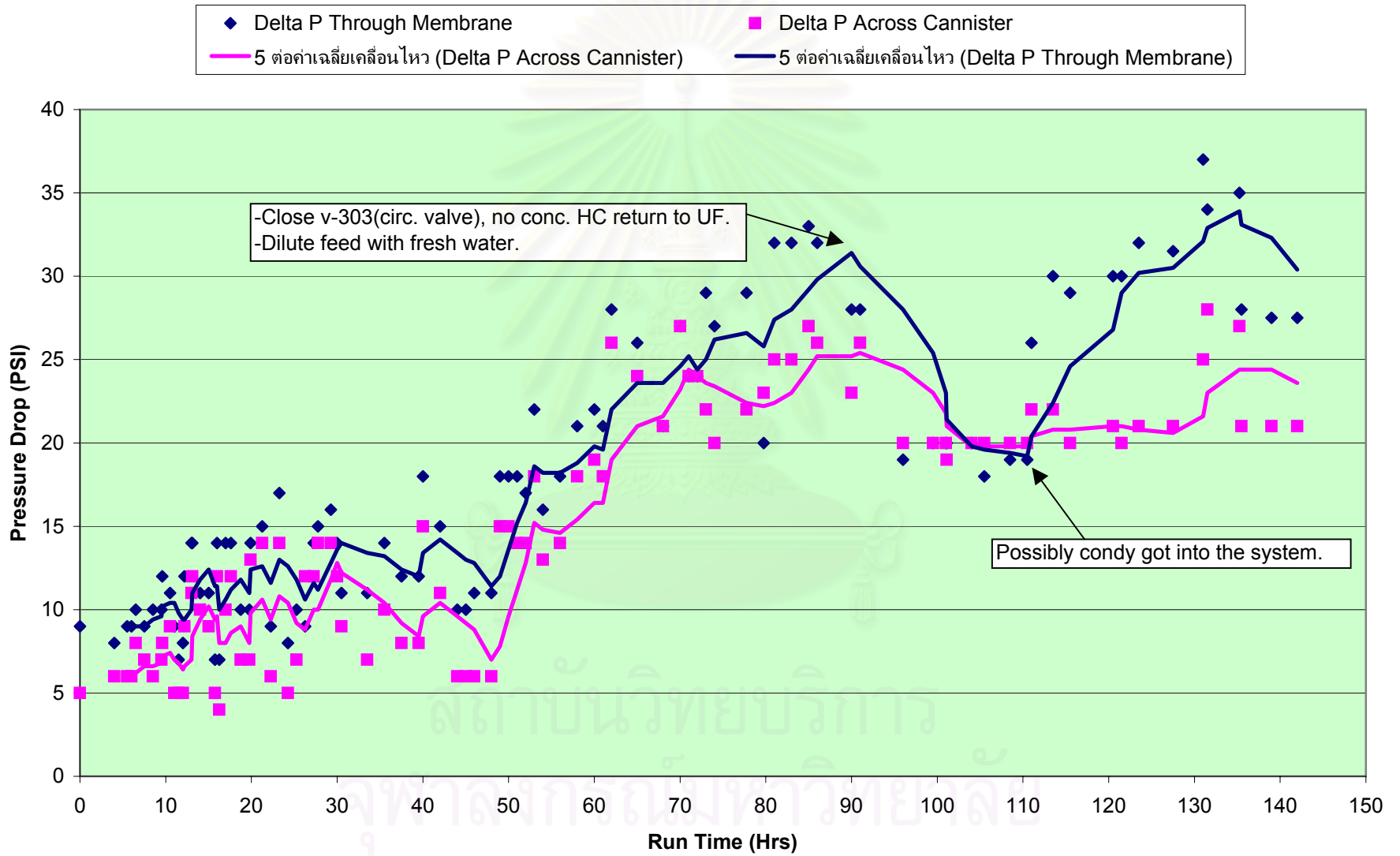
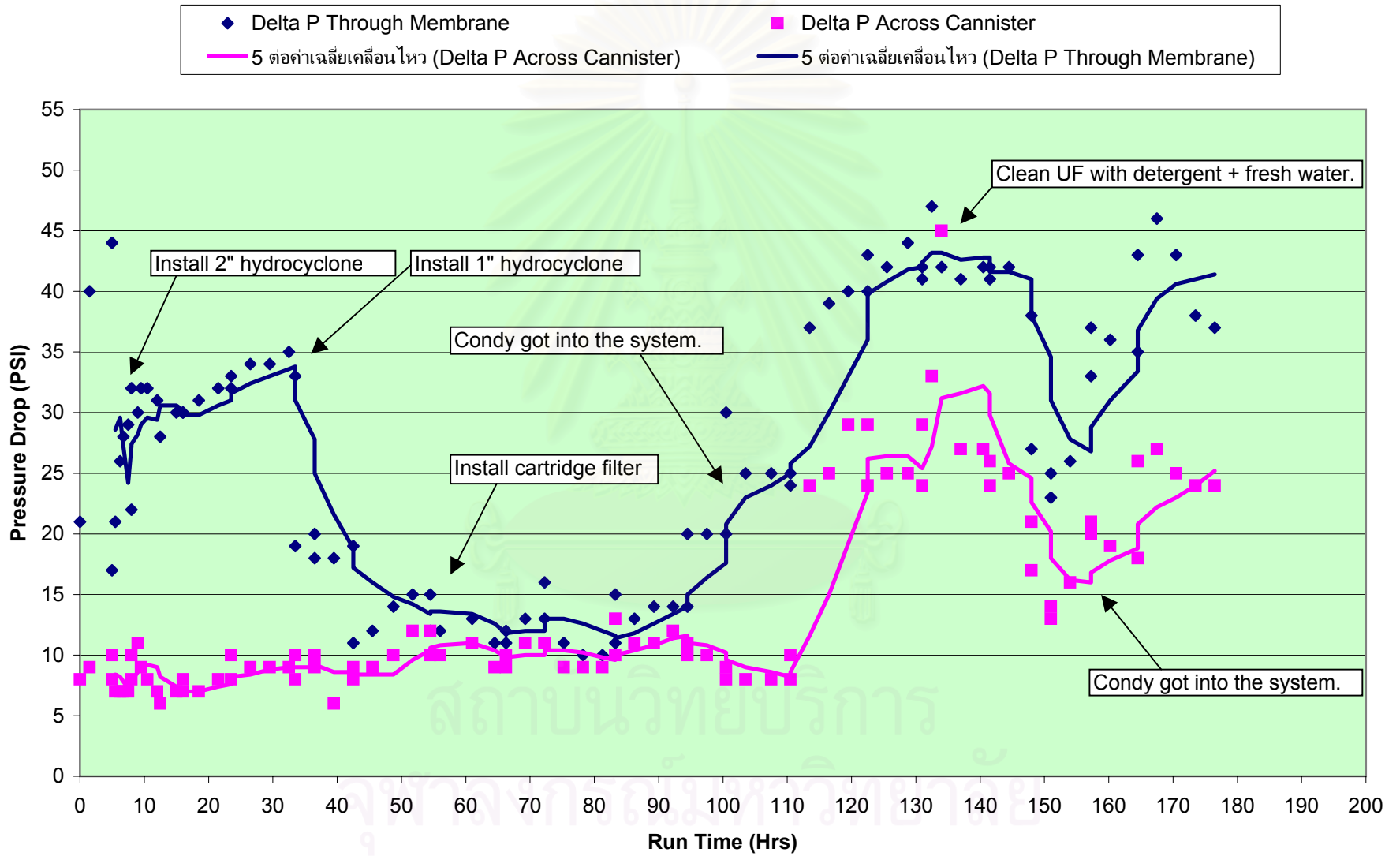


Fig. 5.4 Pressure Drop Across UF Membrane vs. Time (2nd Set)



**Fig. 5.5 Normalized Permeation Rate for RO Membrane vs Time
(Recalculated using calculated Feed and Conc. NaCl Data)**

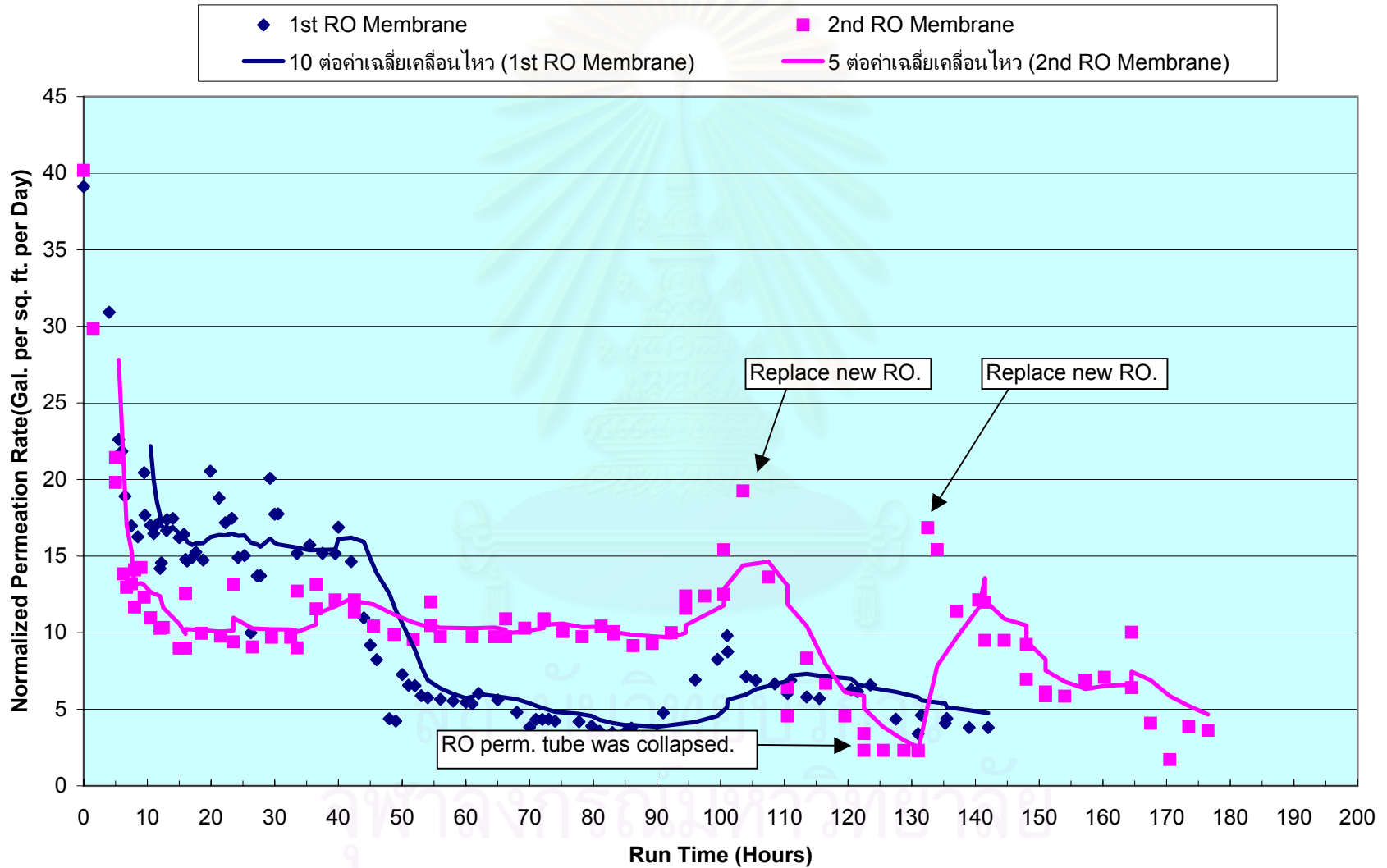


Fig. 5.6 Pressure Drop Across RO Membrane vs. Time (1st Set)

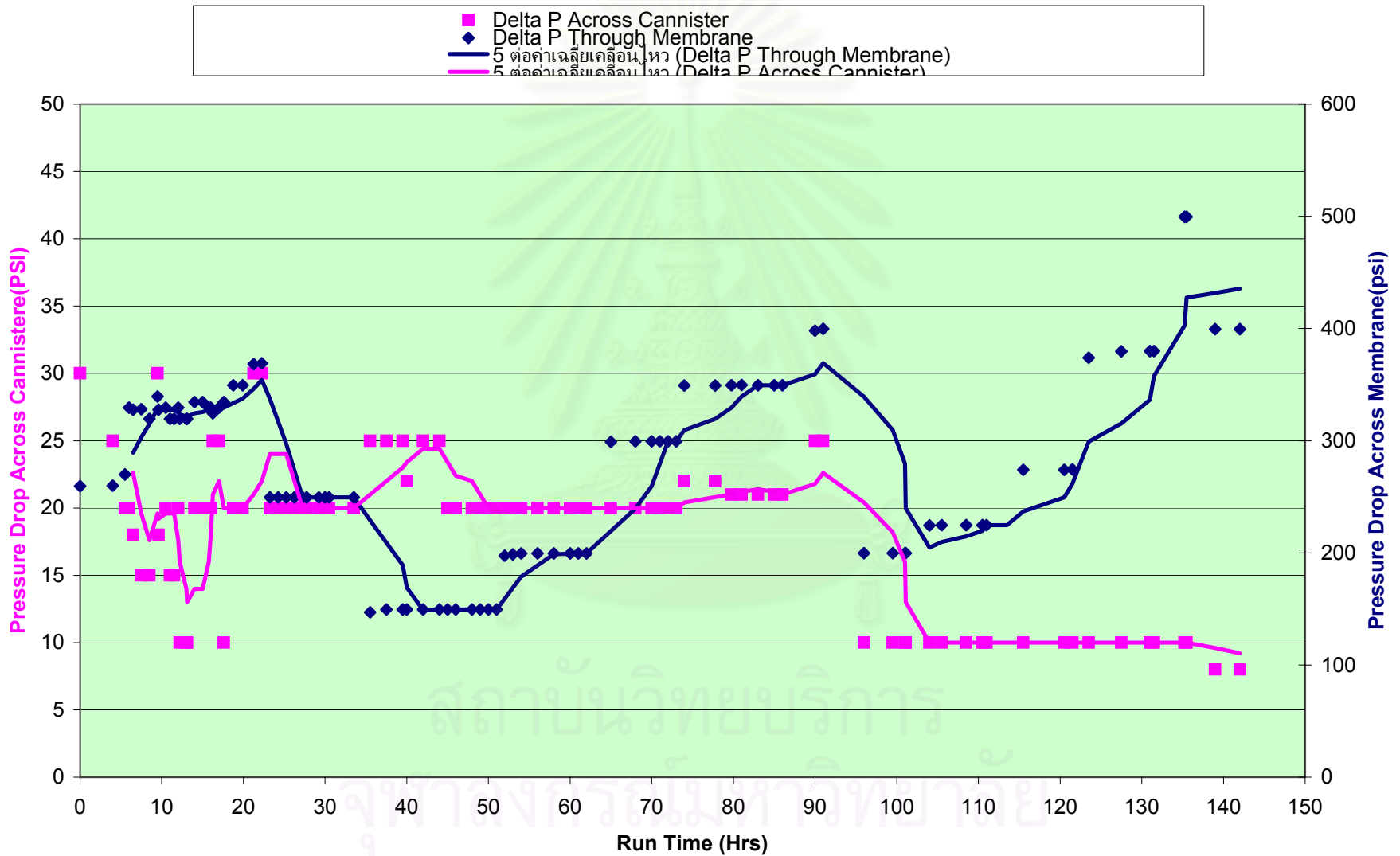
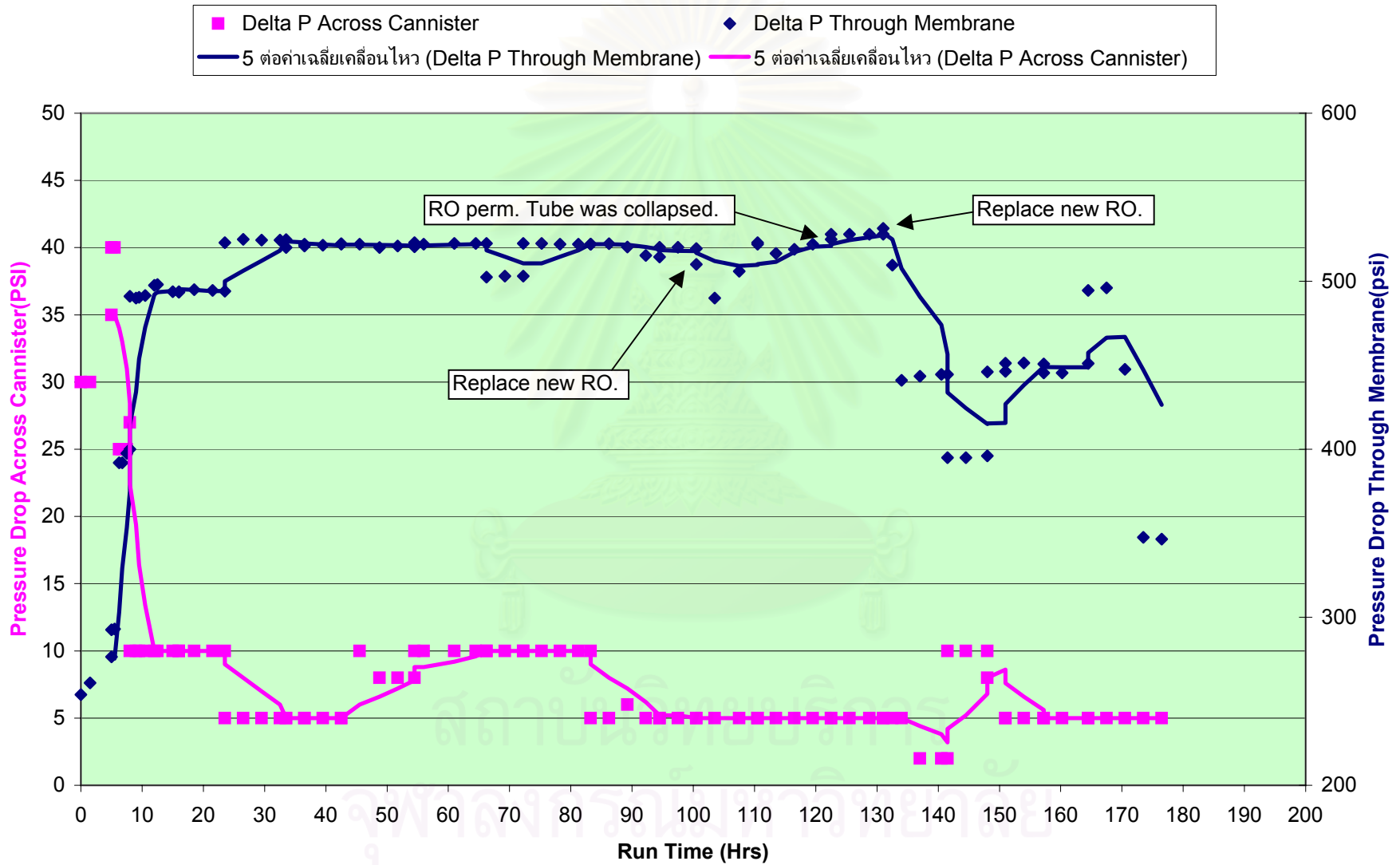


Fig. 5.7 Pressure Drop Across RO Membrane vs. Time (2nd Set)



From its overall performance, general results could be evaluated as follows:

1. UF membrane could consistently reject oil and performed reliable operations without membrane fouling during the 130 and 180 hrs run time.
2. A hydrocyclone and a filter cartridge were able to provide a good pretreatment process and performed better solid separation prior to feeding FSO water to the membrane system.
3. Mercury result in product water was indicated at approx. 0.7 ppb within Unocal self-imposed specification.
4. TPH result in product water was shown at approx. 64 ppm, which was slightly higher than Unocal self-imposed specification.
5. Arsenic was still found at approx. 2,500 ppb in product water. In addition, Arsenic adsorbent beads/Ion exchange resins were ineffective in reducing Arsenic content.
6. The single stage Reverse Osmosis system could not remove Arsenic from 16,800 ppb to achieve 250 ppb. in product water.
7. The 2-stage Reverse Osmosis system was implemented and was able to remove Arsenic down to 40 ppb and Mercury to less than 0.2 ppb.
8. UF membrane performance was limited by deposition of oil-coated solids between the membrane filter sheets. No oil was found in the membrane itself. Some swelling of the membrane due to aromatics in the water may have occurred, but if so, this happened within the first few minutes of exposure to the produced water. Cleaning the membrane first with dilute acid, then with detergent should return the UF membrane to a nearly new condition.
9. It was suspected that the high TPH which was observed in the UF permeate were largely due to dissolved hydrocarbons. The identity of these hydrocarbons is unknown, but ethylene glycol from a gas dehydration system or low MW organic acids would be likely candidates. Without mechanical damage (i.e., the collapsed tubes), the RO membrane should contain and reject these dissolved hydrocarbons and allow the system (even the single pass RO) to meet the 40 PPM TPH discharge limit.
10. The 1st set of polyamide RO membranes were thought to have lost some permeability due to swelling of the membrane from exposure to dissolved aromatics. The returned membrane's permeability was about 50% of the virgin membrane which is normal and indicates there is no evidence of long term damage to the membrane.
11. The 2nd set of cellulose acetate RO membranes were compressed by the high pressure used during the test and thus lost permeability irreversibly. The CA membranes

operate best with a 250 to 300 PSI pressure drop. Thus the CA membranes are not suitable for the 1st stage RO, but they would be quite suitable for the 2nd stage RO.

12. UF membrane was fouling by condensate.

5.2 Full Scale Study

The full scale plant was studied and designed for treating 250 bbl/day water discharge to sea which involved UF filtration and 2 stages of RO filtration. The membrane skid base will include the UF bag and cartridge prefilters, pumps, pressure vessels, and UF membrane elements. Also mounted on the same skid are the first and second pass RO units complete with prefilters, pumps, pressure vessels.

A process flow diagram for the full scale membrane plant is shown in Figure 5.8 Contaminated water will be pumped to a process feed tank through a 1" desanding hydrocyclone by using a submersible pump installed in a dedicated tank. The hydrocyclone will effectively reject solids and coalesce condensate droplets in the process feed tank. In order to prevent the build up of a condensate layer in the process feed tank, a continuous condensate skimming will overflow and return to the FSO tank.

From the process feed tank, water will be pumped through a 50-micron bag filter and then through 4 spiral wound UF membrane elements in series. UF permeate will go to the intermediate tank # 1 while concentrate (non-permeated feed water) will be returned to the process feed tank.

Water from to the intermediate tank # 1 will be pumped through the first pass 4 spiral wound RO membrane elements. The first pass RO concentrate will be recycled to the intermediate tank # 1 while the first pass RO permeate will flow to the intermediate tank # 2. In order to enhance arsenic removal efficiency, water from the intermediate tank # 2 will be pumped to the second pass 4 spiral wound RO membrane elements. The second pass RO concentrate will be returned back to the intermediate tank # 2 while the second pass RO permeate will go to the tank prior to discharging to sea.

Technical specifications show in Table 5.5:

Figure 5.8 : PFD for Full Scale Operation

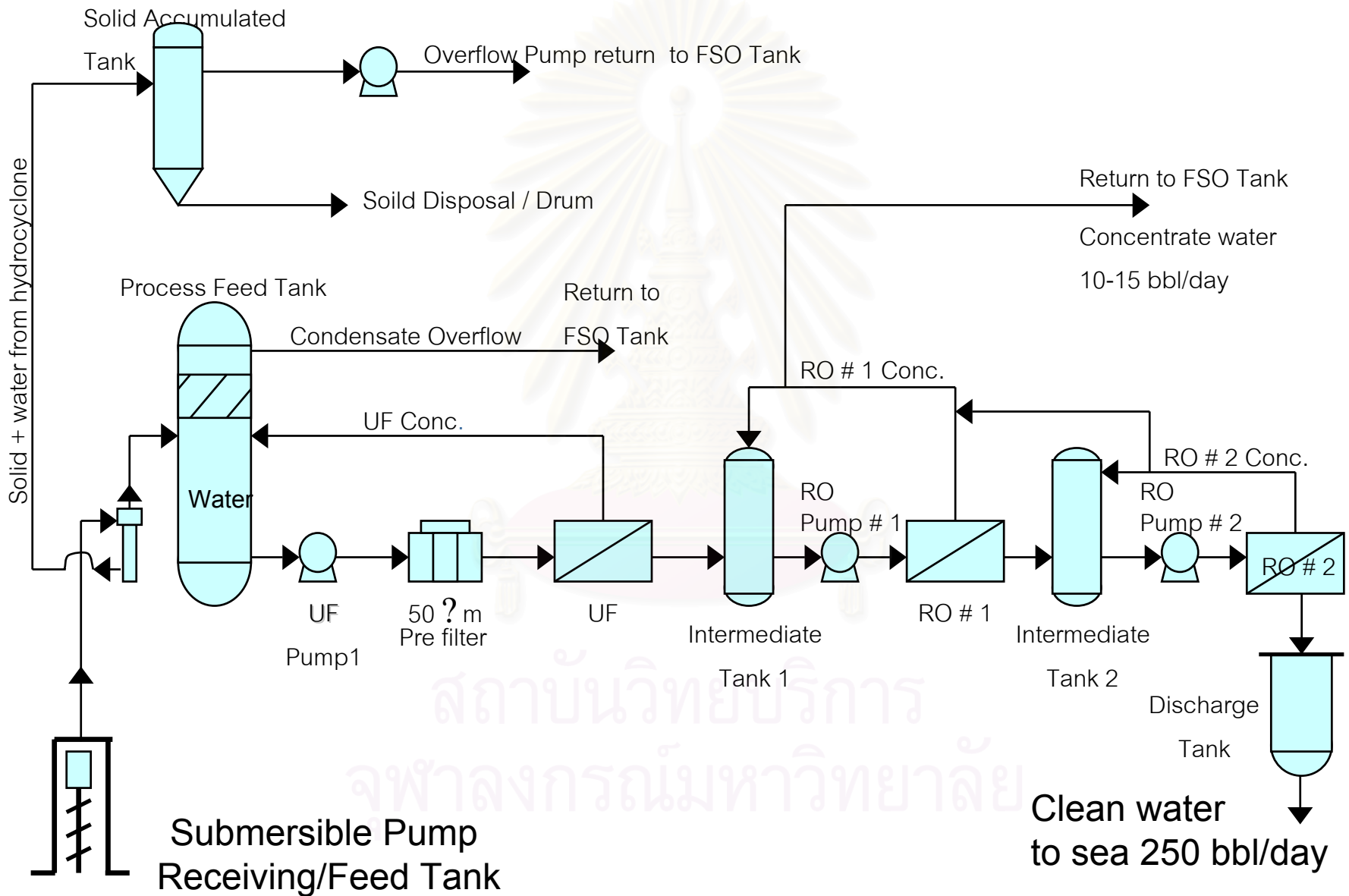


TABLE 5.5 Full Scale Plant Technical Specifications

DESIGN DATA

UF Permeate rate	9.0 gpm
UF Concentrate rate	0.9 gpm
First Pass RO Permeate rate	8.0 gpm
First Pass RO Concentrate rate	1.0 gpm
Second Pass RO Permeate rate	7.5 gpm
Second Pass RO Concentrate rate	0.5 gpm

COMPONENTS

UF Bag Filter Housings

Quantity	2
Bag Filter Rating	50 micron

UF/RO Cartridge Filter Housings

Quantity	4
Bag Filter Rating	2 each 75 micron, 2 each 25 micron

UF Pump

Quantity	1
Motor Horsepower & Type	7.5 Hp, 60 Hz, 460 VAC, 3500 rpm, Class I Group D, Class II Group F & G
Design Flow Rate	80 gpm
Design Boost Pressure	60 psig (discharge pressure – pump inlet pressure)

UF Membrane Elements

Model	8040C MX50 spiral wound elements
Manufacturer	Osmonics/Desal
Quantity	4
Membrane Type	Ultrafiltration

RO#1 Pump

Quantity	1
Motor Horsepower & Type	20 Hp, 60 Hz, 460 VAC, 1150 rpm, Class I Group D, Class II Group F & G
Design Flow Rate	30 gpm
Design Boost Pressure	600 psig (discharge pressure – pump inlet pressure)

TABLE 5.5 Full Scale Plant Technical Specification (continue)

COMPONENTS

RO#2 Pump	
Quantity	1
Motor Horsepower & Type	15 Hp, 60 Hz, 460 VAC, 3500 rpm, Class I Group D, Class II Group F & G
Design Flow Rate	30 gpm
Design Boost Pressure	400 psig (discharge pressure – pump inlet pressure)
RO 1 & 2 Membrane Elements	
Model	AE8040C & AG 8040C spiral wound elements
Manufacturer	Osmonics/Desal
Quantity	8
Membrane Type	Reverse Osmosis

5.3 Economic Study

The preliminary economic study was done, based on the expectation of 6 months membrane lifetime. The replacement cost of the membrane is approximately \$1,000 per element. Thus, if 250 bbl/day were processed for 180 days, then the maximum operating cost for membrane replacement would be \$0.18 per barrel of water processed for the UF membranes and the first stage of the RO membranes. Adding the second stage of the RO membranes would increase the operating cost by an estimated \$0.09 per barrel of water processed. If the membranes last longer than 6 months, operating costs will be lower.

As a cost target, the system should be priced to save the company enough money compared to ship-to-ship transfer and deep-well disposal that the capital cost is "recovered" in savings within one year, after paying for operating costs.

Based on the following assumptions:

- Without a membrane plant, ship-to-ship offloading costs \$70,000 per cargo
- Investment cost for a full scale plant is \$273,000
- Membrane replacement cost is \$24,000 per year
- Opex Cost \$0.27 per barrel
- With a membrane plant, ship-to-ship off-loading is eliminated

Table 5.6 shows the economic study based on one cargo lifting per year:

Opex Saving = \$70,000 - \$24,000
= \$46,000 per year

Investment : \$273,000
NPV Gross : - 64,136 \$ @12%
DPI : - 0.29 %
ROI : - 2.6 %

Table 5.7 shows the economic study based on two cargoes lifting per year:

Opex Saving = \$140,000 - \$24,000
= \$116,000 \$ per year

Investment : \$273,000
NPV Gross : 38,046 \$ @12%
DPI : 0.17 %
ROI : 16.4 %

Based upon this discussion, the operating cost savings for the membrane system compared to water transfer one cargo lifting and two cargoes lifting per year would be \$46,000 and \$116,000 respectively. From Table 5.6 – 5.7, if the cargo lifting were performed once a year, the investment would not be economically viable. However, there are additional benefits to be realized as follows:

- (A) The ability to clean water on the FSO opens up the opportunity to catch solids and water in the condensate as it arrives on the FSO. With topside capture of these contaminants, shipboard operations are simplified and routine COW washing becomes feasible.
- (B) This also opens up the possibility for avoiding costs on the Central Processing Platforms for sludge processing equipment. This could all be handled on the FSO with less equipment, less cost, and a reduced volume of solids heading for disposal.
- (C) Condensate quality is protected from excessive water.
- (D) The cost for installation of any additional equipment on the Central Processing Platforms to reduce water in the condensate is avoided.

Table 5.6 : Economic Case : One Cargo Lifting per Year

Economic Case: **Case Name : One Cargo Lifting Per Year**

Input in Blue Shaded Area

Mid Year Discount (Y/N) **Y** WI % -----> **71.25%**

Year	2000	2001	2002	2003	2004	2005
Investment (\$)	273,000	-	-	-	-	-
Incremental OPEX (\$)	-	(46,000)	(46,000)	(46,000)	(46,000)	(46,000)
-Depreciation	-	(54,600)	(54,600)	(54,600)	(54,600)	(54,600)
Revenue for Gas/Condensate sale (\$)	-	-	-	-	-	-
- Royalty (12.5% of revenue)	-	-	-	-	-	-
Taxable Income	-	(8,600)	(8,600)	(8,600)	(8,600)	(8,600)
Corporate Tax (35%)	-	3,010	3,010	3,010	3,010	3,010
US. State Tax (2%)	-	172	172	172	172	172
Taxable Income for Remit. Tax	-	(5,590)	(5,590)	(5,590)	(5,590)	(5,590)
Remit. Tax (23.08%)	-	1,290.17	1,290.17	1,290.17	1,290.17	1,290.17
Remit. Tax Credit (50% of Royalty Paid)	-	-	-	-	-	-
After Tax Income	-	(4,128)	(4,128)	(4,128)	(4,128)	(4,128)
+Depreciation	-	54,600	54,600	54,600	54,600	54,600
Gross Cash flow (\$)	(273,000)	50,472	50,472	50,472	50,472	50,472

As of 2000

NPV at **12%**
DPI
ROI

Gross

(\$64,136)
-0.29
-2.6%

Net

(\$45,697)
-0.29
-2.6%

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Table 5.7 : Economic Case : Two Cargo Lifting per Year

Economic Case: **Case Name : Two Cargo Lifting Per Year**

Input in Blue Shaded Area

Mid Year Discount (Y/N) **Y** WI % -----> **71.25%**

Year	2000	2001	2002	2003	2004	2005
Investment (\$)	273,000	-	-	-	-	-
Incremental OPEX (\$)	-	(116,000)	(116,000)	(116,000)	(116,000)	(116,000)
-Depreciation	-	(54,600)	(54,600)	(54,600)	(54,600)	(54,600)
Revenue for Gas/Condensate sale (\$)	-	-	-	-	-	-
- Royalty (12.5% of revenue)	-	-	-	-	-	-
Taxable Income	-	61,400	61,400	61,400	61,400	61,400
Corporate Tax (35%)	-	(21,490)	(21,490)	(21,490)	(21,490)	(21,490)
US. State Tax (2%)	-	(1,228)	(1,228)	(1,228)	(1,228)	(1,228)
Taxable Income for Remit. Tax	-	39,910	39,910	39,910	39,910	39,910
Remit. Tax (23.08%)	-	(9,211.23)	(9,211.23)	(9,211.23)	(9,211.23)	(9,211.23)
Remit. Tax Credit (50% of Royalty Paid)	-	-	-	-	-	-
After Tax Income	-	29,471	29,471	29,471	29,471	29,471
+Depreciation	-	54,600	54,600	54,600	54,600	54,600
Gross Cash flow (\$)	(273,000)	84,071	84,071	84,071	84,071	84,071

As of 2000

NPV at **12%**
DPI
ROI

Gross

\$38,046
0.17
16.4%

Net

\$27,108
0.17
16.4%

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CHAPTER VI

CONCLUSION

The pilot test of a tandem UF and RO membrane system for cleaning highly contaminated produced water successfully demonstrated the capability of the subject technology. Controlling the solids content of feed to the membrane was the most important parameter for maintaining system performance. The UF membrane was resistant to fouling by dispersed hydrocarbons and successfully protected the RO membrane from exposure to liquid organics.

The presence of substantial levels of dissolved organic compounds limited the ability of the membranes to meet the Unocal Thailand discharge TPH standard of < 40 PPM. Under some running conditions, the UF membrane rejected in excess of 90% of the hydrocarbons in the process feed water. The tandem membranes together typically rejected 95% to 99% of the hydrocarbons in the feed water.

Mercury removal from produced water exceeded 99%. This result is in line with expectations since earlier work demonstrated that the mercury was either colloidal in nature or associated with dispersed hydrocarbons and solids.

Arsenic rejection was unexpectedly high across the UF membrane, exceeding 80% at times. Possibly the arsenic rejection resulted from the precipitation of ferric arsenite on iron-based solids trapped in the spiral wound UF membrane. Together, the RO and UF membranes generally rejected over 95% of the arsenic in the process feed water. However, residual arsenic levels in the product water still exceeded Unocal Thailand's self-imposed discharge standard of 250 PPB.

Although the pilot testing of the UF/RO membrane water treatment was considered technically successful, the final permeate did not meet Unocal Thailand's standard for arsenic in discharge water. Accordingly, the decision was made to proceed with disposal of ship-retained water by deep-well injection.

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CHAPTER VII

RECOMMENDATIONS

In case incoming water to the FSO continues at about 200 bbl/day, a huge amount of free water will be stored on-board the FSO within a year. As a result, the existing water removal by ship-to-ship offloading, then disposal elsewhere, is required once a year or two, even though it is a high cost and complicated process.

On the other hand, water treatment by the membrane technology is proven, and it is feasible to install on-board the FSO with a full scale operation. The greatest advantage is that the system provides a friendly user operation and cost reduction benefit. In addition, the need of future FSO water lifting may be eliminated or extended.

However the following factors are recommended for consideration:

1. Pretreatment processing is very important in order to remove solid particles down to 10 micron prior to feeding water to a membrane system. A good pretreatment process, e.g. a hydrocyclone and a filter cartridge, can prevent membrane fouling by solid entrapment, resulting in membrane lifetime extension.
2. Due to the fact that membrane is fouled by condensate, a separation tank is required in order to prevent condensate breaking into the system otherwise membranes will be severely deteriorated.
3. The 2-stage Reverse Osmosis process is required in order to achieve Unocal specified discharge quality listed below:

As	less than	250 ppb
Hg	less than	10 ppb
TPH	less than	40 ppm
4. Based on 250 bbl/day discharge capacity for a full scale membrane plant, the estimated cost breakdown is as follows:

Hydraulic Power Pack & Submersible Pump	\$70,000
Hydrocyclone	\$3,000
UF - 2 stages RO	\$150,000
Installation	\$50,000
Total	\$273,000

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APPENDICES

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จุฬาลงกรณ์มหาวิทยาลัย



Appendix A : MATERIALS

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย

Appendix A : MATERIALS

Qty	Tag	Part No.	Description	Vendor
1	T-2	Chemtainer TC2236CA	Tank, 55 Gallon capacity, PE cylindrical cone bottom 22" dia x 36" HT	Chemtainer
1	T-2A	Chemtainer TC2235CK	Tank stand, for above tank	Chemtainer
1	BF-4A	Mc Master-carr 5168K235	Bag filter housing, 1 ¹ / ₂ " FNPT connection, SS construction, 1/2" FNPT drain connection 0-50 GPM, w/quick clamp opening, 12" long basket	Mc Master
1	BF-4B	Mc Master-carr 5162K22	Polyester felt filter bag, 50 micron, trade size 4	Mc Master
1	P-10	Tonkaflow AS1645D	Pump, 316SS body, with noryl impeller 10 GPM @ 525 PSI max., 1 ¹ / ₄ " victaulic suction and discharge, with 7 ¹ / ₂ HP 230/460 VAC 3 phase, SF=1.0, 213TC frame 3450 RPM, FLA=18.6/9.3, explosion proof	By Others
2	ES-5, ES-6	SEi 10910-8	4" pressure vessel, single element, 1" victaulic feed/concentrate connection, end cap dwg# 11093-3, 316 SS construction	SEi
1	ES-11	ASI 4UB	4" element membrane shell, FRP construction, single element, 3/4" FNPT feed/concentrate, 1/2" FNPT permeate connection, 600 PSI rated	ASI
3	E-5, E-6, E-11	Osmonics	4" element membrane	By Others
1	P-3	Widen P2-P-P-P-P-WF-WF-PWF-40 0	1" polypropylene air operated diaphragm pump, with Wilflex diaphragm, ball and o-rings, 1/4" air inlet, 1/2" air outlet with exhaust muffler. 1" flange connection	Phoenix
1	P-7	Wilden P025-P-P-P-P-WF-TF-PWF	1/4" polypropylene air operated diaphragm pump, with Wilflex diaphragm, and o-rings, teflon ball 1/8" air inlet, 1/4" air outlet with exhaust muffler. 1/4" FNPT connection	Phoenix

Appendix A : MATERIALS

Qty	Tag	Part No.	Description	Vendor
1	T-8	Nalgene 14100-0010	Chemical tank, 12 x 12 x 12 HDPE w/cover, 7 gallon capacity	Harrington
1	S-9	Amiad 115-0059-030	1 ¹ / ₂ " Strainer, glass fiber polyamid body, 1 ¹ / ₂ " MPT connection, w/300 micron weave ss screen, Y-pattern	Stock
2	TI-107 TAKE-OUT	Ashcroft 30-EI-60-R-040, 30/1	Temperature indicator, bimetal, 3" dial, 1 ¹ / ₂ " center rear connection, 1 ¹ / ₄ " dia.x 4" long stem, range 30-130F	Scaler
2	TW-107 TAKE-OUT	Ashcroft 75-W-025-ST-260-S	316SS thermowell, 1 ¹ / ₂ " instument connection, 3 ³ / ₄ " process connection U dimension = 2 ¹ / ₂ ", straight shank	Scaler
1	PI-100	Ashcroft 25-1009-SWL-02B XUC 0-100 PSI	Pressure indicator, 2 ¹ / ₂ " dial, style 1009, 316SS bourdon tube and socket, glycerine filled, 1 ¹ / ₄ " MPT back connection, range 0-100 psi w/panel u-clamp	Scaler
1	PI-103	Ashcroft 25-1009-SWL-02B XUC 0-600 PSI	Pressure indicator, 2 ¹ / ₂ " dial, style 1009, 316SS bourdon tube and socket, glycerine filled, 1 ¹ / ₄ " MPT back connection, range 0-600 psi w/panel u-clamp	Scaler
1	PI-105	Ashcroft 25-1009-SWL-02? 0-30 PSI	Pressure indicator, 2 ¹ / ₂ " dial, style 1009, 316SS bourdon tube and socket, glycerine filled, 1 ¹ / ₄ " MPT???? connection, range 0-30 psi	Scaler
1	FI-102	Blue-White F-45500LHN-8	Flow meter, range .5-5 gpm, 1 ¹ / ₂ " MPT connection Polysulfone body and adapters, 316SS float and guide rod, Viton o-ring seals	Harrington
1	FI-106	Blue-White F-45376LHN-8	Flow meter, range .2-2 gpm, 1 ¹ / ₂ " MPT connection Polysulfone body and adapters, 316SS float and guide rod, Viton o-ring seals	Harrington

Appendix A : MATERIALS

Qty	Tag	Part No.	Description	Vendor
2	FI-104, FI-108	Blue-White F-45750LHN-12	Flow meter, range .1-10 gpm, 3/4" MPT connection Polysulfone body and adapters, 316SS float and guide rod, Viton o-ring seals	Harrington
1	FI-101	Mc Master	Flow meter with rotary scale, brass body, OAL=4.9" range 6-30 GPM 1" FNPT connection	Mc Master 4948K18
1	1/2" V307	Mc Master-Carr	1/2" check valve, kynar body, spring loaded, 316SS spring, Viton O-ring	Mc Master 46505K35
1	1/2" V305	Asahi 1265005	1/2" Globe valve, PP body disc, FNPT connection	Harrington
1	1/2" V302	Asahi 1265010	1" Globe valve, PP body disc, FNPT connection	Harrington
3	1/2" V320, 1/2" V321, 1/2" V322	GF 163.560.002	1/2" True union ball valve, CPVC body, teflon seat, EPDM seals	Pen Valve
1	1V310	GF 163.560.004	1" True union ball valve, CPVC body, teflon seat, EPDM seals	Pen Valve
4	1 1/2" V301, 1 1/2" V303, 1 1/2" V304, 1 1/2" V309	GF 163.560.006	1 1/2" True union ball valve, CPVC body, teflon seat, EPDM seals	Pen Valve
2	2V300, 1 1/2" V303	GF 163.560.006	1 1/2" True union ball valve, CPVC body, teflon seat, EPDM seals	Pen Valve
2	1/4" V311, 1/4" V318	SMC 5741590	1/4" PP filled MPT x MPT valve, Viton seal	SMC
1	1/2" V319	GF 163.360.562	1/2" Ball check valve, CPVC construction, EPDM seal, socket connection	Pen Valve
2	1/2" V314, 1/2" V323	Mc Master-Carr	1/2" needle valve, 316 SS construction, 1/2" FNPT connection, Cv=1.35	Mc Master 4644K34
1	1V313	Mc Master-Carr	1" needed valve, 316 SS construction, 1" FNPT connection, Cv=3.6	Mc Master 4644K36

Appendix A : MATERIALS

Qty	Tag	Part No.	Description	Vendor
1	1V312	Mc Master	1" check valve, SS construction, 1" FNPT	Mc Master
1	1/4" V317	Whitey SS-43XS4	1/4" 3-way ball valve, 316 SS construction, 1/4" swage-lok connection rated 2500 PSI @ 100 F.	SD Valve
1	1/8" V306	Whitey SS-43ZF2	1/8" 5-way ball valve, 316 SS construction, 1/8" FNPT connection, Rated 2500 PSI @ 100 F.	SD Valve
2	AR-12, AR-13	Norgren B07-234-A1KA	Main air filter, regulator w/o lubricator, 20 CFM max. pressure regulator, 1/4" self relieving, 2-125 psi, with air filter automatic drain gauge 0-160 psi, 2" dial 1/4" back connection	Norgren

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Appendix B : DRAWING PACKAGE

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จุฬาลงกรณ์มหาวิทยาลัย

Y-1
FEED TANK
SUPPLIED BY CUSTOMER
XX GAL

R-3
AIR PUMP
20 GAL @ 50P

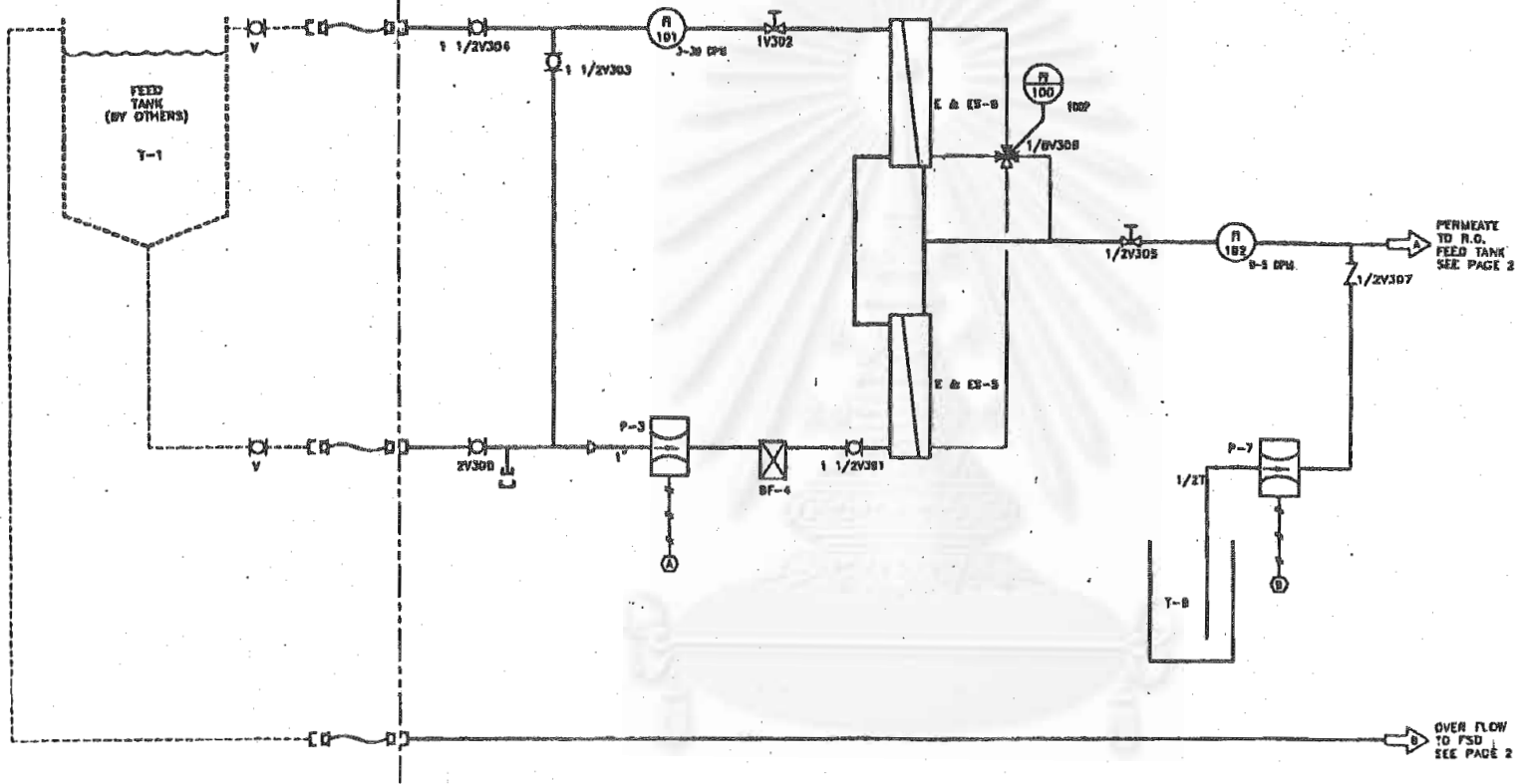
R-4
BAG FILTER
50 MICRON

ES-5 & 6
MEMBRANE HOUSING
4-40

Y-6
CHEMICAL TANK
XX GAL

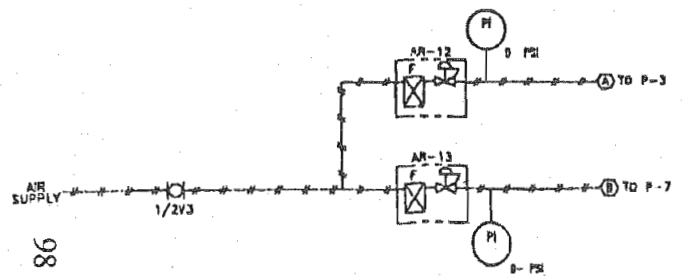
P-7
CHEMICAL PUMP
XX GAL

UNDCAL DSMONICS



PERMEATE
TO R.O.
FEED TANK
SEE PAGE 2

OVER FLOW
TO FSD
SEE PAGE 2

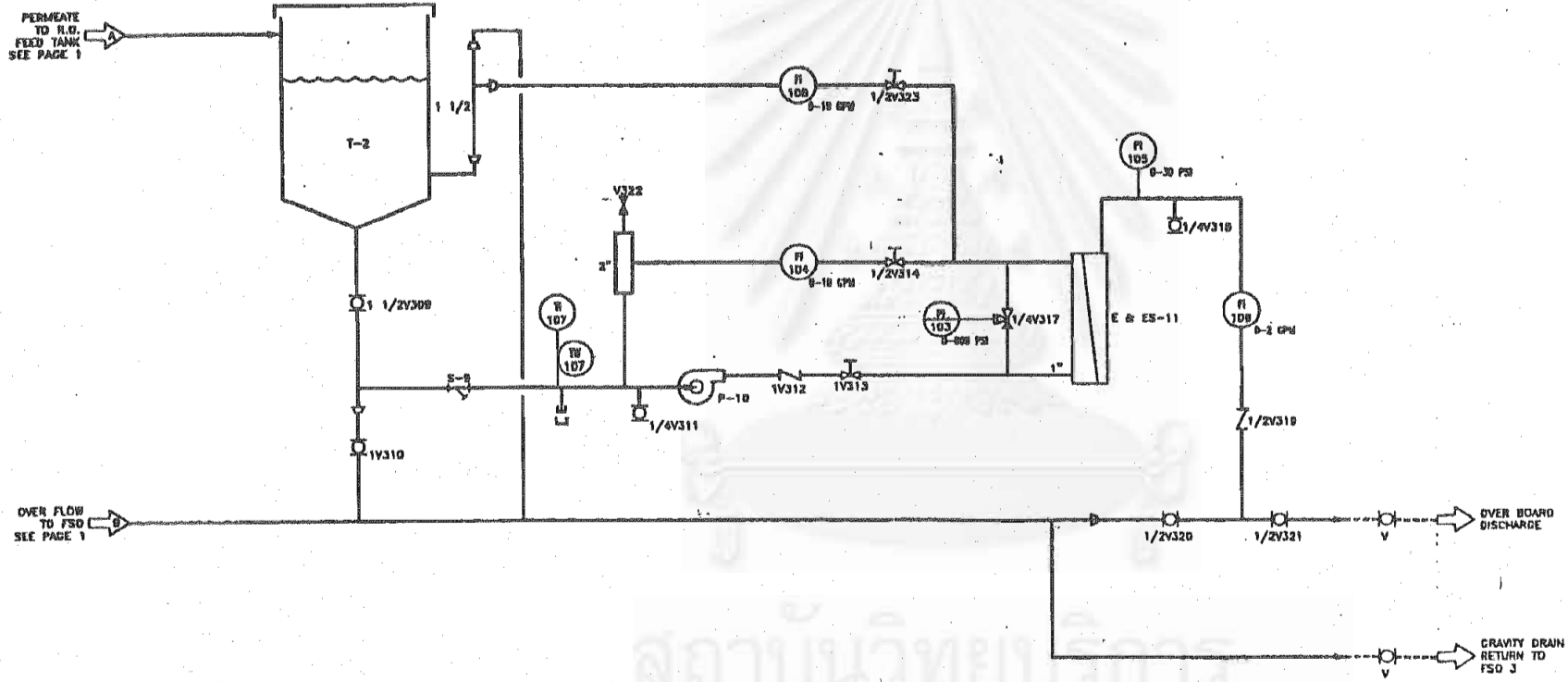


T-2
FEED TANK
50 GAL.

AIR SEPARATOR

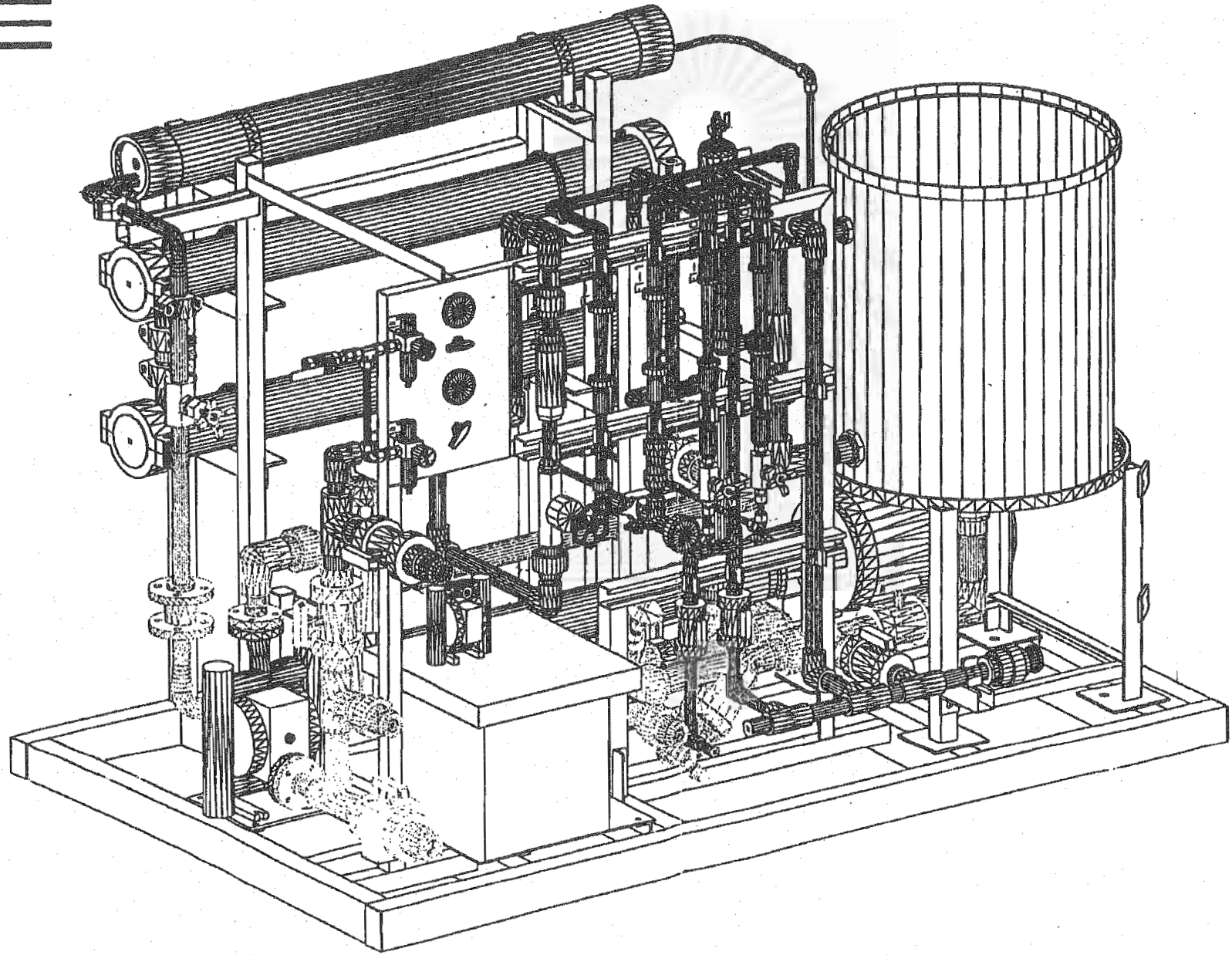
P-10
FEED PUMP
10 GAL. @ 525 PSI

ES-11
MEMBRANE HOUSING
6-40

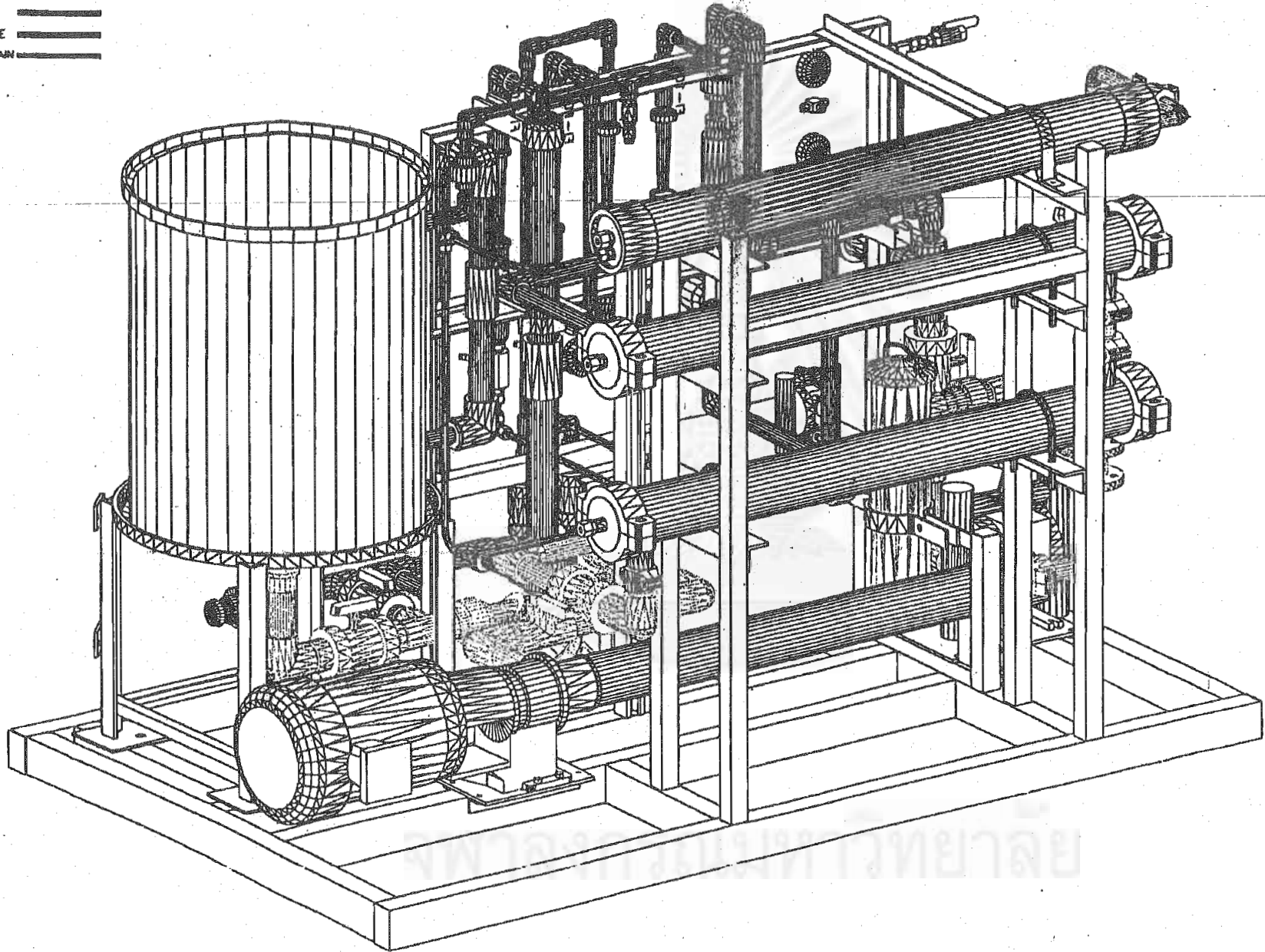


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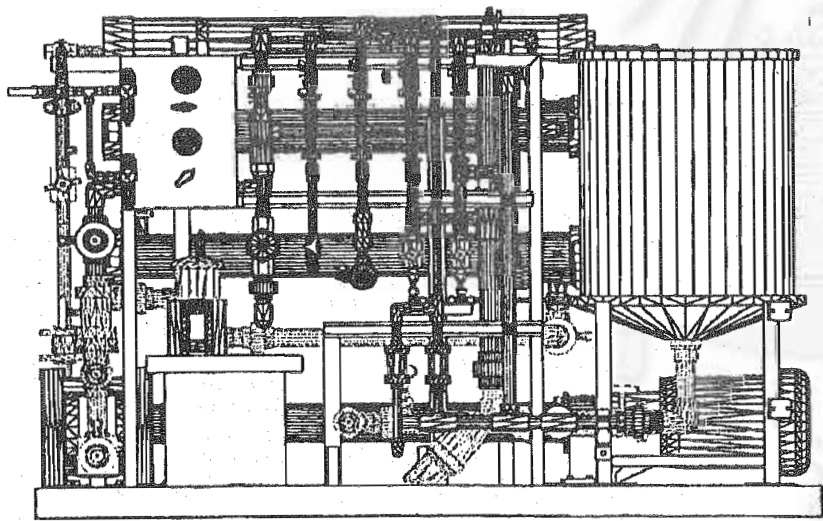
FEED CPVC
FEED SS
PERMATE
CONCENTRATE
OVERFLOW/DRAW



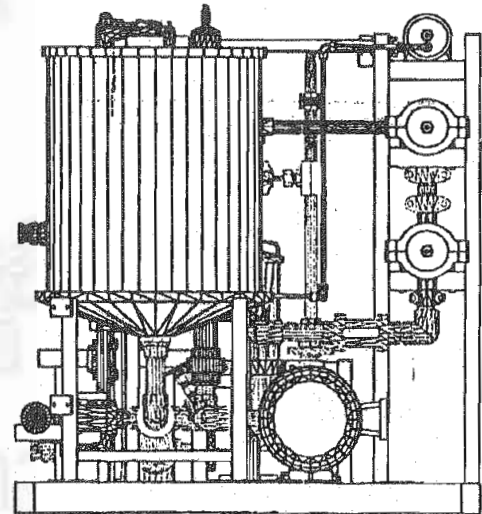
FEED CPVC
FEED SS
PERMEATE
CONCENTRATE
OVERFLOW/DRAIN



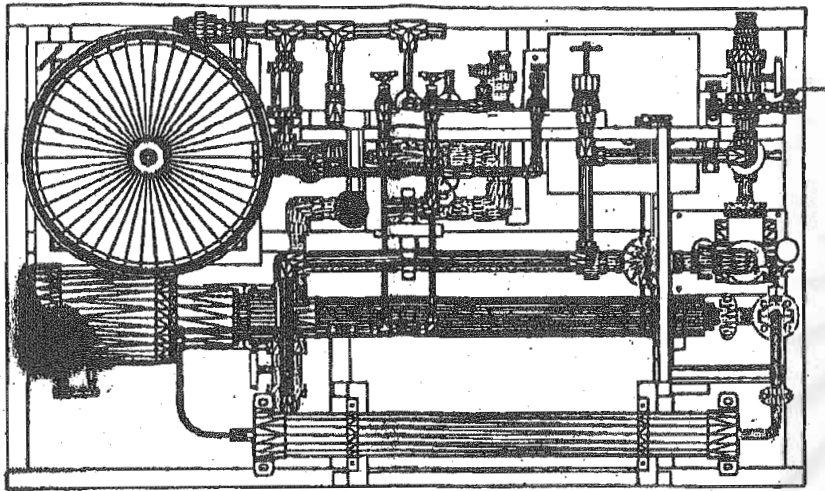
FEED CPVC ██████████
 FEED SS ██████████
 PERMEATE ██████████
 CONCENTRATE ██████████
 OVERFLOW/DRAIN ██████████



FRONT ELEVATION

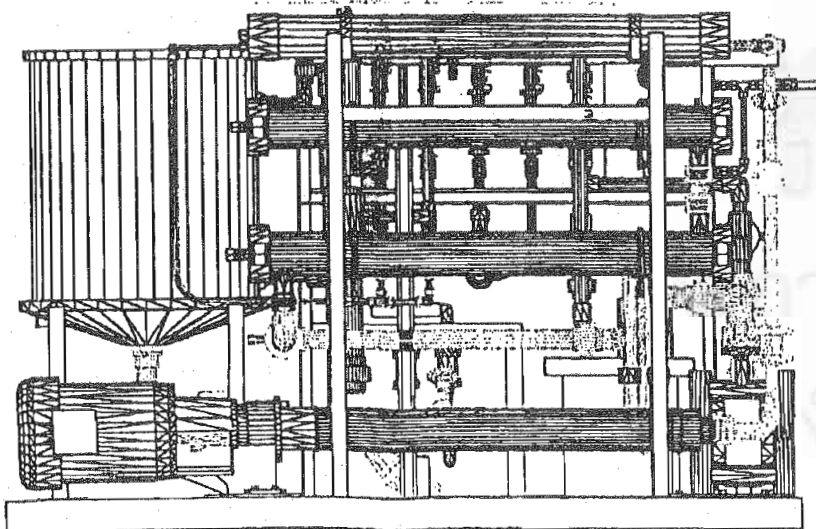


RIGHT ELEVATION



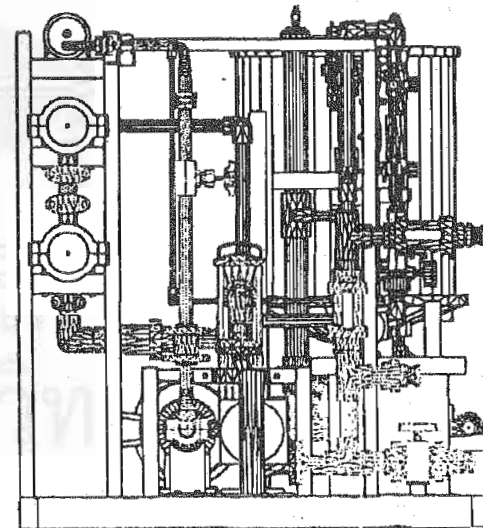
PLAN VIEW

FEED CPVC ██████████
 FEED SS. ██████████
 PERMEATE ██████████
 CONCENTRATE ██████████
 OVERFLOW/DRAIN ██████████



REAR ELEVATION

LEFT ELEVATION





Appendix C : OTC 8712, Upgrading Production Facility on the Funan Platform to Remove Hydrocarbons and Heavy Metals from Produced Water

สถาบันวิทยบริการ
จุฬาลงกรณ์มหาวิทยาลัย



OTC 8712

Upgrading Production Facilities on the Funan Platform to Remove Hydrocarbons and Heavy Metals from Produced Water

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Abstract

Unocal Thailand has been producing natural gas in the Gulf of Thailand since 1981. In recent years, with increasing natural gas production, the volume of produced water has also been increasing. Contaminants in the water include hydrocarbons and heavy metals. The original platform design did not contemplate the need to handle and remediate high volumes of produced water. Characterization of the produced water determined that hydrocarbons were present as stabilized emulsions, mercury was present in elemental form, and arsenic was present in water soluble form. The objective is to reduce contaminants in the produced water to the following levels: Hydrocarbons to < 40 PPB, Mercury to <10 PPB, and Arsenic to < 250 PPB.

In 1995, Unocal Thailand initiated a program to upgrade water handling facilities on its central processing platforms. On Funan, this involved upgrades to the high pressure inlet separators, improvements to the original skim tank, and the installation of hydrocyclones as well as induced gas flotation equipment. The latter were required along with additional facilities to treat the water for heavy metals removal. The vessel upgrades are described in this paper along with a review of the complete water cleaning train. Operational data illustrating the performance of the Unocal Thailand Water Cleaning Process are also presented.

Introduction

Unocal Thailand, a subsidiary of Unocal Corporation, produces natural gas and condensate from nine fields in the Gulf of Thailand. Since 1981, Unocal has drilled over 1000 wells. Production from 60 remote wellhead platforms and is pipelined to four production and four central processing platforms. In 1997 Unocal Thailand natural gas production averaged 970 MMSCFD

while accompanying liquid hydrocarbon (condensate) production averaged 34,600 bbls per day. Figure 1 illustrates how fluid flow from the remote platforms to the production and central processing platforms. Also in 1997, Unocal Thailand platform produced an average of 35,850 bbls of water per day. However, with the introduction of new gas production technology and new development strategies, the volume of produced water is expected to increase over the next 2 years to as much as 75,000 bbls of water per day.

To ensure that all future Thailand national environmental discharge regulations are observed, Unocal Thailand has, over the past three years, developed, tested, and installed technology for removing contaminants from co-produced water. The goal of the Unocal water-cleaning project was to reduce the levels of these contaminants in overboard discharge water to the following (1):

Mercury	≤	10 PPB
Arsenic	≤	250 PPB
Hydrocarbons	≤	40 PPM

Where feasible, Unocal Thailand is pursuing a "zero discharge" philosophy which entails re-injecting co-produced water back into the formations from which it originated. Unfortunately, the re-injection of all produced water is not feasible given the large geographic area over which gas production occurs. Thus the development of surface cleaning technology was also necessary.

This upgrade project increased the produced water handling capacity on Funan from its original design limit of 4800 BWPD to the new target level of 25,000 BWPD. Also, all installed equipment had to be compatible with the chemistry required for heavy metals removal.

Chemical Basis for Cleaning Funan Produced Water

The first step in the development of a technically and economically viable water cleaning process is to have a strong fundamental understanding of the physical chemical characteristics of both the produced water and the contained contaminants. Only then can optimal process chemistry and equipment be selected for contaminant removal.

understanding of the physical chemistry of the produced water and the contaminants.

Once fully commissioned in early 1998, Unocal Thailand expects to be in full compliance with all proposed discharge water quality requirements for the Gulf of Thailand.

Nomenclature

PPB	= parts per billion, micrograms/liter
PPM	= parts per million, milligrams/liter
H	= height, ft
L	= length, ft
Q	= flow rate, ft ³ /second
P	= pressure, psi
ρ	= density

Acknowledgements

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Table 1. Summary of Data on the Emulsion Forming Tendency of Condensate in Water in the Presence of Corrosion Inhibitors

Condensate-water mixed in ratio 1:4. Inhibitor dosage 150 ppm for water soluble and 200 ppm for oil soluble.

Platong Alpha 13 ("A" Zone)

Nephelometer used to measure turbidity

Water Soluble Products

	<u>Water Turbidity</u>	<u>Remarks</u>
Blank	5	
WS-A	69	Clear cond.
WS-B	20	Slight cond. emulsion
WS-C	41	Clear cond.
WS-D	76	Clear cond.
WS-E	80	Clear cond.

Oil Soluble Products

	<u>Water Turbidity</u>	<u>Remarks</u>
OS-A	77	Clear cond.
OS-B	14	Clear cond.
OS-C	95	15% Rag layer
OS-D	32	40% Rag layer
OS-E	38	40% Rag layer

Table 2. Diagnostic Tests Indicate that Organic Acids Along with Corrosion Inhibitor are Primarily Responsible for the Stability of the Condensate in Water Emulsions

<u>Test Procedure</u>	<u>Affect Tested</u>	<u>Result</u>
Solvent Extraction	Wax Dissolution Asphaltene Dissolution	Modest/none
Cationic/Anionic Flocculents	Charge or Solids Stabilization	None
pH or Ionic Strength Change	Charge Stabilization	None
FeCl ₃ addition	Coordinate Organic Acids Coordinate Corrosion Inhibitors	Very Effective

Table 3. Filtration was Effective at Removing Mercury From Produced Water

<u>Sample</u>	<u>Solids Removed</u> <u>mg / liter</u>	<u>Hg in Water</u> <u>Conc., ppb</u>
Platong Skim Tank Water	--	155
3.0 μ filtrate	30	12
0.8 μ filtrate	104	2
0.45 μ filtrate	136	<1

Table 4. Arsenic Cannot be Removed by Simple Filtration

<u>Funan Water</u>	<u>Arsenic</u>	<u>Mercury</u>	<u>TPH</u>
As taken	382 PPB	11.2 PPB	545 PPM
15 min. of settling	305		191
5 μ filtrate	255	3.7	
1.2 μ filtrate	232	3.7	
0.45 μ filtrate	251	1.9	9

Table 5. Performance Data are summarized for the Funan Inlet Separators in the as-built and upgraded configurations

	<u>Liquid Flow Rates</u>		<u>Residence Time & Liquid Space Velocity</u>	<u>Cond. Pad</u>
	<u>Cond. BOPD</u>	<u>Water BWPD</u>	<u>Water (min) / (ft/min)</u>	<u>IN.</u>
As-Built	4,800	4,800	2.7 / 6.9	18.6
Up-Graded				
Case 1	10,000	10,000	5.4 / 3.4	18.6
Case 2	5,000	10,000	5.7 / 3.3	17.4
Case 3	5,000	20,000	3.2 / 5.8	15.0
Case 4	10,000	20,000	3.0 / 6.0	16.3

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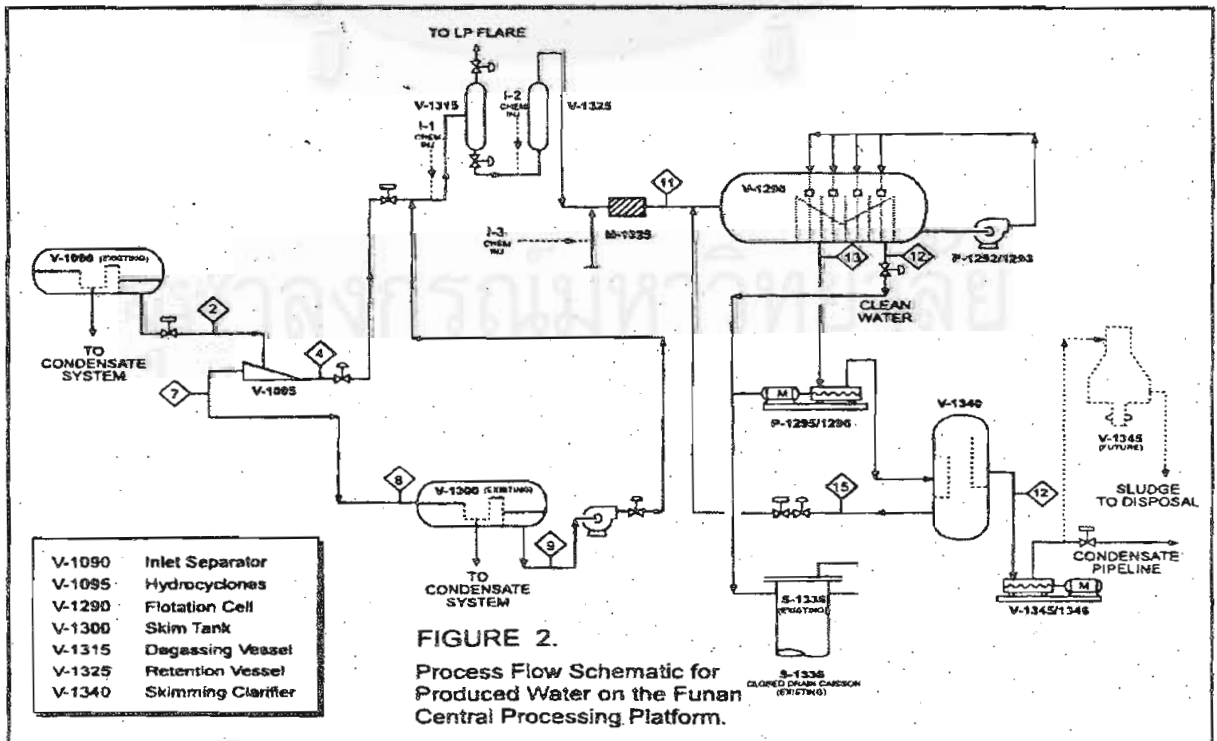
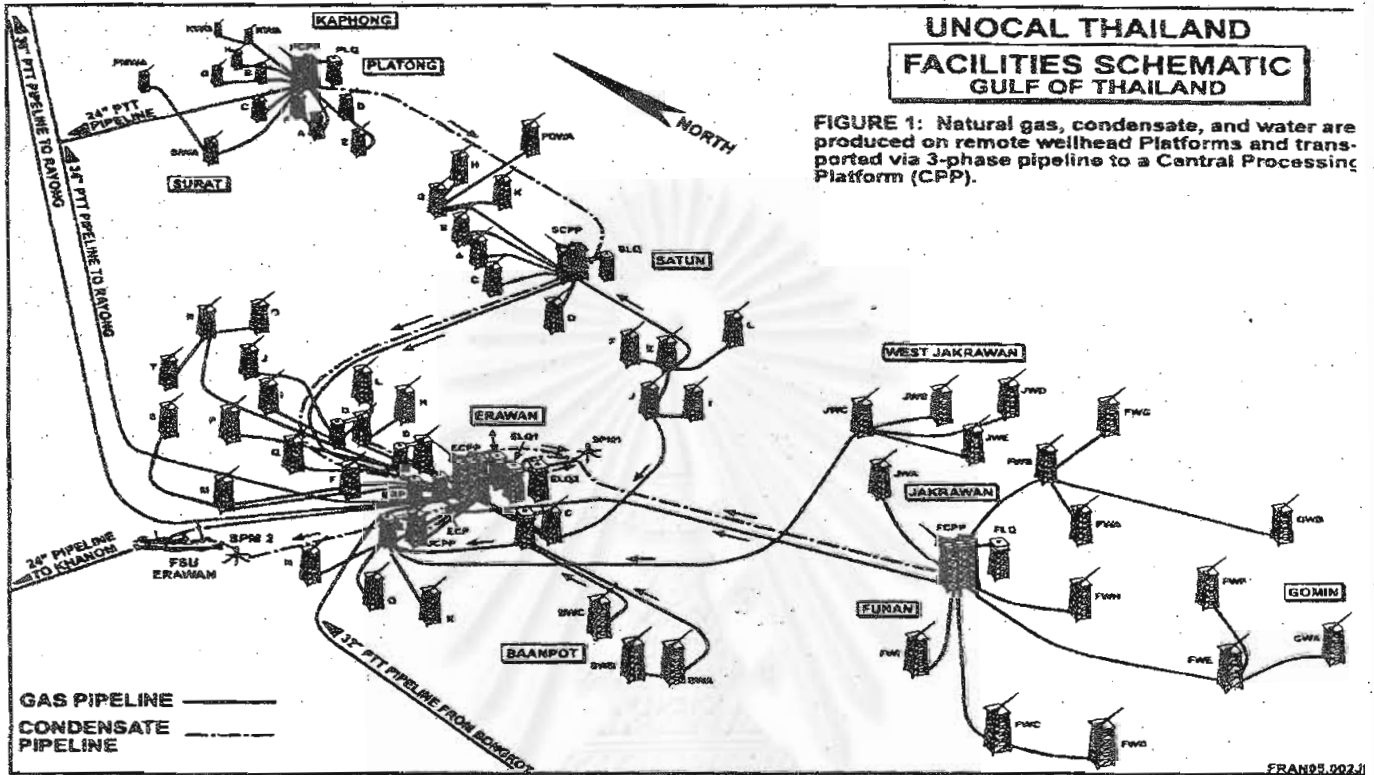


FIGURE 3. Liquid Head Ht. vs Flow Rate for the Funan Inlet Separator with Original and Modified Weir Locations

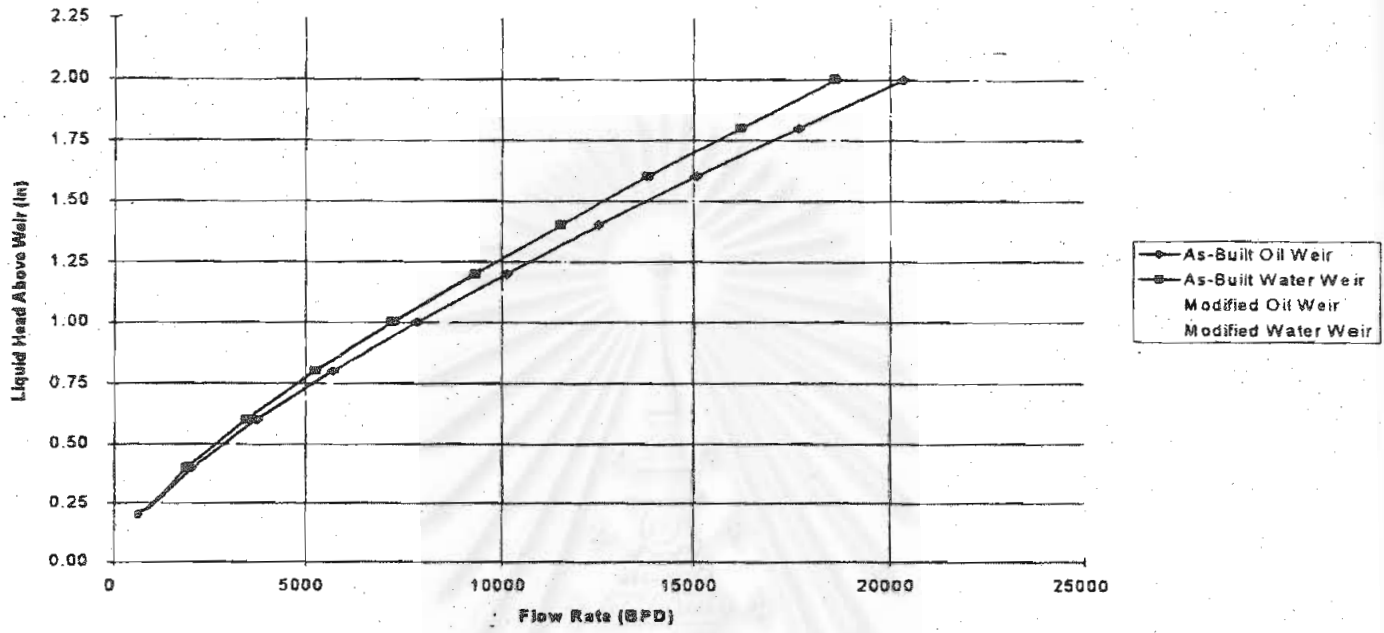
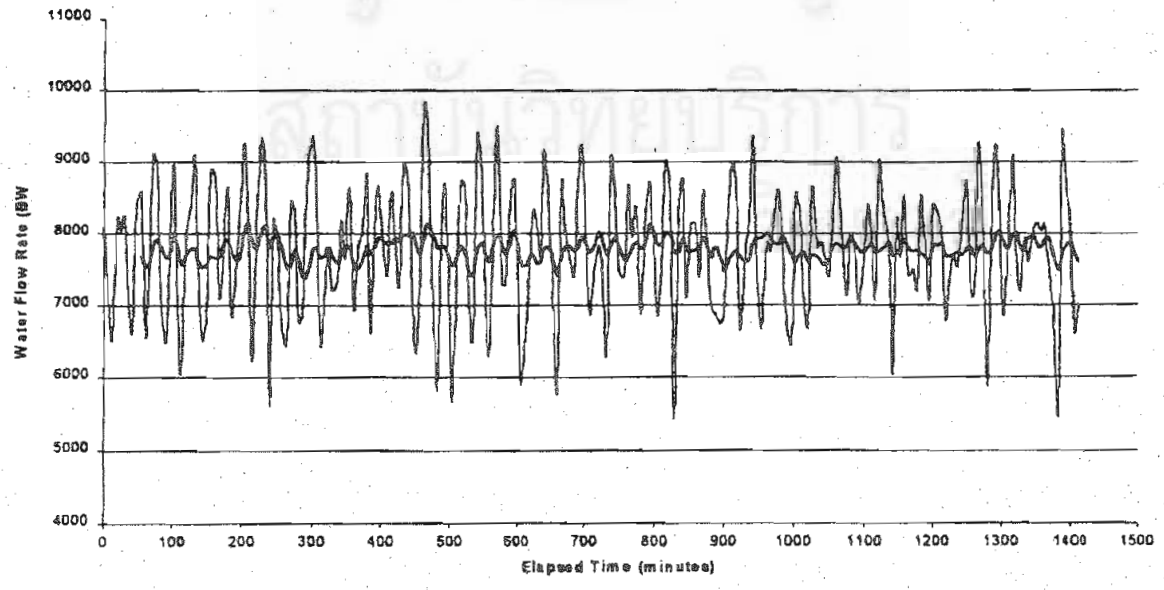


FIGURE 4. 12/18/97 Data for Water Flow from Funan Inlet Separator #1 versus Time with 60 min. Running Average also Plotted



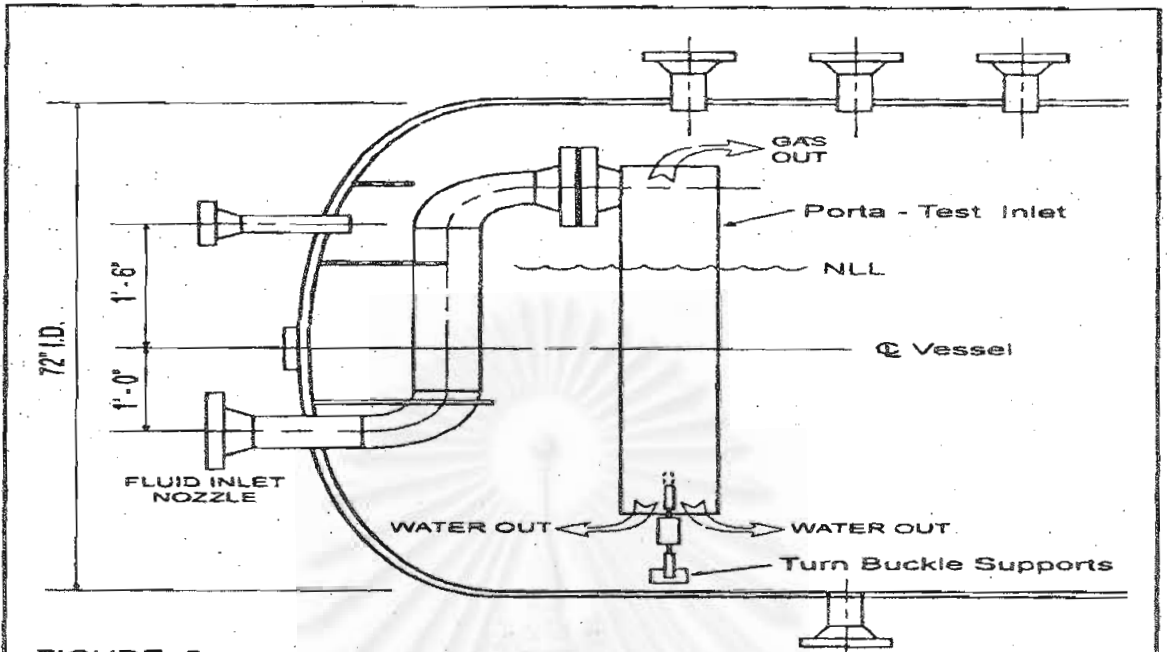


FIGURE 5.

The Installation of Cyclonic Gas/Liquid Disengagement Tubes on the Funan Skim Tank Inlet Significantly Improved its Condensate/Water Separation Performance.

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FIGURE 6. Hydrocarbon Content in Discharged Water (Funan)
(December 1992 - December 1995)

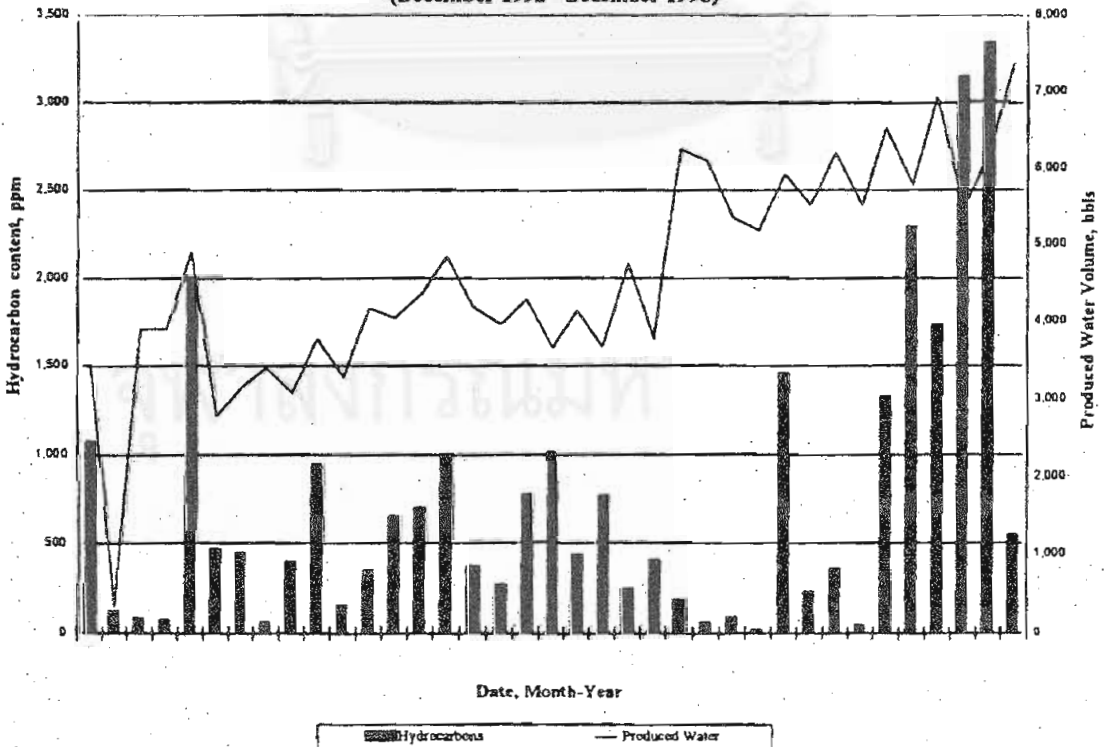


FIGURE 7. Distribution of TPH Analytical Data for IGF Samples from 69 Valid Wa 2 Tests failed to Meet the Target TPH of < 40 PPM. A Total of 87 Tests were conducted during the Pilot Plant Campaign

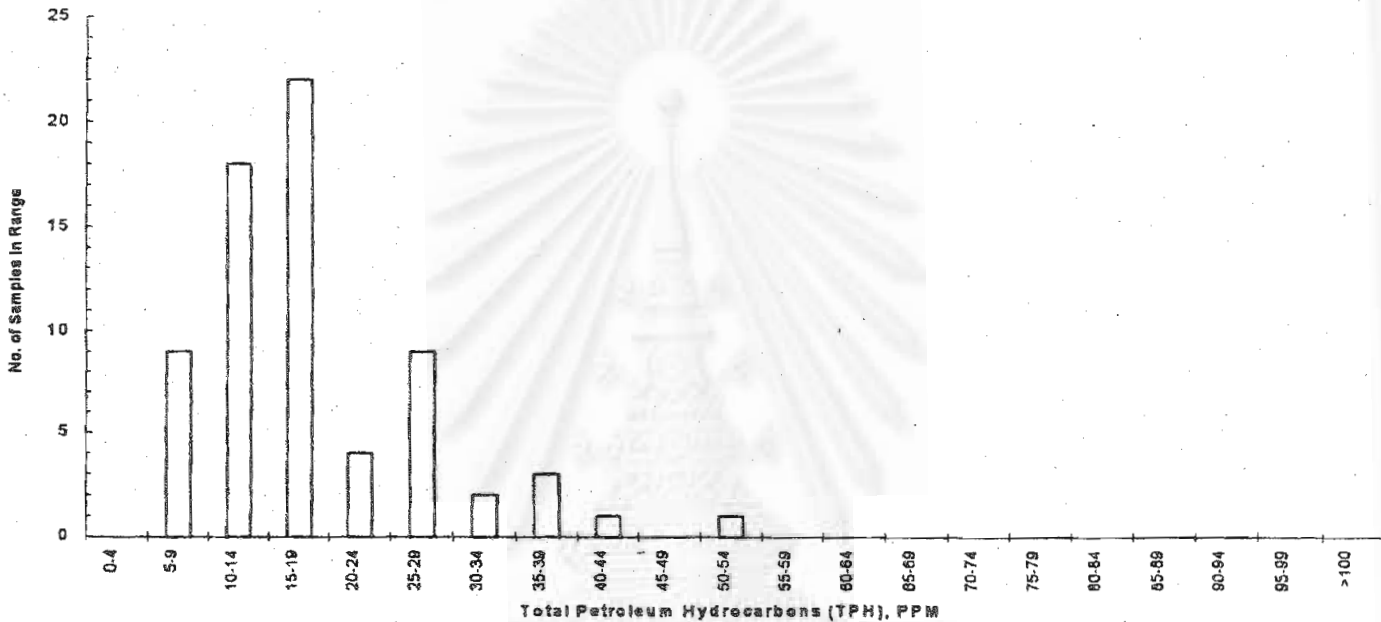


FIGURE 8. Distribution of Mercury Analytical Data for IGF Discharge Samples from 71 Valid Water Cleaning Pilot Tests. A Total of 87 Tests were Conducted during the Pilot Plant Campaign

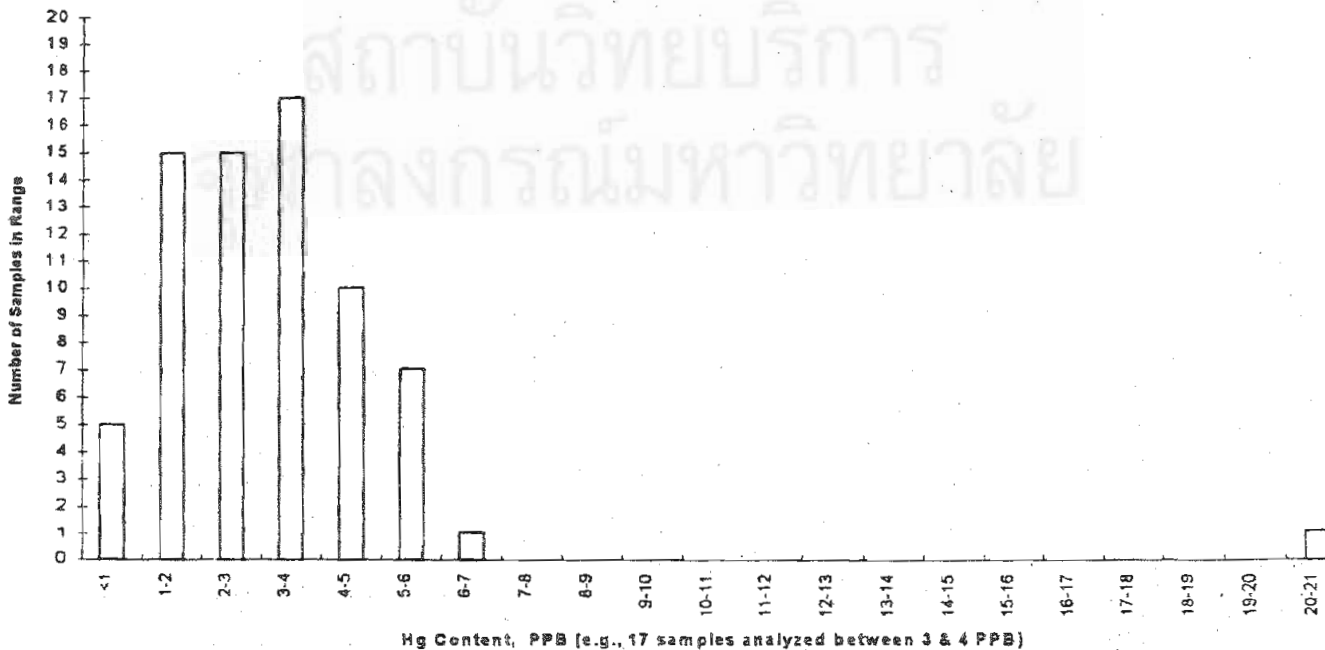
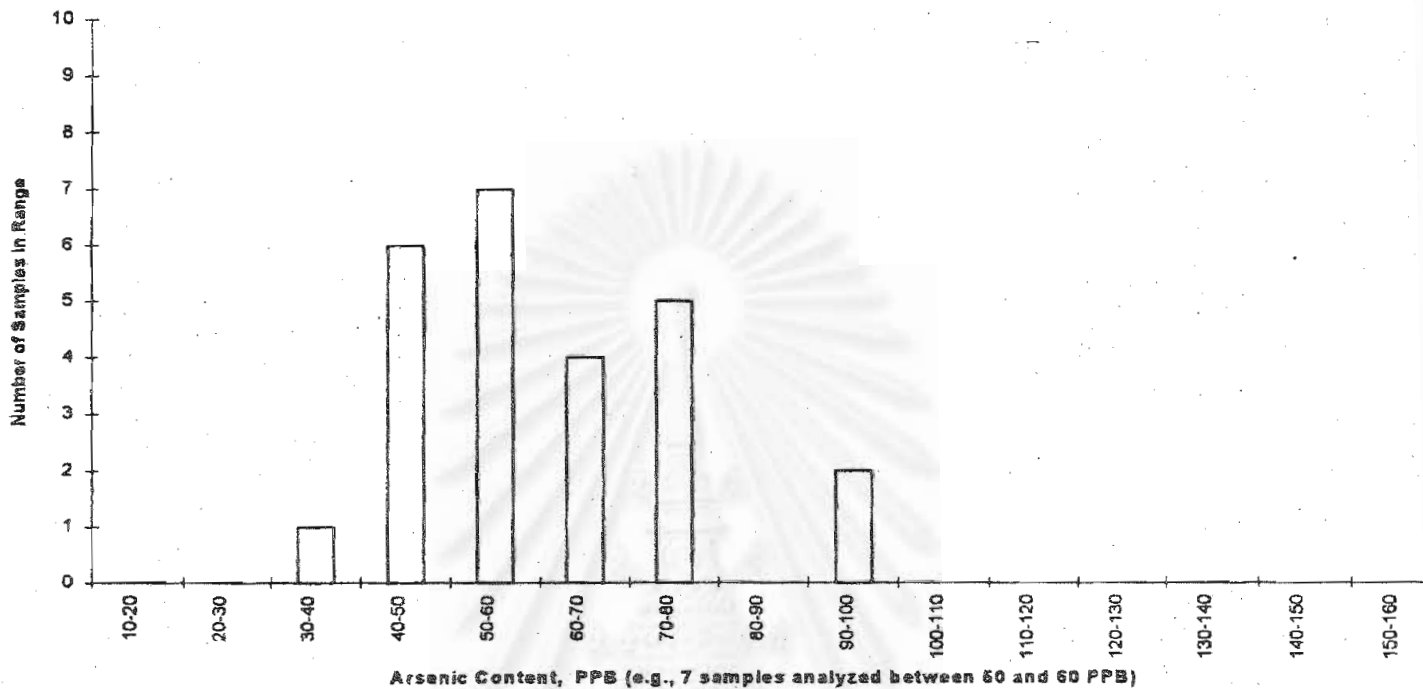
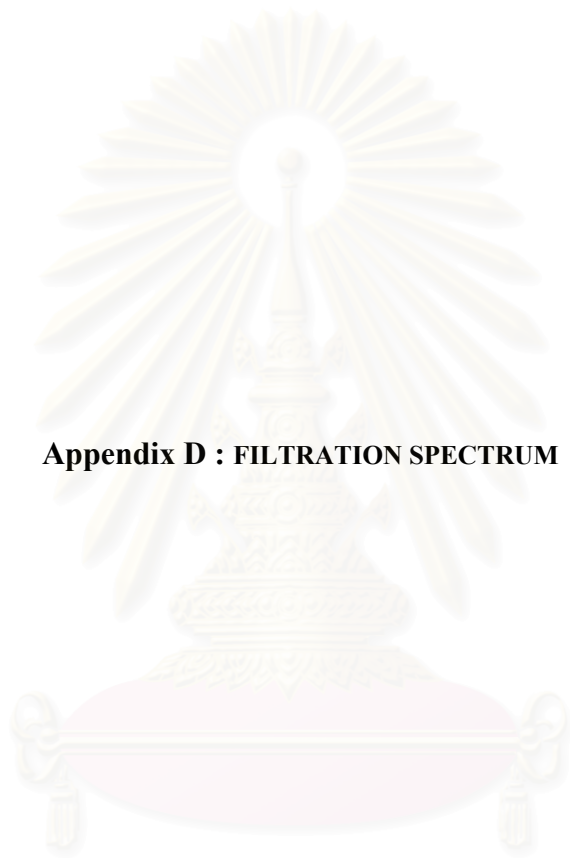


FIGURE 9. Distribution of Arsenic Analytical Data for IGF Discharge Samples from 25 Valid Water Cleaning Pilot Tests Where Arsenic Removal was an Objective. Significant Arsenic Reduction was obtained in all Tests.

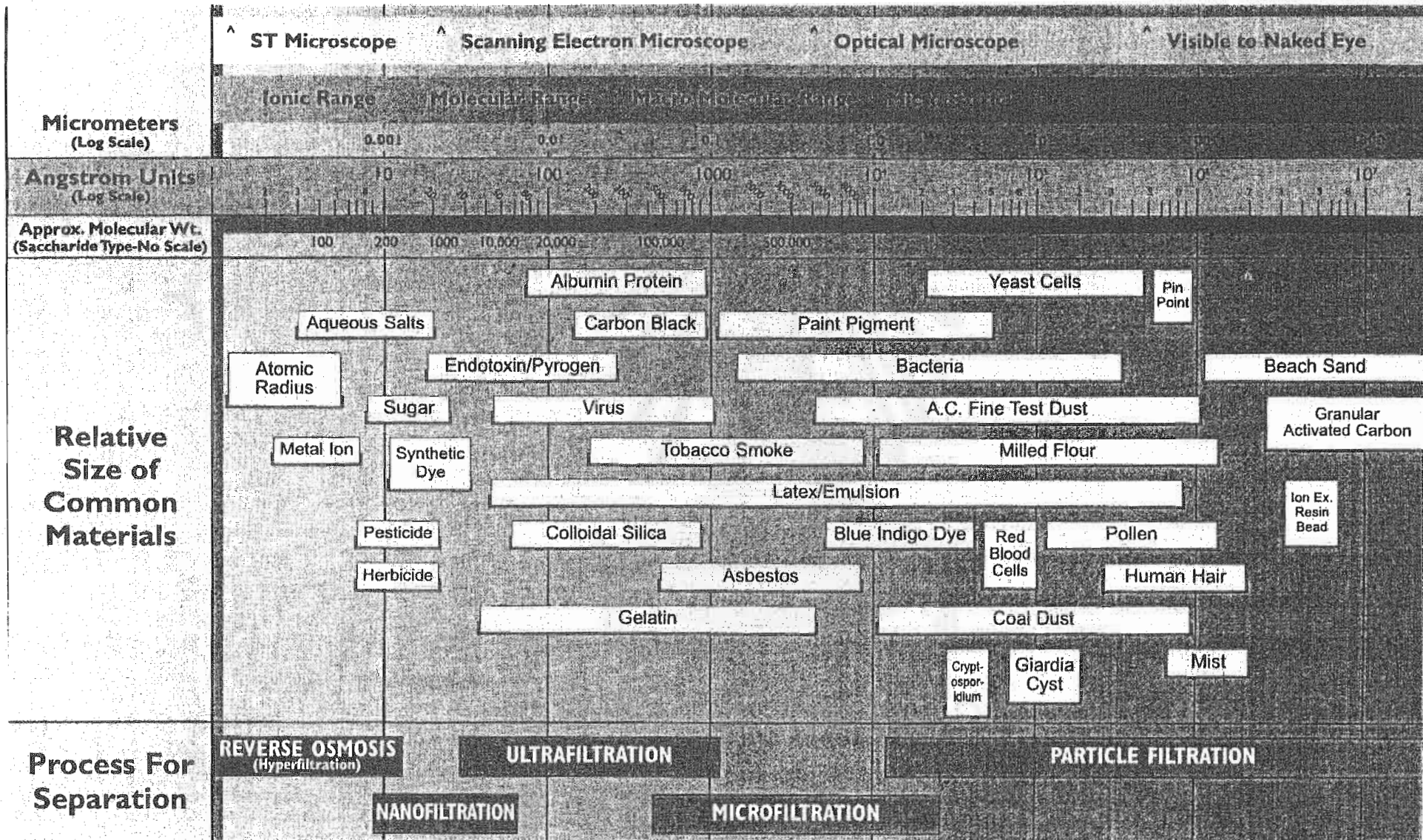


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Appendix D : FILTRATION SPECTRUM

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Note: 1 Micron (1×10^{-6} Meters) $\sim 4 \times 10^{-5}$ Inches (0.00004 Inches)
 1 Angstrom Unit = 10^{-10} Meters = 10^{-4} Micrometers (Microns)

Filtration Spectrum

APPENDIX E FSO WATER CHEMISTRY

Calcium	85	mg/liter
Magnesium	60	
Sodium	2400	
Iron	37	
Chloride	1690	mg/liter
Sulfate	21	
Bicarbonate	3900	
Total Alkalinity as CaCO ₃	3200	
Total Suspended Solids	175 – 10,000	mg/liter
Hydrocarbon	1,000 – 10,000	
Arsenic	15 – 28	
Mercury	0.4 – 9.2	

- Hydrocarbons
 - Present as chemically stabilized reverse emulsion (5 – 20 μ droplets) and as oil-coated scale mineral solids
- Mercury
 - Present as colloidal Hg⁰, chemisorbed Hg, and as Hg⁰ dissolved in condensate
- Arsenic
 - Present in water soluble, ionic form (As⁺³, AsO₃³⁻)

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