



**The Massachusetts Toxics Use Reduction Institute
University of Massachusetts Lowell**

**DIFFUSION DIALYSIS AND ACID RECOVERY
IN METAL OPERATIONS**

**TOXICS USE REDUCTION INSTITUTE
UNIVERSITY RESEARCH IN SUSTAINABLE
TECHNOLOGIES PROGRAM**

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University of Massachusetts Lowell

Diffusion Dialysis and Acid Recovery in Metal Operations

**Dr. Francis J. Bonner and Dr. Alfred A. Donatelli
Department of Chemical and Nuclear Engineering
University of Massachusetts Lowell**

**The Toxics Use Reduction Institute
University Research in Sustainable Technologies Program**

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The Toxics Use Reduction Institute is a multi-disciplinary research, education, and policy center established by the Massachusetts Toxics Use Reduction Act of 1989. The Institute sponsors and conducts research, organizes education and training programs, and provides technical support to promote the reduction in the use of toxic chemicals or the generation of toxic chemical byproducts in industry and commerce. Further information can be obtained by writing the Toxics Use Reduction Institute, University of Massachusetts Lowell, One University Avenue, Lowell, Massachusetts 01854.

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University Research in Sustainable Technologies

The University Research in Sustainable Technologies program is a joint project of the Toxics Use Reduction Institute (TURI) and the Center for Environmentally Appropriate Materials (CEAM) at the University of Massachusetts Lowell, with support from the Commonwealth's Strategic Envirotechnology Partnership (STEP).

The program taps the research capabilities of the University of Massachusetts to advance the investigation, development and evaluation of sustainable technologies that are environmentally, occupationally and economically sound. The program provides research funding to UMass faculty from all campuses, annually, on a competitive basis and encourages faculty/industry partnerships and cross-campus collaboration. Industry partners provide guidance, propose applications for new technologies, and, in some cases, evaluate and/or adopt processes and technologies resulting from research.

Following is a list of the Fiscal Year 2000 projects.

- ❑ **Diffusion Dialysis and Acid Recovery in Metal Working and Finishing** - Prof. Francis J. Bonner and Prof. Alfred A. Donatelli, UMass Lowell, Department of Chemical and Nuclear Engineering
- ❑ **Solar Fuel Cell System** - Prof. John Duffy, UMass Lowell, Department of Mechanical Engineering, Solar Engineering Program
- ❑ **Optical Information Processing with Environmentally Friendly Organic Materials** - Prof. D.V.G.L.N. Rao, UMass Boston, Department of Physics
- ❑ **Developing and Analyzing Lead-Free Soldering Processes for Printed Wiring Boards** - Prof. Sammy G. Shina, UMass Lowell, Department of Mechanical Engineering
- ❑ **Environmentally Benign Control of Polymer Solubility: Photoresist Materials Using DNA Mimics** - Prof. John C. Warner, UMass Boston, Department of Chemistry
- ❑ **Integration of Pollution Prevention and Occupational Health and Safety** - Prof. Rafael Moure-Eraso, UMass Lowell, Department of Work Environment
- ❑ **Synthesis of Conjugated Polymers and Molecules Using Sugar Reagents and Solventless Reactions** - Prof. Daniel J. Sandman, UMass Lowell, Department of Chemistry

Notice

This report has been reviewed by the Institute and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Toxics Use Reduction Institute, nor does the mention of trade names or commercial products constitute endorsement or recommendation for use.

Related Work on Diffusion Dialysis by the Toxics Use Reduction Institute

The Toxics Use Reduction Institute has provided various grants and been involved in projects on diffusion dialysis technology research and implementation efforts.

In 1995, through the Toxics Use Reduction Institute's Industry Matching Grants Program, Printed Circuit Corporation of Woburn, Mass. evaluated a diffusion dialysis unit to process 50 gallons per day of a nitric acid solder stripping bath. Testing found nitric acid reclaim efficiencies ranging from 87-89% and metal rejection rates for copper, lead and tin of 75-90%. The project approximated a nitric acid use reduction of 74% and a first year savings for the company of \$47,000. For more details, see Toxics Use Reduction Institute's Technical Report Number 26: "Reclamation of Nitric Acid from Solder Strip."

In 1996, through the Toxics Use Reduction Institute's Demonstration Sites Program, Danaher Tool Group of Springfield, Mass. demonstrated diffusion dialysis of 15 gallons per day of a nitric acid stripping bath used to strip nickel and chrome plate off of stainless steel plating racks. Testing found nitric acid reclaim efficiencies ranging from 80-95% and nickel rejection rates of 60-70%. Implementation of the dialysis unit resulted in a 54% decrease in the use of nitric acid and a project payback of 2.1 years. For more details, see Toxics Use Reduction Institute's Technical Report Number 32: "Nitric Acid Recovery Using Diffusion Dialysis."

In 1999, the Environmental Protection Agency Region 1 supported research to test the utility of the Pollution Prevention Technology Application Analysis Template. The technology chosen for documentation was the diffusion dialysis acid recovery system. The resulting report documented eight applications of diffusion dialysis at four companies, including the Danaher Tool Group installation. The results of seven applications (not including Danaher Tool Group) are summarized below.

Acid	Acid recovery (%)	Contaminant	Contaminant reduction (%)
Nitric	96	Nickel, iron, copper	66-86
Nitric	80	Copper	88
Hydrochloric	89-91	Chromium, iron	72-80
Hydrochloric	76	Copper, iron	78-89
Sulfuric	94	Copper	91
Sulfuric	89	Nickel, iron, chromium	76-91
Sulfuric	90	Aluminum, copper	89-94

For more details, contact the Commonwealth's Strategic Envirotechnology Partnership at the Executive Office of Environmental Affairs at 617-626-1052.

The Institute has worked closely with the following two Massachusetts vendors of the technology:

Pure Cycle Environmental Technologies, Inc.
20 Wilbraham Street
Palmer, Mass. 01069
Contact: Dan Bailey
Phone: 413-283-8939
<http://www.purecycle.com>
email: purecycle@purecycle.com

Zero Discharge Technologies
2096 Westover Rd.
Westover Industrial Airpark
Chicopee, Mass. 01022
Contact: Tony D'Amato
Phone: 413-592-4242

Introduction

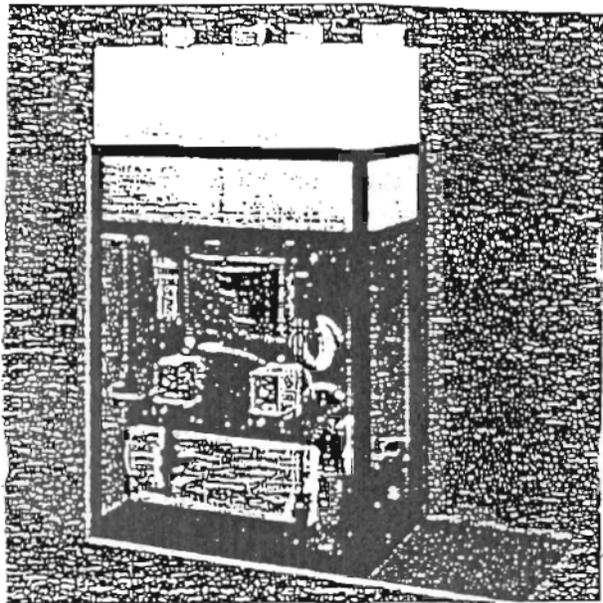
This is the final report of work performed by the Separations and Interfacial Science and Engineering Laboratory in the Department of Chemical and Nuclear Engineering, University of Massachusetts Lowell during the academic year 1999-2000 for the second year of the Toxics Use Reduction Institute University Research in Sustainable Technologies Program. The purpose of this research was to develop information and understanding that would lead to improvements in commercial equipment and procedures currently used to reclaim spent acid from metal treating operations using anion exchange membranes in the absence of external electric fields. Industry partners in this project are Daniel E. Bailey (Pure Cycle Environmental Technologies, Inc.) and Anthony D'Amato (Zero Discharge Technologies, Inc.).

Acid baths are used within the electronics and metalworking and plating industries for a variety of metal etching and stripping processes. The bath removes unwanted substances such as metals from a product. These substances are then trapped within the bath usually in a dissolved state. With each use, the concentration of the contaminants increases. Once the contamination level reaches a point in which the bath is no longer functional for meeting process specifications, the bath is considered spent. The spent bath is then disposed, and fresh acid and possibly other additives are mixed together to create a new bath for processing. The spent bath containing several types of dissolved metals and other contaminants is then shipped off-site for treatment or treated on-site creating solid and liquid waste. The liquid waste is neutralized and released with discharge water, while the solid waste is sent for disposal or reprocessing.

Innovative technologies are available for recycling a spent bath for reuse in order to provide for an increase in bath life. One of these technologies uses the concept of diffusion dialysis through anion exchange membranes, which is the method investigated in this research.

Technology Description

Commercial equipment utilizes a stack of membranes with countercurrent flow of the permeate and retentate back and forth over opposite sides of the membrane surface. A pilot scale/small works unit is shown in Figure 1 and was provided by Pure Cycle Environmental Technologies, Inc. A miniature 3-pass countercurrent flow membrane test cell, shown in Figure 2, had been used in the previous first year study to resemble commercial multi-pass equipment while conserving membrane and reagents and minimizing waste. The operating parameters for that test cell are given in Table 1. The test cell for the second year of the study was further reduced to a one-pass system. An exploded view of the test cell is shown in Figure 3, and a description of the cell is given in Table 2.



Pure Cycle Environmental technologies, Inc., Palmer, MA.

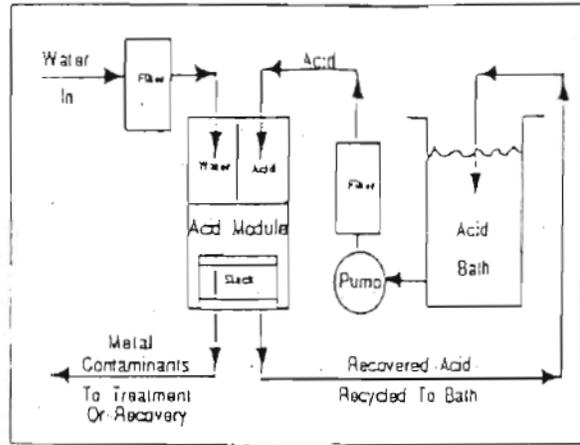
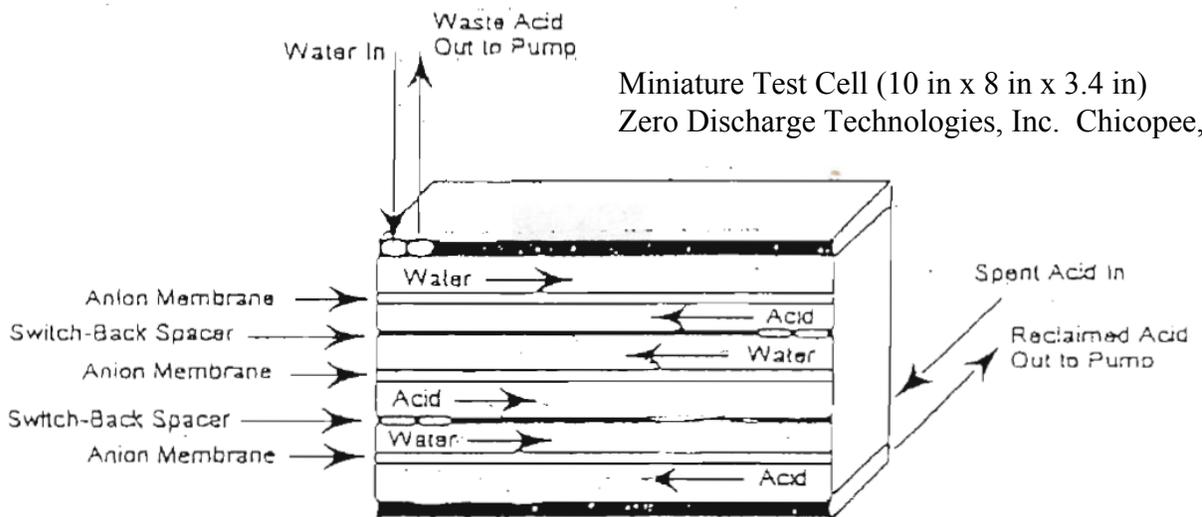


Figure 1. Pilot Scale Diffusion Dialysis Unit



Miniature Test Cell (10 in x 8 in x 3.4 in)
Zero Discharge Technologies, Inc. Chicopee, MA

Figure 2. Schematic of three-pass countercurrent flow bench scale diffusion unit

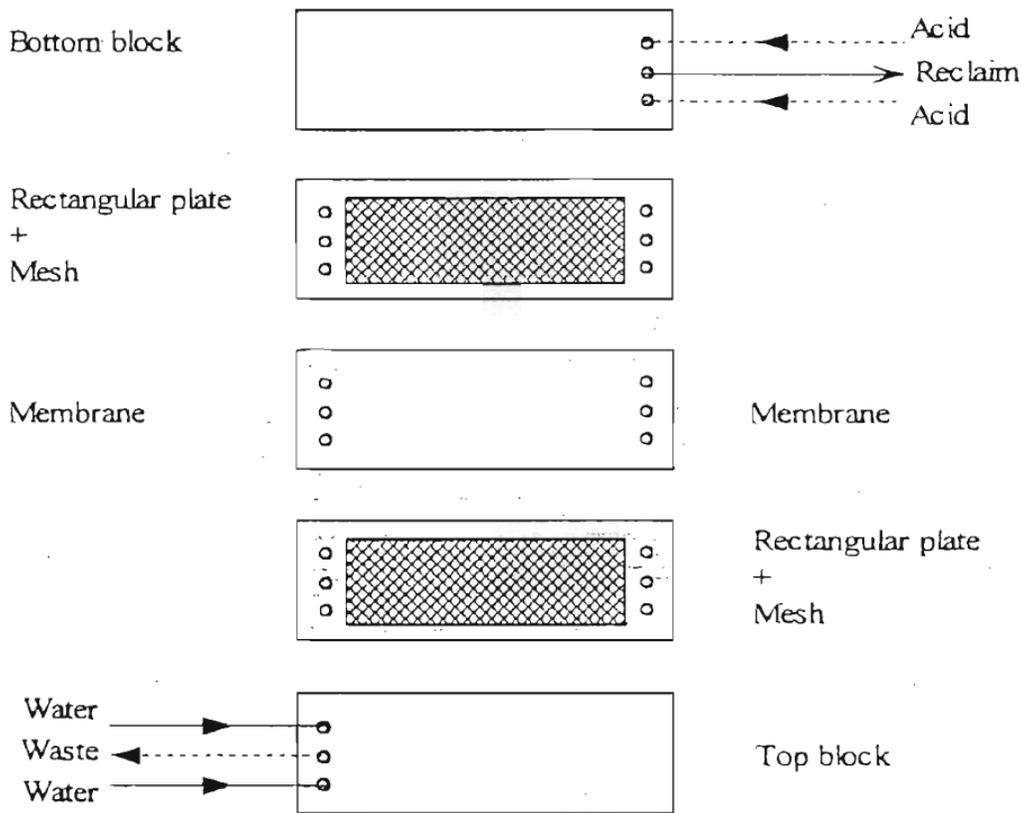


Figure 3. Exploded view of one-pass test cell

Table 1. Operating Parameters for Three-Pass Bench Scale Diffusion Unit	
Cell Pairs	3
Cell Gap (cm)	0.066
Flow Rate (ml/min)	1.0
Velocity (cm/min)	1.0
Residence Time (hr)	1.0
Total Active Membrane Area (cm ²)	445

Table 2. Description of One-Pass Test Cell	
Number of Membranes	1
Cell Gap (cm)	0.5
Active Membrane Area (cm ²)	150

Technology Application and Applicability

Cation exchange membranes are used to reclaim metals with the process generally being termed Donnan dialysis. Anion exchange membranes are used to reclaim acids with the process generally referred to as diffusion dialysis. The distinction is arbitrary since both are basically diffusion dialysis and both are subject to the same Donnan criteria of co-ion rejection and preservation of electrical neutrality. As already noted, acid recovery by means of anion exchange membranes is the subject of this report.

Some of the more common applications of diffusion dialysis include the recovery of mixed acids of stainless steel pickling baths, recovery of sulfuric acid/hydrochloric acid or sulfuric acid/nitric acid of pickling plants for non-ferrous metals such as zinc and aluminum, recovery of sulfuric acid and hydrochloric acid of steel and non-ferrous pickling baths, hydrochloric acid and nitric acid rack strips, and sulfuric acid anodizing solutions (1). Using pilot scale diffusion dialysis equipment from Pure Cycle Environmental Technologies, Inc. similar to that shown in Figure 1, Freshour and Thornton (2) found good nitric acid recovery and iron and nickel rejection but relatively poor phosphoric acid recovery and titanium rejection. They detail their experiences with the recoveries of (a) nitric acid, phosphoric acid and sodium chloride mixtures used in metals cleaning, (b) nitric acid and hydrofluoric acid mixtures used for iron and nickel alloy cleaning, (c) nitric acid and hydrofluoric acid mixtures for titanium etching. The very low rejection of titanium ions was attributed to the formation of an ion complex with fluoride ion that can then diffuse through the anion exchange membrane. Leakage of other metals is often assumed to occur because of complexation.

As discussed by Bailey and Howard (3) and Bailey (4), diffusion dialysis can be a very effective way of recovering mineral acids from acid solutions containing dissolved metals. In a hydrochloric acid chromium rack strip application, more than 90% of the acid was recovered and metals rejection approached 80%. For a sulfuric acid anodizing application, which is one of the most proven and trouble-free examples of acid recovery using anion exchange membranes, acid recovery was around 90% and metals rejection was greater than 90%. Examples of commercial usage and favorable comparisons with the competing technology of resin sorption are also given.

Anion exchange membrane dialysis for acid recovery is potentially applicable to a wide variety of acid-metal salt combinations, but in some cases metal rejection can be limited by metal complexation with the anions that are present in the solutions.

Research Plan

Due to availability and because of prevalent use, Neosepta anion exchange membranes in the chloride form (Tokuyama Soda Co., Ltd.) were used in the present study. See Table 3 for a description of the membrane. In keeping with available literature (5) and scanning electron microscope investigations of the present study, the Neosepta membranes are presently considered to be colloidal dispersions of a polystyrene/divinyl benzene copolymer anion

exchange resin in a microporous polyvinyl chloride (PVC) gel supported by plasticized PVC cloth.

Table 3 Membrane Description
<ul style="list-style-type: none">❑ Neosepta type AFN (Tokuyama Soda Co., Ltd.)❑ Polystyrene/divinyl benzene copolymer❑ Anion exchange-chloride form❑ Microporous❑ 0.2 mm thickness❑ Morphology: colloidal dispersion of ion exchange resin particles in PVC gel supported by and infused into PVC cloth

One theory tested was whether it was possible to replace the exchangeable chloride ions in the membrane with sulfate ions either by soaking the membranes in concentrated sulfuric acid or by adding a salt of the acid anion. If this was possible, it was thought that this replacement would improve the recovery of sulfuric acid.

To test the presoaking theory, the following concentrations and durations were tested: 36 N for 12 hours, 36 N for 30 minutes, and 5 N for 12 hours. Scanning electron microscope (SEM) was used to determine sulfur content on the membrane. To test acid recovery, 5 N sulfuric acid feed solution at a flow rate of 0.5 cc/min was used on membranes soaked in 5 N sulfuric acid for 0, 2, 4, 6, and 8 days. In the acid anion test, 1/3 M aluminum sulfate was added to the 5 N sulfuric acid.

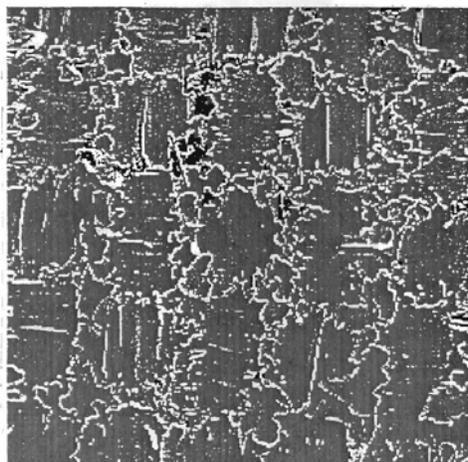
Using 2.5 N HCl and 0.052 M FeCl₃ at a flow rate of 1 cc/min., acid recovery and salt rejection was determined. Subsequently four acids at 5 N and a flow rate of 0.5 cc/min. were compared for % acid recovery. Those acids were hydrochloric, nitric, sulfuric, and phosphoric.

The chlorine content of the membrane was studied by examining X-ray emission scans, carried-out as part of the SEM investigation. Researchers were interested in obtaining a better understanding of the structure of the membrane. The membrane contains a colloidal dispersion of the component that contains that active material, and it is not dispersed uniformly throughout the membrane.

Finally the effect of feed flow rate was examined for 1, 3 and 5 N hydrochloric acid to determine its effect on acid recovery.

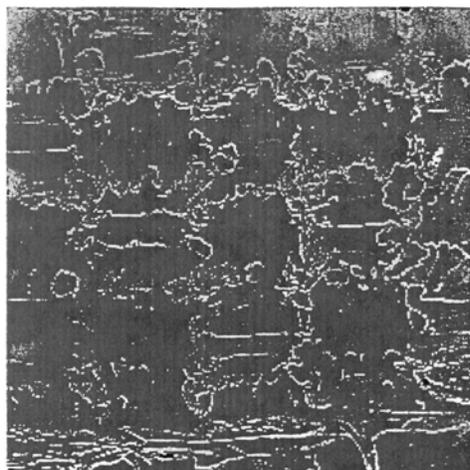
Results and Discussion

Scanning electron microscope (SEM) photos, Figures 4 and 5, clearly show the PVC cloth weave was attacked and degraded by concentrated sulfuric acid (36 N). Moderately concentrated sulfuric acid (5 N), but still more concentrated than in anodizing baths, did not visibly attack the membrane as evidenced in Figure 6.



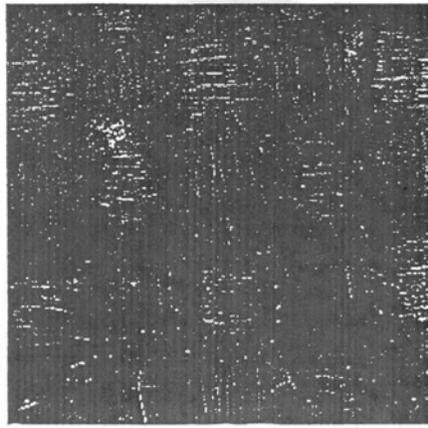
CAM-UML 100 μ m 20KeV X 100

Figure 4. Appearance of membrane surface after soaking in concentrated sulfuric acid (approximately 36N) for 12 hours



CAM-UML 100 μ m 20KeV X 100

Figure 5. Appearance of membrane surface after soaking in concentrated sulfuric acid (approximately 36N) for 30 minutes



CAM-UML 100µm 20KeV X 100

Figure 6. Appearance of membrane surface after soaking in sulfuric acid (approximately 5N) for 12 hours.

For feed solutions containing either 2.5 or 5 N hydrochloric acid (HCl) with 0.052 M ferric chloride (FeCl₃), HCl recovery was about 60% and FeCl₃ rejection was approximately 80% using a flow rate of 1 cc/min to the membrane cell as shown in Figure 7.

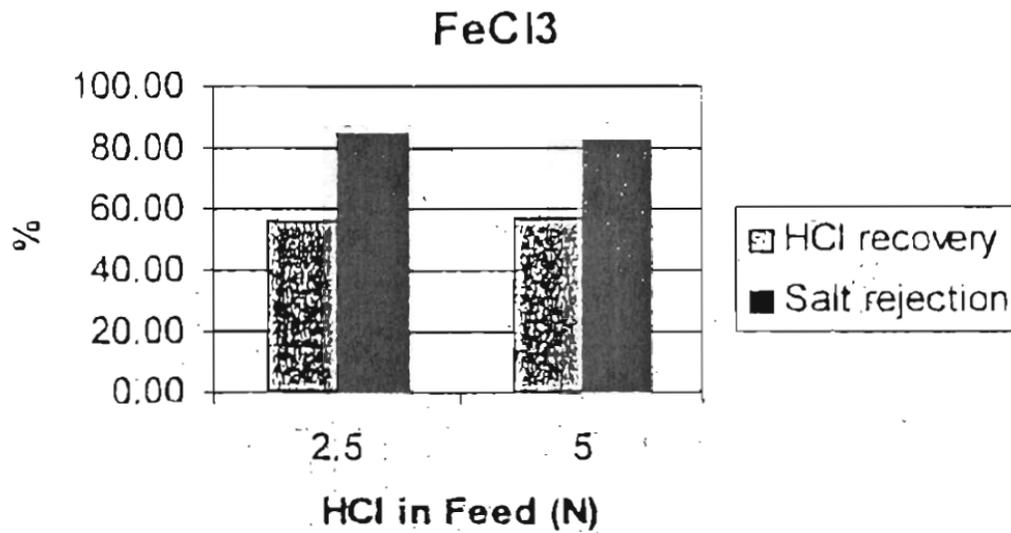


Figure 7. HCl recovery and FeCl₃ rejection at a flow rate of 1 cc/min. Feed solutions contained either 2.5 or 5 N HCl with 0.052 M FeCl₃

Figure 8 shows that recovery was similar for hydrochloric and nitric acids, significantly less for sulfuric acid and much less for phosphoric acid. Apparently acid recovery decreases as the number of hydrogen ions on the acid increases.

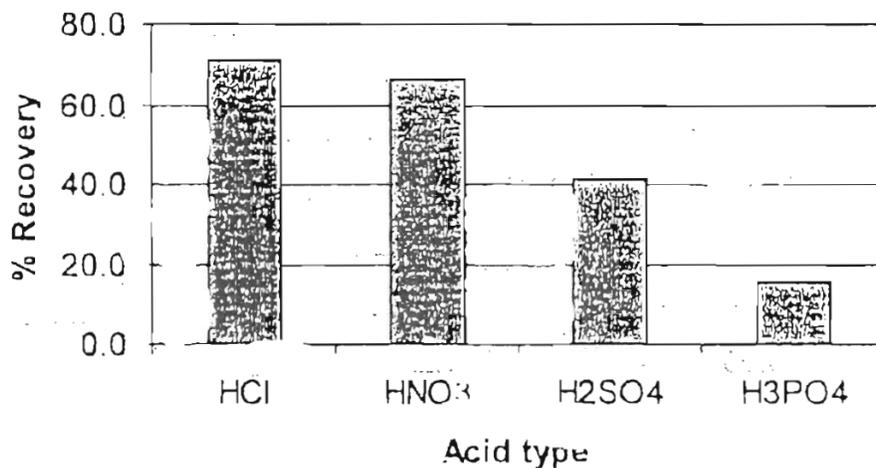


Figure 8. Comparison of acid recovery for 5 N hydrochloric, nitric, sulfuric and phosphoric acids at a flow rate of 0.5 cc/min.

There were some indications that increasing the concentration of the acid anion by adding another salt of that anion or by presoaking the membrane in the acid could somewhat increase acid recovery. Figure 9 compares the recovery of a 5 N sulfuric acid (H₂SO₄) feed solution at a flow rate of 0.5 cc/min with a solution containing the same acid concentration but with 1/3 M aluminum sulfate. The system containing additional sulfate ion in the solution showed a slightly higher recovery of H₂SO₄. Figure 10 shows the recovery of 5 N H₂SO₄ at a flow rate of 2 cc/min. when the membrane was presoaked from 0 to 8 days in the acid. The recovery of H₂SO₄ may have increased slightly with the presoaking time.

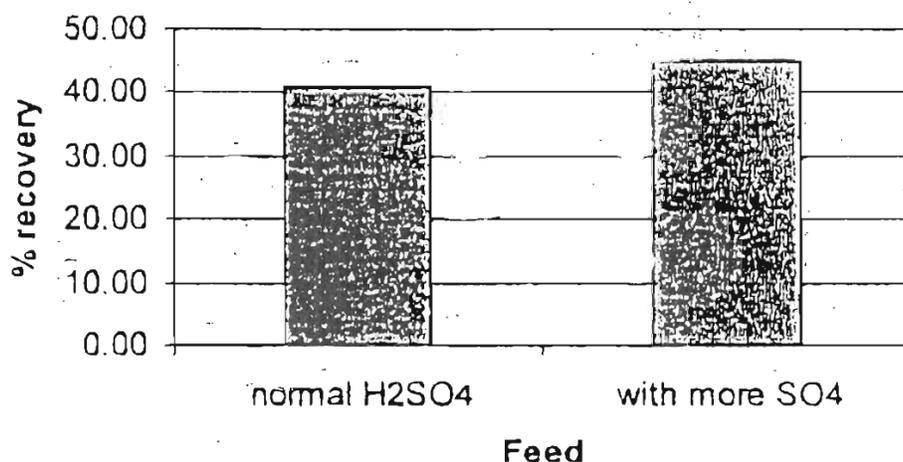


Figure 9. Effect of the addition of aluminum sulfate on the recovery of sulfuric acid.

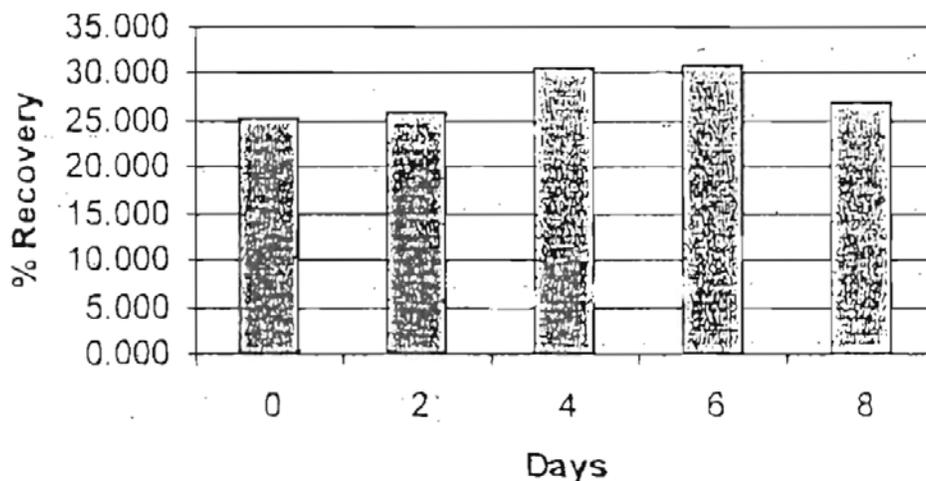


Figure 10. Effect of membrane soaking time on the recovery of sulfuric acid.

X-ray emission scans, carried-out as part of the SEM investigation, revealed a periodicity in the distribution of chlorine over and through the membrane surface. Figure 11 is a diagram of the scanning points along the cloth weave on the membrane surface. Figure 12 shows the intensity of the chlorine signal at the various scanning points on the membrane surface. Scans performed through the membrane thickness showed some displacement of the chloride ion by the corresponding anion after soaking in nitric, sulfuric and phosphoric acids as revealed in Figure 13.

The effect of feed rate to the membrane cell was examined for 1, 3 and 5 N hydrochloric acid solutions as shown in Figure 14. HCl recovery consistently decreased with a decrease in residence time in the cell as the feed rate increased from 0.5 to 2.0 cc/min. This behavior suggests that transport through the membrane was not influenced by an external boundary layer for the range of flow rates investigated. Rather recovery was affected by transport solely through the membrane.

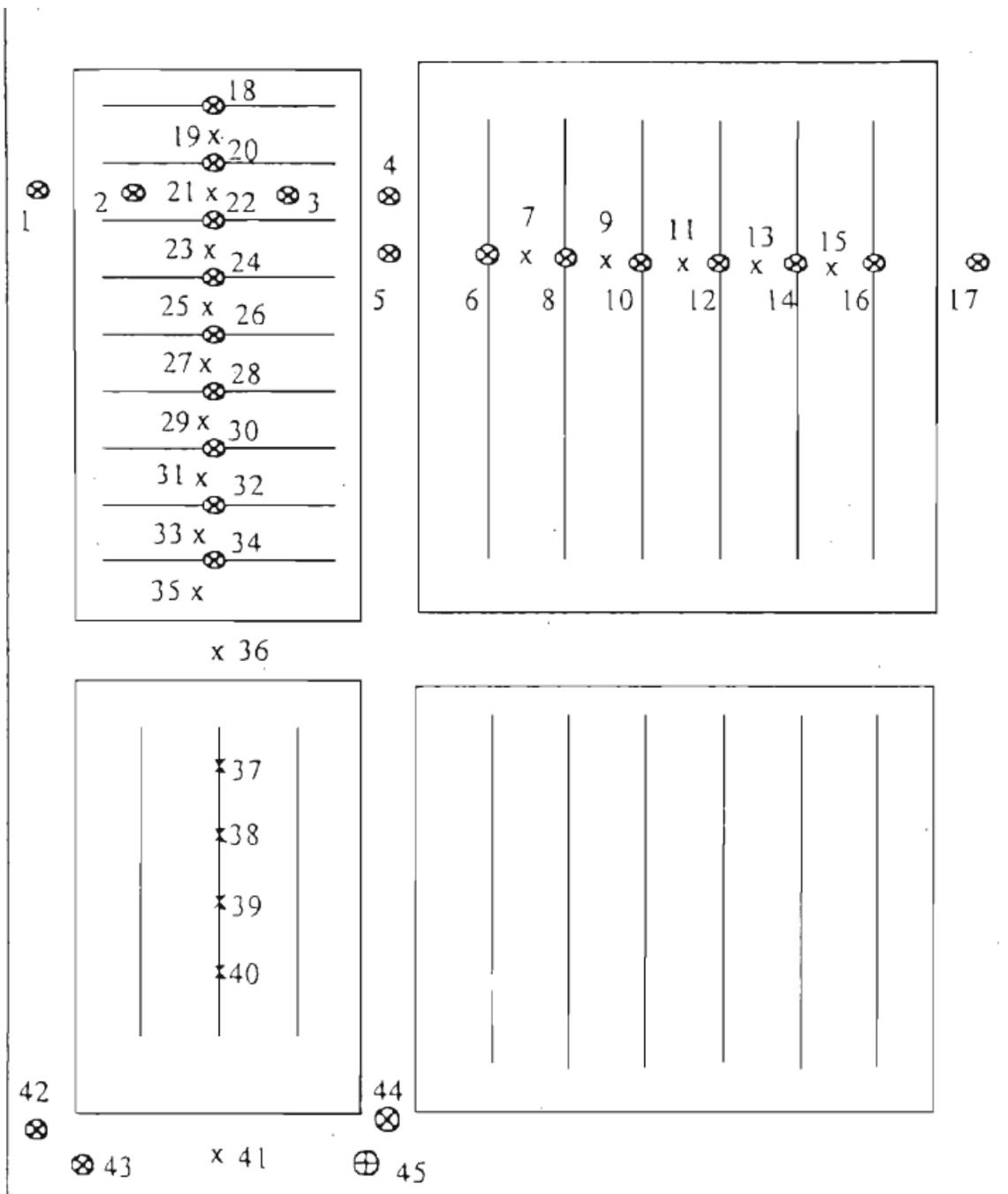


Figure 11. Diagram of scanning points on membrane surface

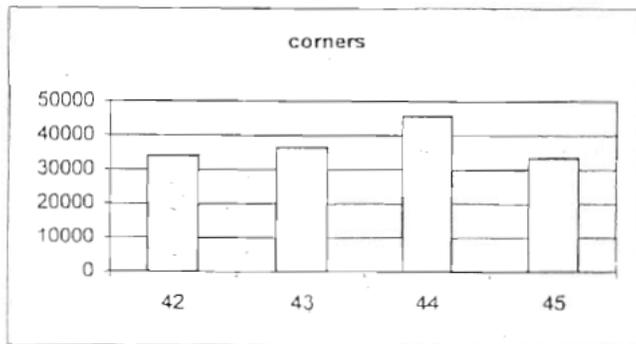
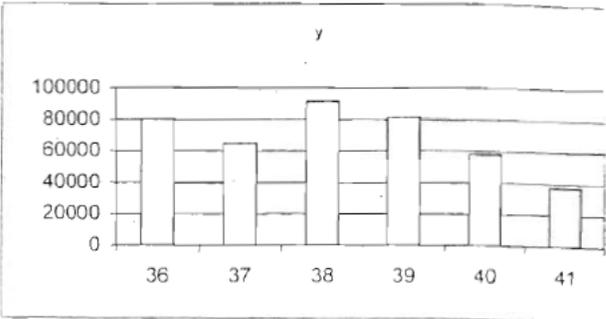
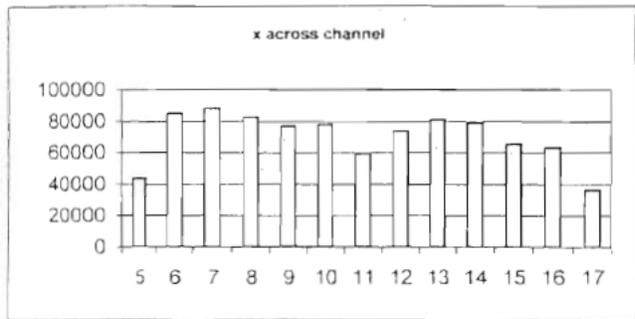
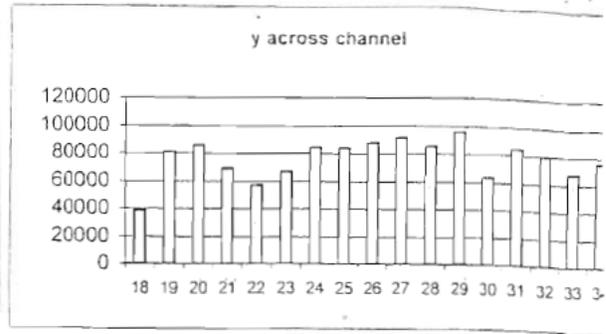
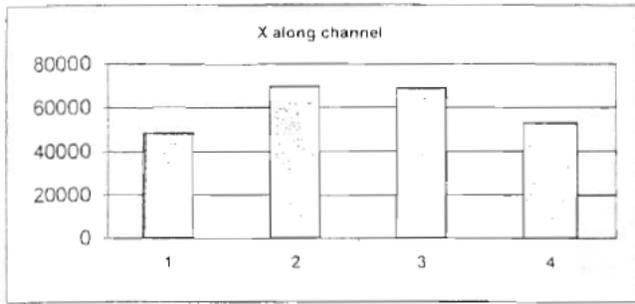
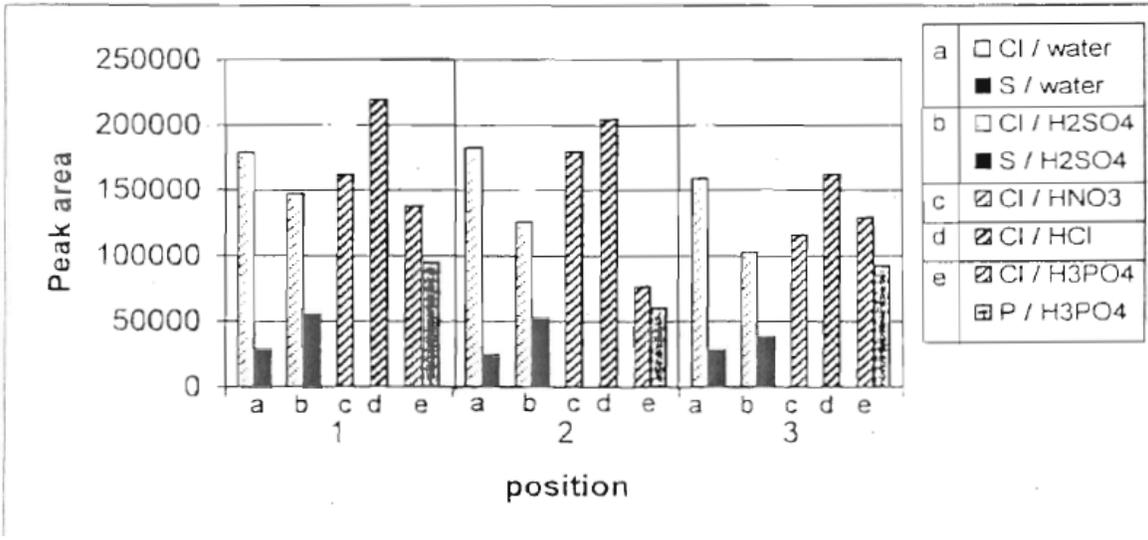


Figure 12. Intensity of chlorine signal on the membrane surface at locations given in Figure 11.

No	Soaked	position	Peak area					
			Cl	AVG	S	AVG	P	AVG
a	water	1	178588	173229.0	28382	27021.0	0	
		2	182139		24515		0	
		3	158960		28166		0	
b	H2SO4 5 N	1	146928	125145.33	55178	48617.7	0	
		2	125786		52046		0	
		3	102722		38629		0	
c	HNO3 5 N	1	161816	152323.0	0		0	
		2	179306		0		0	
		3	115847		0		0	
d	HCL 5 N	1	219469	195302.0	0		0	
		2	204492		0		0	
		3	161945		0		0	
e	H3PO4 5 N	1	137621	114578.7	0		94918	82510.0
		2	76852		0		60338	
		3	129263		0		92274	

Note: 1-left, 2-middle, 3-right



X-Section EDX from soaked membrane

Figure 13. Intensity of chlorine, sulfur and phosphorous signals through membrane cross-section after soaking in water and in hydrochloric, nitric, sulfuric and phosphoric acids.

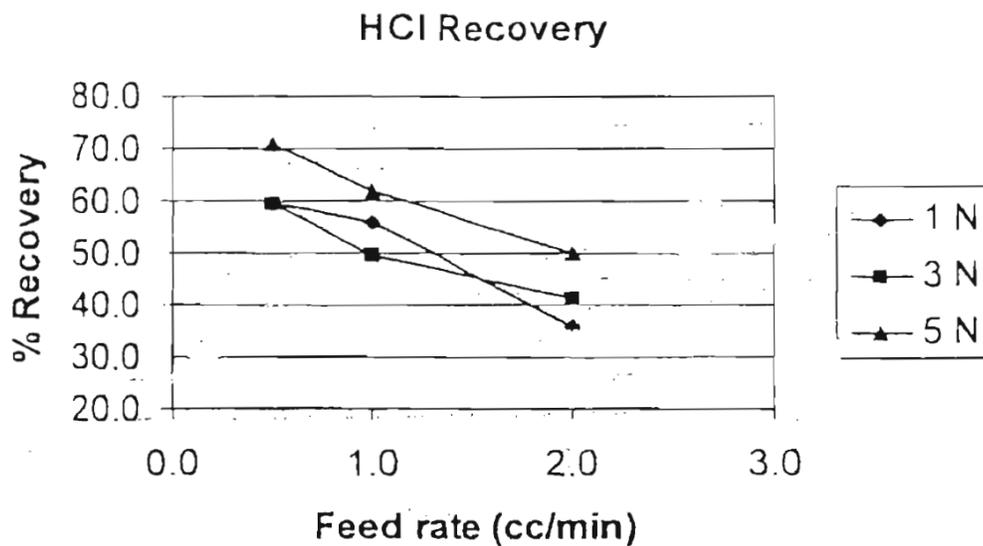


Figure 14. Effect of feed flow rate to the membrane cell on hydrochloric acid recovery.

Future Work

Plans for future work are as follows:

- ❑ Study the implication of complexation in important acid/metal combinations and attempt to modify those systems to reduce metal leakage across the membrane.
- ❑ Examine the scale-up issue in detail to increase the laboratory system from a one-pass up to six passes and then to an industrial application
- ❑ Fabricate membranes in-house to be able to control the structural parameters of the membranes and to gain a better understanding of the transport mechanisms through the membranes

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- (3) Bailey, D. and Howard, T., *Acid Recovery with Diffusion Dialysis*, Metal Finishing (Nov. 1992) 21-23.
- (4) Bailey, D. E., *Optimizing Anodizing Baths with Diffusion Dialysis*, Metal Finishing (Dec. 1998) 14-17.
- (5) Mizutani, Y., Hirayama, K., Nago, S., *Preparation of microporous membranes by paste method*, Journal of Membrane Science, 135 (1997) 129-133.