

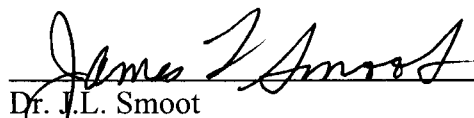
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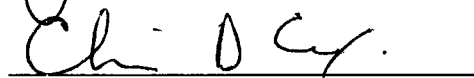


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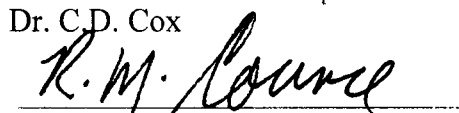
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FACILITATED TRANSPORT OF SODIUM PERRHENATE ACROSS  
SUPPORTED LIQUID MEMBRANES

A Dissertation  
Presented for the  
Doctor of Philosophy Degree  
The University of Tennessee, Knoxville

SRINIVAS KILAMBI

May, 1996

# ACKNOWLEDGEMENTS

First and foremost, I wish to thank my academic advisor, Dr. Robert Bruce Robinson, for his valued guidance, support, cooperation, and patience. Without Dr. Robinson's support this dissertation would have remained only a distant dream. Thank you very much Dr. Robinson.

Next, I wish to thank Dr. Cox, Dr. Smoot and Dr. Counce for agreeing to serve on my committee. I also wish to thank Dr. Bruce Moyer of ORNL for his guidance and financial support. I also wish to thank my colleagues at ORNL, Dr. Fred Sloop, Dr. Peter Bonnessen, Dr. Rick Sachlaben, Dr. Yon Fu Sun, Tammy Haverlock and Derrick Presley for their friendship, support and cooperation. I also wish to thank Annette Costar for her support.

I wish to thank my parents for all their love and support throughout these 30 odd years. Finally, I wish to thank my wife, Jaya Kilambi, who was responsible for my doing a Ph.D. She instilled in me the confidence that I could do a Ph.D., offered me unwavering support and always stood by my side through all the up and downs in my career. I dedicate this dissertation to her.

## Abstract

Technetium ( $^{99}\text{Tc}$ ), an uranium fission product, is a waste material left over after reprocessing fuel rods for plutonium production. The nuclear tank waste present at all the Department of Energy (DOE) sites contains an estimated 1.8 metric tons of Tc mostly present as the pertechnetate anion,  $\text{TcO}_4^-$ . Technetium is environmentally mobile, has a half life of  $2.13 \times 10^5$  years and is volatile upon vitrification. Existing techniques for Tc removal include solvent extraction, ion exchange, and reduction/precipitation. An alternative technique for the removal of pertechnetate\*\* present in waste streams, is to employ supported liquid membranes (SLMs). This research aims at examining the feasibility of extracting Tc in SLMs using crown ethers as extractants. SLMs consist of a solvent contained in the pores of a polymeric membrane between two aqueous solutions (feed and strip). Crown ethers form a complex with sodium and technetium at the extraction interface. This complex diffuses across the membrane and is then stripped at the strip interface.

SLM mass transfer models available in literature have either focussed only on the extraction side kinetics, or considered stripping side solute concentrations to be negligible, or have assumed identical solute distribution coefficients on the extraction and strip side. They have been unanimous in their claim that a solute cannot be transferred against its concentration gradient in cocurrent transport. The model developed by the author has eliminated all these deficiencies by considering finite concentrations of the

solute in the strip, and different feed and strip side distribution coefficients. Also, as per the model technetium can be transported against its apparent concentration gradient even in cocurrent transport and without any pH effects

Experiments were conducted at the Oak Ridge National Laboratory, Oak Ridge, TN on flat sheet SLMs. The first set of experiments involved the determination of the optimum Extractant (E), Diluent (D), and Modifier (M) combination. Crown Ethers (CE) were selected as the broad extractant category. CEs selected for the study included bis-4, 4' (s')[(tert-butyl)cyclohexano]-18-crown-6 (Eichrom Industries, Inc.) abbreviated di-t-Bu CH18C6, dicyclohexano-18-crown-6 (Parish Chemical) abbreviated DCH18C6, and cis-sym-bis-(tert-octyl benzo)-14-crown-4-dial (synthesized at Oak Ridge) abbreviated BOB14C4dial. di-t-Bu CH18C6 was selected, for most studies, over DCH18C6 because of its higher lipophilicity and higher lipophilicity resulted in lower aqueous solvent losses. Diluents systems studied included blends of 2-octanone with Isopar M, blends of 4-(1-butyl pentyl) pyridine (4-BPP) with Isopar-M or Isopar-V Nitrophenyloctylether (NPOE), and Nitrophenylpentylether (NPPE). Only NPOE and NPPE showed technetium transport and hence were chosen as the desired diluent. The 4-BPP and 2-

A set of experiments using d-t-Bu CH18C6 in NPOE was conducted to study the effect of initial CE concentration on Na and Re Flux. CE concentration was varied from 0.0 M (only NPOE) to 0.2 M. Na flux increased slowly between 0.0 and 0.1 M and then very rapidly between 0.1 and 0.2 M while the Re flux behaved in the exact opposite manner. Selectivity, defined as the ratio of Re over nitrate flux, reached a constant maximum value between 0.01 and 0.1 M. A second set of experiments involved studying the effect of flow rates on Na and Re flux. Fluxes increased and selectivity dropped with increasing flow rates. This shows that aqueous boundary layer resistances dropped with increasing flow rates, though not in a linear fashion, and the increase in nitrate flux was more than the increase in technetium flux. Na flux approximates nitrate flux as sodium nitrate is abundant over sodium perrhenate by over four orders of magnitude in the feed solution. A third set of experiments involved studying the effect of varying Re and Na concentrations in the feed solution on Na and Re flux. Re and Na fluxes increased by 20 and 6 times, respectively, and selectivity dropped by 15 times when the initial Re concentration in the feed was increased by 50 times. Na concentration in the feed and the strip and had no appreciable impact on either Na or Re flux. Experiments were conducted to demonstrate that Re can be transported against its concentration gradient.

**\*\*Sodium perrhenate was used as a surrogate for sodium perrhenate in all experiments as the former is not radioactive.**

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# LIST OF ABBREVIATIONS

## Abbreviation

|            |                                         |
|------------|-----------------------------------------|
| MTF        | Mass Transfer Flux                      |
| MTC        | Mass Transfer Coefficient               |
| SLM        | Supported Liquid Membrane               |
| EDM        | Extractant-Diluent-Modifier             |
| BLM        | Bulk Liquid Membrane                    |
| HLM        | Hybrid Liquid Membrane                  |
| ODE        | Ordinary Differential Equation          |
| PDE        | Partial Differential Equation           |
| MVWS       | Melton Valley Waste Simulant            |
| Tc         | Technetium                              |
| Re         | Rhenium                                 |
| CE         | Crown Ether                             |
| dtbDCH18C6 | Di-tert-butyl-Di-Cyclohexano-18-Crown-6 |
| DOE        | Department of Energy                    |
| QSS        | Quasi Steady State                      |
| NPOE       | Nitrophenyloctylether                   |
| NPPE       | Nitrophenylpentylether                  |
| ORNL       | Oak Ridge National Laboratory           |

|          |                                  |
|----------|----------------------------------|
| ICAP/ICP | Inductively Coupled Argon Plasma |
| PE       | Polyethylene                     |
| DI       | Deionized                        |
| SAS      | Statistical Analysis System      |
| J        | Diffusive MTF                    |
| N        | Total MTF                        |
| QA       | Quality Assurance                |
| QC       | Quality Control                  |
| CL       | Confidence Level                 |
| GLM      | General Linear Model             |
| REG      | Regression                       |
| ANL      | Argonne National Laboratory      |
| CI       | Condition Index                  |
| VIF      | Variance Inflation Factor        |
| TOL      | Tolerance                        |

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# LIST OF SYMBOLS

## Symbol

|                |                                                   |
|----------------|---------------------------------------------------|
| K              | Overall mass transfer coefficient                 |
| K*             | Apparent overall mass transfer coefficient        |
| F              | Facilitation factor                               |
| K <sub>d</sub> | Distribution coefficients                         |
| C              | Concentration                                     |
| a              | activity                                          |
| J              | Mass transfer flux                                |
| D              | Diffusion coefficient                             |
| d              | Membrane thickness                                |
| V              | Volume                                            |
| A              | Membrane area                                     |
| $\delta \pi$   | Osmotic Pressure                                  |
| t              | Time                                              |
| s              | Ratio of strip over feed distribution coefficient |
| P              | Overall MTC                                       |
| CE             | Crown Ether                                       |
| [CE]           | Crown Ether Concentration                         |
| E or B         | Extractant                                        |

|            |                                      |
|------------|--------------------------------------|
| $k$        | individual mass transfer coefficient |
| $\epsilon$ | Porosity                             |
| $T$        | Tortuosity                           |
| $Re$       | Rhenium                              |
| $ReO_4$    | perrhenate                           |
| $Tc$       | Technetium/pertechnetate             |
| $U$        | Velocity                             |
| $Y$        | Degree of Extraction (Efficiency)    |
| $n$        | Number of Loops                      |
| $w$        | Width of Channel                     |
| $L$        | Length of channel                    |
| $\gamma$   | Activity Coefficient                 |
| $K_x, K_y$ | Equilibrium Constants                |
| $X_A$      | Mole Fraction of A                   |

### Subscripts

|         |           |
|---------|-----------|
| $F,1,a$ | Feed      |
| $S,2,b$ | Strip     |
| $eff$   | Effective |
| $M,m$   | Membrane  |

|       |                                 |
|-------|---------------------------------|
| Re    | Rhenium, perrhenate             |
| I     | Anion                           |
| eq,Eq | Equilibrium                     |
| ext   | Extraction                      |
| si    | Strip Side Interface            |
| O     | At length $z=0$ or time $t = 0$ |
| aq    | Aqueous                         |
| org   | Organic                         |

#### **superscripts**

|   |                                  |
|---|----------------------------------|
| 0 | Initial state (at time $t = 0$ ) |
|---|----------------------------------|

# CHAPTER I

## INTRODUCTION

Radioactive metals in wastes from past and present activities pose major treatment and disposal problems. One type of radioactive waste found at the U.S. Department of Energy (DOE) sites, is "tank wastes" and constitutes about 100,000,000 gallons. Technetium (Tc) is one of the primary radio nuclides found in significant concentrations in these tank wastes. Technetium in these wastes occurs as pertechnetate,  $\text{TcO}_4^-$ . Technetium (VII) is highly water soluble and hence is highly mobile, besides technetium has a very long half life of 200,000 years which makes it a very persistent chemical in the environment (Sheppard, M.I., 1991).

Currently there are no viable technologies for treating technetium. The potential volatilization of technetium poses problems for any thermal treatment of tank wastes (Schulte, E.H., 1984). Ion exchange and precipitation processes are not very selective, have loading limitations, and lead to build-up of technetium. Ion exchange and precipitation also generate large volumes of residuals requiring further treatment and disposal. These process limitations warrant the development of a new process which can accept high loading rates, has no emulsion problems, is very selective, and has high mass

transfer rates. Supported Liquid Membranes (SLMs) offer a new and promising technology for selective separation of technetium from high level tank wastes. SLM technology involves the saturation of the pores of a hydrophobic membrane (polypropylene) with a water immiscible solution of an extracting chemical (extractant), which is typically dissolved in an appropriate diluent (Danesi, 1985). The extractant forms a complex with sodium and pertechnetate ions at the extraction interface. This complex diffuses across the membrane and is stripped at the strip interface. The SLM process takes advantage of high mass transfer coefficients (MTC) and mass transfer area/unit volume possible with micro-porous hollow fiber membrane contactors. Numerous studies have demonstrated that these contactors can achieve more than an order of magnitude greater mass transfer rates than can be achieved in conventional mass transfer equipment such as mixer settlers, packed bed columns etc. (Danesi, 1985; Cussler, 1972). There is also a reduced dependency of the overall mass transfer coefficient ( $K_L a$ ) on flow rates (Danesi, 1985), and a much higher upper limits on pumping rates. Emulsion formation, a common problem in conventional solvent extraction, can be eliminated by proper control of operating pressure (Cussler, 1972; Danesi, 1985; Sirkar et al., 1984; Yang and Cussler, 1986; ). It can be inferred from the preceding discussion that all conventional technetium treatment processes have process and safety limitations and that membrane processes can to a large extent overcome most of these process limitations. Membrane processes also have high selectivity, mass transfer rates and extraction efficiencies. In SLMs, the extractant and diluent are held in a thin membrane, allowing minimal inventory of expensive reagents and low loss of

reagents to the raffinate (treated waste water). Solvent extraction itself is not new and is commonly used in industry including recovery of metals in mining, biochemical production, treatment of metals in mine and industrial wastes, nuclear fuel separations, recovery of uranium and thorium from ores. The use of SLMs for technetium removal is new. Hence the development of an SLM process would offer a potentially economical and feasible technology for technetium removal from tank wastes.

### **1.1 Advantages of SLM Separations**

Some of the advantages of SLM systems include:

1. High selectivities
2. Ions can be pumped "uphill" or against their concentration gradient
3. Higher fluxes than with solid membranes
4. Lower capital and operating cost
5. Expensive extractants can be utilized
6. High separation factors can be achieved in a single stage
7. Potentially high feed/strip volume ratios

### **1.2 Unanswered Questions on the SLM Process**

Even though researchers have developed SLM techniques for the removal of americium and other radio nuclides (Danesi, 1986), there are a number of questions yet

unanswered about the SLM process. Some of these questions include:

1. Is the SLM process technically and economically viable for technetium removal from tank wastes? The answer to this question can be considered yes, if near total removal of technetium is possible at a minimum cost. Most of the research done till now (Danesi, 1985; D'Elia and Cussler, 1986) have focussed on the extraction permeability in SLMs. Very little has been done to determine the overall process efficiency, design parameters, and cost. This investigation aims at initially determining the basic mass transport parameters which would be incorporated in an engineering model to predict design parameters for any waste. Objective 2.2.2 outlined in Chapter 2.0 aims at answering this question.
2. Is it possible to transport technetium against its concentration gradients without an hydrogen or hydroxide driving force (pH effects)? Past research by Cussler (1972), Danesi (1985), predict that it is impossible to transport an ion against its gradient in co-transport (without pH effects) which involves simultaneous transport of a cation and anion across a membrane to maintain electroneutrality. The model presented in Chapter 5 however, shows that such an "up-hill" transport is possible if the ratio of strip over feed distribution coefficient ( $K_{d2}/K_{d1}$ ) is made smaller than the ratio of feed concentration over the strip concentration. Such a transport would result in substantial reduction in waste volume. "Up-Hill" transport

is defined as the diffusion of a component against its apparent concentration gradient. The driving force for such an uphill transport is provided by the term in the parenthesis of Equation 5.8 ( $C - C^*$ ).

Objective 2.2.3, Chapter 2 aims at answering this question.

3. Do the stripping process variables such as velocity, chemical composition and distribution coefficients have any influence on the overall mass transfer coefficients and mass transfer flux? Danesi's model is based on the assumption that stripping process has no significant effects on overall mass transport. Objective 2.2.2, Chapter 2 aims at answering this question.
4. Is the membrane stable during continuous operations? One of the primary reasons for the limited use of SLMs is the lack of information on the stability of the membrane over an extended time period. Solvent losses due to capillary pressure effects in the pores of the membranes can prove to be very costly and could impact the overall process economics. Objective 2.2.5, Chapter 2 aims at answering this question.
5. Can an SLM model be developed which can predict process performance, supply design data and estimate system cost? The author recognizes that it is practically impossible to determine all design parameters experimentally

for all different technetium removal scenarios. Objective 2.2.1, Chapter 2

aims at determining a comprehensive mathematical model.

This proposed investigation will aim at providing answers to most of these unanswered questions.

### **1.3 Process Overview**

Figure 1.1 shows a schematic of a flow through SLM system. The feed laden with the contaminants (in the present case, sodium nitrate and sodium perrhenate) enters on one side of the membrane and exits from the SLM as the raffinate (a term, usually is used for a solution devoid of the solute, or having a solute concentration less than the feed solution). The strip solution, deionized water, is introduced in a co-current manner on the other side of the membrane and exits as the extract (a solution rich in solute concentration). The SLM pores are saturated with the Extractant-Diluent-Modifier (EDM) organic solution. Facilitated or extractant mediated diffusion based transport occurs from the feed to the strip side of the membrane.

### **1.4 Crown Ether and the Choice of Rhenium as Technetium Surrogate**

Figure 1.2 shows the structure of dtbDCH18C6 (crown ether) used in this study (Bonnessen, P.V., 1995). DtbDCH18C6 has 6 oxygen atoms each connected to two carbon atoms, besides two cyclo hexano rings and two tert butyl groups. This crown

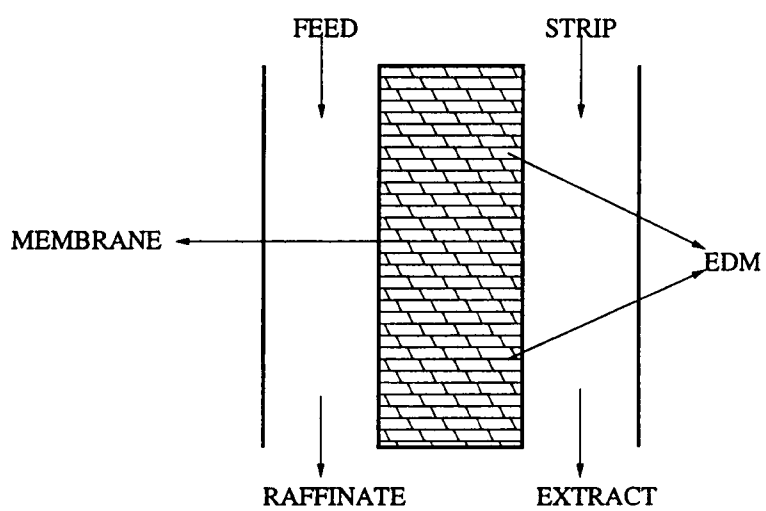


FIGURE 1.1: SCHEMATIC OF PROCESS FLOW STREAMS IN AN SLM

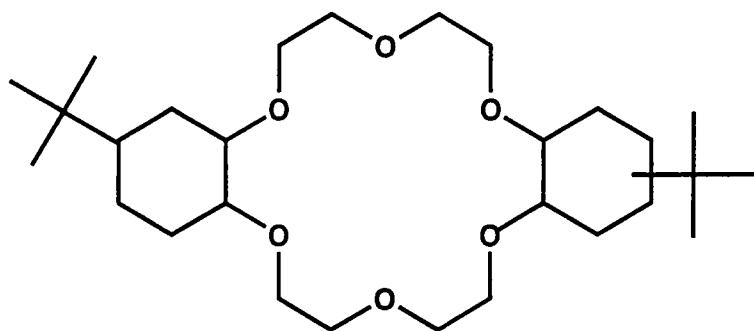


Figure 1.2. 4,4',5'-di(*t*-butyldicyclohexano)-18-crown-6 (abbreviated di-*t*-BuCH18C6).

ether has a ring size which matches very well with potassium and strontium atomic sizes but it also can very effectively bind sodium (Bonnessen, P.V., 1995). Since the actual DOE wastes contain both potassium and sodium ions, dtbDCH18C6 was selected for the study. The presence of other divalent ions like calcium, magnesium in the waste does not have any impact on the system as dtbDCH18C6 does not transport divalent ions because of their larger atomic sizes. Perrhenate was preferred over its competitor nitrate because organic solvents prefer lower hydration energy, more oxygenated anions and larger size anions. Perrhenate is larger in size, has one more oxygen atom and has less hydration energy than nitrate and hence was the preferred anion.

Rhenium was used as the surrogate for technetium because technetium is radioactive and rhenium, technetium and manganese all belong to the same group VIIB. Elements of the same group in the periodic table exhibit similar properties and can often be used as surrogates for each other. In the present case manganese was not used because its anion, permanganate, is a strong oxidizing agent. It is interesting to note that batch tests at ORNL have shown that Tc was always extracted more than rhenium by a factor of 2.

## **CHAPTER 2**

### **RESEARCH OVERVIEW**

#### **2.1 Goal**

The overall goal of the research project was to determine the technical feasibility of selective perrhenate extraction, transport and concentration across a supported liquid membrane.

#### **2.2 Project Objectives**

The following specific objectives and tasks were established in order to accomplish the overall goal of the research project.

##### **2.2.1 Comprehensive Mass Transport Model**

Development and testing of a mass transfer model for rhenium/technetium removal in an SLM. Such a model would allow calculations for scale-up to full scale equipment.

###### **2.2.1.1 Tasks**

Task 1. Development of a mass transfer model from fundamental

principles for open and closed loop SLMs.

- Task 2. Development of a statistical model based on multiple regression of mass transfer flux (MTF) data.

## **2.2.2 Determination of Optimal Mass Transport Parameters**

Determination of the mass transfer coefficients for the optimal extractant and diluent concentrations for simulated rhenium containing wastes. Determination of the optimum extractant, modifier and diluent concentrations, and the effect of flow rate, and anion and cation concentration in the feed and strip solutions on technetium extraction in a flat sheet SLM.

### **2.2.2.1 Tasks**

- Task 3. Determination of the optimum extractant-diluent-modifier (EDM) combination in terms of their relative overall MTCs and selectivity.
- Task 4. Determination of the optimal crown ether concentration in terms of mass transfer flux and process selectivity.
- Task 5. Determination of the optimal feed and strip flow velocities which yield the highest MTC and selectivity.
- Task 6. Determination of the effect of change in sodium and rhenium ion concentrations in the feed solution on MTC

and selectivity.

- Task 7. Conduction of computer simulations on steady-state open-loop mass transport in an SLM and to experimentally verify the results.
- Task 8. Determination of the overall MTC, P, aqueous feed, membrane phase and overall mass transfer coefficients and mass transfer flux for perrhenate in a tank waste simulant.
- Task 9. Development of a correlation between open-and closed-loop MTCs.
- Task 10. Determination of the relationship between MTC and membrane thickness.
- Task 11. Determination of MTCs for Nitrophenylpentylether (NPPE) systems.

### **2.2.3 Up-Hill Transport**

Determination of the conditions by which rhenium/technetium can be concentrated in the stripping solution thereby resulting in a reduction in waste volume.

#### **2.2.3.1 Tasks**

- Task 12. Determination of conditions for "up-hill" transport of

perrhenate in a simple waste simulant across an SLM.

- Task 13. Determination of the conditions for up-hill transport using Melton Valley Waste Simulant (MVWS), a simulant of an actual DOE Oak Ridge waste.
- Task 14. Determination of equilibrium or "Quasi Steady State" (QSS) concentration in an SLM.

#### **2.2.4 Kinetic Analysis**

Determination of the apparent equilibrium constants using kinetic analysis on MTF data and the determination of the diffusion coefficients without the need for any batch solvent extraction experiments.

##### **2.2.4.1 Tasks**

- Task 15. Determination of the distribution coefficients using batch experiments and apparent equilibrium constants and diffusion coefficients of perrhenate (Tc surrogate) in advanced extractants using kinetic analysis on mass transfer flux data.
- Task 16. Determination of whether free ions or ion pair transport constitute the predominant means of mass transport in the membrane when Nitrophenyloctylether (NPOE) is used as a

diluent.

- Task 17. Determination of the average crown ether loading, complexation constants and diffusion coefficients using kinetic analysis.

### **2.2.5 SLM Stability**

Determination of the stability of the membrane under actual operating conditions. Gradual loss of the extractants and diluents is called membrane instability and would limit the run time of a membrane as well as increase costs and potentially release undesirable contaminants in to the raffinate.

#### **2.2.5.1 Tasks**

- Task 18. Determination of the long term stability of the SLM.

## **2.3 Phases of Study**

### **2.3.1 Mathematical Mass Transport Model**

The objective of this phase was to develop a comprehensive mathematical model capable of predicting mass transfer flux and mass transfer coefficients for open- and

closed-loop SLMs. Such a model would be extremely useful for process scale-up and also for parameter predictions and extrapolations.

### **2.3.2 Mass Transfer Flux (MTF) Experiments**

The objective of these set of experiments was to determine the best membrane phase composition from a series of extractants and diluents, and to determine the mass transfer fluxes for the best membrane composition as a function of extractant concentration, feed and strip velocities, feed and strip composition and 4) membrane thickness.

### **2.3.3. Mass Transfer Coefficients (MTC) Experiments**

The objective of this set of experiments was to determine the overall MTC and the individual aqueous feed and strip MTCs as a function of Reynolds number and the membrane MTC. These data were later compared with the computer simulation data based on the mass transfer model.

### **2.3.4 Melton Valley Waste Simulant Experiments**

The objective of this set of experiments was to determine the feasibility of the SLM system studied thus far in selectively extracting, and transporting perhenate from a

simulant of an actual complex waste stored at the Melton Valley complex in Oak Ridge, TN.

#### **2.3.5 Statistical Analysis**

The objective of this phase was to obtain a multiple regression of MTF with all its predictor variables and to statistically determine which variables are significant at a 95% confidence level in predicting MTF. This statistical model could also be used for predicting MTF through intrapolation without the need for any experiments.

## **CHAPTER 3**

### **LITERATURE REVIEW**

#### **3.1 Supported Liquid Membranes**

##### **3.1.1 An Overview**

Liquid membrane transport process is an emerging new technology where specific material species are transported selectively and rapidly across a liquid membrane. Though SLMs were invented in the early 1970s, the bulk of experimental studies involving SLMs for metal removal have been carried out in the last ten years, e.g. Danesi (1986c), Chirazia (1991a), Stolwijk et al. (1987). Way et al. (1982) surveyed the applications of liquid membranes in general including those for metal ion removal. Schultz and Goddard (1974a,b), and Goddard (1977) reviewed both the theoretical and experimental aspects of general facilitated transport systems. Danesi (1985) both reviewed the work being carried out at the Argonne National Laboratory on separation of metal species by SLMs, and also developed simple equations to describe the metal ions transport by SLMs. Yinger's paper (1987) describes the basic principles involved in the application of SLM transport processes for recovery and separation of metals from aqueous solutions which include passive and active transport, aqueous and membrane diffusion, and chemical reactions.

As indicated in Yinger's paper (1987), transport of a metal ion across an SLM is accompanied by transport of another ion either in the same (co-transport) or in the opposite direction (counter-transport) of the metal ion transport. The concentration gradient of this second ion often provides the driving force for the transport of metal ions, thus making possible the transport of metal species from dilute to concentrated solutions. Such "uphill" transport is a remarkable feature of facilitated transport. A liquid membrane combines solvent extraction and stripping operations in one unit and ideally can hold the organic phase extractant and diluent indefinitely. Hence, as per Yinger (1987), SLMs have several advantages over conventional solvent extraction systems.

Utilization of an SLM, as per Danesi and Vandegrift (1986a), is especially suitable for recovery of metals, since the metal species usually are in aqueous phases and also prefer to be in aqueous over organic phase, and a variety of organic phase extractant/diluent combinations relatively immiscible in water have been identified, thus satisfying a key condition for an SLM. Compared to emulsion membranes, SLMs have an additional mass transfer resistance but avoid problems associated with emulsification, demulsification and emulsion stability. A number of laboratory studies have been made to assess the effectiveness of SLMs for metal separation, concentration and recovery for a number of metals. For example: Richley Yinger (1987)- Co/Ni; Danesi (1984)- Cu, An/Cd, Ni/Co, Eu/Am, and Lanthanides/Actinides; Nishiki and Bautista (1985)- Pt; Takahasi and Takeuchi - Cu (1985); Harada (1984)- Fe, Zn, Fe/Zn; Pearson (1983)- Cu, Cr; Babcock et al. (1980 a&b)- U; and Stolwijk et al. (1987)- K.

A simple SLM is essentially a single stage operation thus limiting the achievable separation. A novel idea developed by Danesi was that of a composite SLM. A composite SLM combines a simple SLM with a complementary SLM such that the strip solution of the first SLM acts as the feed solution of the second SLM. A complementary SLM requires a second reagent which can further extract the target species from the stripping solution of the first SLM. Several composite SLMs can be arranged in series to improve separation efficiency. Another idea tried by Harada was to use a second reagent in the simple SLM which will back transport the competing species from stripping solution.

### **3.1.2 SLM Applications**

Supported Liquid Membranes have applications in the following chemical and environmental engineering unit operations.

1. Supported Liquid Membranes can be used for metal ion recovery from electroplating, hydro metallurgy, and mining process waste streams. SLMs can also be used for separation and recovery of rare earth metals, precious metals namely platinum, palladium and silver. However membrane stability must be improved before the process can be commercialized (Danesi, 1985; Danesi and Chirazia, 1987).

2. SLMs can also be used for cyanide and other anions recovery from iron & steel, photographic bleaching, metal plating and finishing industries (Danesi and Vandegrift, 1986 a).
3. SLMs can also be used for pigment recovery from automobile and paint industry wastes, ink and dyes recovery from textile and paper industry wastes (DOE Report, 1990).
4. Facilitated SLM transport is viewed as a natural separation technique for unstable, costly biochemicals such as proteins, amino acids, antibiotics, glycerides where fast high purity separation are imperative (DOE Report, 1990).
5. Radio nuclides and transuranics separation can also be very effectively accomplished in an SLM (Danesi, 1984, 1985).
6. Finally, gas separation offers significant potential for the commercialization of the SLM process. Some of the interesting gas separations which can be very effectively accomplished in an SLM include, oxygen separation from air, carbon monoxide separation from natural gas, hexane recovery from polyolefin degassing units, and hydrogen sulfide separations (DOE Report, 1990).

### 3.1.3 Cussler and Facilitated Transport

Cussler (1972) pioneered facilitated transport and SLM research by formulating the mass transport model involving the transport of an ion pair complex inside the pores of the membrane. He used the distributed parameter approach based on the continuity equations and Ficks second law to describe such a transport. Several other researchers including Goddard (1977), Smith et al. (1977) and Smith & Quinn (1980) also followed a similar modeling approach. Others, most notably Ward (1970) transformed Cussler's model in a dimensionless form to predict steady state membrane concentrations. Cussler also pioneered the process of liquid-liquid extraction with microporous hollow fibers. These reactions are unusually fast because of the large surface area per unit volume in these modules. He found that extractions in hollow fibers were fastest when the fibers were wet by the fluid in which the solute was most soluble. D'Elia and Cussler (1986) found that when the Reynolds number within the fibers is less than 400, the flow is laminar and the mass transfer coefficient is given by the Sherwood equation.

Cussler also authored a book "Diffusion", wherein he described in detail the mechanics of facilitated transport in SLMs. In it a complete chapter has been devoted to facilitated transport. As per the book facilitated transport is by far the most complex of all membrane based unit processes. As per Cussler, Stein was the first to point out some of the salient features of facilitated transport which are:

1. Fluxes can be much more strongly coupled than is expected from in vitro

experiments of multi component diffusion.

2. Fluxes vary linearly with small concentration differences across membranes, but reach a maximum value at large concentration differences.
3. Fluxes are much larger than expected from the solubility of the solutes in the principal membrane components.
4. The transport can be very selective but can be poisoned.

This process can be explained by small amounts of reactive molecules, or "mobile extractants", moving within the membrane. Also facilitated transport shows many characteristics of enzyme kinetics and so can be interpreted with familiar mathematical equations developed for enzyme kinetics. Cussler happens to be one the few researchers who has attempted to model facilitated transport on the basis of Michaelis Menton equation (1984). Equation 6.10 in Chapter 6, describes the MTF in the form of the Michaelis-Menton Equation. He was also the first researcher who correctly stated that the driving force in coupled ion co-transport is based on the difference between the product of the activities of the coupled anion and the cation across the membrane and not on the individual activities of the cation or the anion (1984).

Cussler (1972) also offered solutions to the peculiar phenomena unique to facilitated transport observed by Stein while studying facilitated transport in biological systems. These solutions are:

1. Solute-extractant complex formation can explain all the above mentioned points

observed by Stein during his study of multi component diffusion (Cussler, 1984).

Fluxes can be very strongly coupled when two diffusing solutes react competitively or cooperatively with the mobile extractant.

2. Fluxes reach saturation limits if there is insufficient amount of the mobile extractant present in the membrane to carry the solutes and the complex.
  3. Fluxes are much larger than expected because of the small amounts of mobile extractant solubilizing the diffusing solute.
  4. The transport can be selective because the extractant-solute reaction is selective.
- However irreversible reactions can easily poison facilitated transport.

Cussler was also the first to point out that in membranes of high dielectric constants, ionic solutes will be the dominant means of facilitated transport and in low dielectric constant membranes ion pair form the predominant means of membrane transport. Cussler was also the first to present in detail the contrasts between co- and counter-ion transport both mathematically and experimentally (1984). He was also one of the first to define that the energy for facilitated transport or the driving force for a non ionic solute is obtained from the concentration difference of the diffusing solute (1984).

Cussler also studied in detail the transport of electrolytes across SLMs containing membrane solution of low dielectric constant (1978). In such a membrane, transport can occur by diffusion of both free ions and ion pairs. This process is called as "parallel transport". In this process, transport begins when ions from the concentrated aqueous

solution are dissolved in the membrane. Once inside, they may react to form ion pairs. However, since ion pairs form quickly, this fraction is close to equilibrium throughout the membrane. After diffusion across the membrane, both ions and ion pairs move out of the membrane into a much more dilute aqueous solution. This diffusion mechanism is similar to facilitated transport with the exception that the electrolyte acts as its own mobile extractant thus obviating the need for any external extractant. The mechanism is also similar to conductance in films of low dielectric constant. This work is less common with diffusion across ion exchange membranes, in which the ions interact electrostatically with fixed charges in the membrane. Cussler also found that fewer membranes allow simultaneous transport of free ions and ion pairs across membranes. This is possible only if the electrolyte shows sufficient solubility in both the membrane solvent and in water and when the membrane solvent has a dielectric constant around 10-15 so that both ion pairs and free ions are present in significant concentrations. The solvent must be relatively insoluble in water, show a low vapor pressure and have a high viscosity. The fast flux in electrolyte transport is because of the formation of ion pairs and can be even an order of magnitude greater than the flux associated with free ion transport alone. However, contrary to facilitated transport, the flux would not reach a maximum because one cannot add solute without adding more extractant. Similarly the extractant cannot be poisoned without poisoning the solute as the solute also happens to be the extractant (Cussler, 1984).

Cussler also showed that facilitated transport is possible even when the extractant

is covalently bound to a solid membrane if the extractants still have some limited mobility. The solute flux across such chained extractant membranes varies with solute concentration just like the flux across mobile extractant membranes. Chained extractant membranes are getting popular because they significantly enhance membrane stability. The mechanism is labeled as the "bucket brigade" in which a solute bucket is passed from one extractant hand to the next. It is less like an exchange reaction in surface diffusion, because the reaction and diffusion steps are separately regarded. It is also unlike polymer diffusion by reptation, a process involving the movement of an entire polymer molecule. Surprisingly however, Cussler found that chained membrane transport behaves very similarly in some ways to facilitated transport involving mobile extractants (1989). Solute fluxes vary linearly with solute concentrations at low concentrations while reaching an asymptote value at high solute concentrations. They will have fluxes which increase with the extractant concentration, possibly at greater than the first power. These fluxes are also very selective. The similarities with mobile extractant based transport end there and the differences show up. These differences are 1) chained extractant membranes may show a percolation threshold. This can occur when one chained extractant can just reach the other extractant, 2) chained extractant must have some mobility as when there is no mobility there is no facilitated diffusion and these extractants show facilitated diffusion, 3) apparent diffusion coefficients in chained extractants may reflect chemical kinetics and not diffusion.

Kalachev et al. (1992) extracted and transported cobalt and iron across SLMs.

They obtained a local maximum in flux at initially a low extractant concentration and then a sharp increase in flux followed by a global maximum at a much higher extractant concentration in the membrane solution. This phenomenon was explained by connecting it with the "jumping mechanism" membrane transport which had earlier been theoretically predicted by Cussler, as opposed to the more common facilitated transport mechanism. Such a membrane transport is realized in a narrow interval of the extractant, is more effective than the conventional mechanism. As per the authors, to obtain the desired effect one needs to hold such an SLM under transfer conditions during a certain period of time, in order for the membrane medium in the "jumping" region to become self organized and self-fitted for the membrane transport process. The mechanism involves the following:

1. Flooding the membrane pores with such a high concentration of the extractant in the diluent so that the extractant molecules virtually arrange themselves as a chain from one end to the other end of the membrane.
2. The solute molecule is passed from one extractant molecule to other similar to goods being passed from hand to hand in a human chain.

#### **3.1.4 Danesi and the Lumped Parameter Model**

After Cussler, the research group at the Chemistry Division at the Argonne National Laboratory initially headed by Dr. Danesi and later by Dr. Chirazia have conducted some of the most significant research in the areas of facilitated transport and

SLMs. In one of his most important papers, "Separation of metal species in SLMs", Danesi (1984-85) remodeled facilitated diffusion transport across an SLM using the lumped parameter approach. This model is one of the most widely quoted and popular models in SLM literature since 1984 and is the basis of the model developed by the author in this dissertation. Danesi subdivided the SLM facilitated transport into various subprocess involving aqueous boundary layer effects, interfacial chemical reactions, membrane diffusion, and feed and strip side distribution coefficients. This at steady state, resulted in a simple yet experimentally verifiable permeability expression. The paper discussed separate equations for dilute and concentrated solutions. Equations 3.1 and 3.2 describe the mass transfer coefficient for dilute and concentrated solutions, respectively.

$$\ln \frac{C}{C_o} = -\frac{A}{V} P t \quad (3.1)$$

$$C = C_o - [E] k_m \frac{A}{V} t \quad (3.2)$$

where:

|             |   |                                                              |
|-------------|---|--------------------------------------------------------------|
| P           | = | The overall MTC, cm/s                                        |
| $k_m$       | = | The membrane mass transfer coefficient, cm/s                 |
| C and $C_o$ | = | Concentrations at ant time t and time t=0<br>respectively, M |
| [E]         | = | The concentration of the extractant, M                       |

A = Membrane surface area,  $\text{cm}^2$

V = Volume of the feed tank,  $\text{cm}^3$

The only limitations in the whole design were that 1. Danesi ignored the strip side resistance in the overall MTC as he considered the strip side distribution coefficients and/or the strip side concentrations to be negligible (1984), which are true only in some cases and 2. The fundamental principle governing facilitated transport, as outlined by Cussler, which states that in co-transport of an anion and a cation the product of the activities of the cation and anion and not the individual concentrations, dictate transport kinetics was ignored. Danesi's model involves the concentration of only the transportable ion. This model is valid only when a neutral organic solute is being transported across an SLM. For ionic transport this model at best can serve only as an approximation.

Danesi (1985) experimentally verified their model using both flat sheet and hollow fiber SLM modules on several SLM systems utilizing a variety of membrane extractants and metal species. By using derived permeability equations, simple mathematical expressions were also developed for the separation factors or selectivity. Their model could predict the extent of separation that is achievable in an SLM and how this separation was affected by concentrations and hydrodynamic conditions. As per Danesi's research results, use of a single SLM is insufficient to obtain clean separation between similar metals say sodium and potassium. In this case composite SLMs, consisting of two complementary SLMs sandwiching a suitable aqueous solution, can be

used in series to perform a multistage separation. They also concluded that:

1. Membrane stability is decreased when one of the aqueous solutions contains high pH solution as the water solubility of the membrane solutions increase with pH.
2. SLM life-times of over two months are obtained with their diluent/extractant when Accurel polypropylene hollow fibers are used and when the outside and the inside hydraulic pressures are balanced.

Danesi (1986 c) in another paper addressed the issues when the strip side distribution coefficients and/or concentrations were not negligible. A new equation, very similar to the equation developed by the author of this dissertation, describing the permeation rates under such conditions was developed and was experimentally verified by measuring the distribution ratios and the permeability rates. The conclusions reached were that deviations from the first order rate law, often observed when measuring the coupled transport of metal species at low concentrations through SLMs, originate because of the non-negligible distribution ratio at the SLM-strip solution interface. Nevertheless, these deviations can easily be taken into account in a quantitative way and, by an appropriate linearization of the permeability data, information can now be obtained on an actual overall MTC (1986). However, even after the publication of this paper in 1986, subsequent research models developed by the same group and by other groups have ignored this deviation.

Danesi and Chirizia (1983 a) also experimentally verified the fundamental

principles involving the selective separation of Cadmium from zinc in a composite and simple SLM. They concluded that separation of metal ions from aqueous solutions can be done in SLMs when sufficiently different overall MTCs,  $P$ , are exhibited by the metal species. In a separate study the same set of researchers found out that under cases of high concentrations in the aqueous feed solutions, where the extractant molecule is completely converted into the metal-extractant complex, the membrane flux becomes independent of the metal feed concentration and reaches a limiting value which only depends on the extractant concentration, the diffusion coefficient of the metal-extractant complex and the membrane thickness (Danesi and Chirizia, 1982).

After the departure of Danesi from Argonne National Laboratory (ANL) to Europe, Chirazia headed the SLM group at ANL. Chirazia (1991) studied technetium extraction in SLMs from DOE Hanford wastes. The aqueous feed solutions used in that study were highly acidic at a pH of 2 as compared to highly alkaline/neutral wastes used in the present study. Chirazia used amines for technetium extraction and found that the amine with the lowest basic strength showed the highest Tc extraction and the order of extraction was reverse of the nitrate anion extraction. The diffusion coefficient was smaller than the nitrate distribution coefficient (1991).

### 3.1.5 Solvent Extraction and SLMs

Significant research on SLMs has also been done at the Stevens Institute of Technology and at NJIT by the group headed by Sirkar. This group has studied SLM transport from mass transfer coefficients point of view. Most of their work has focussed on using hollow fiber membranes for liquid-liquid extraction. They did not impregnate the membrane with organic solution but instead, the organic solution was pumped either through the shell or the tubes of the module. Their system required separate extraction and stripping modules. They found that solvent extraction can easily be accomplished in a hollow fiber membrane system by maintaining the aqueous phase at any pressure greater than that of the solvent but lower than that necessary for displacement of solvent from the pores by water. They modeled the transport on the basis of unhindered diffusion of a solute through solvent filled tortuous pores of a microporous medium of uniform pore size (Sirkar et al., 1984, 1986). Sirkar and Basu (1991) in a recent study also introduced a new type of membrane system namely the "Hybrid Liquid Membrane (HLM)". HLMs can be configured in a flat sheet mode or in a hollow fiber mode. HLMs are different from SLMs because they do not contain a solution of the extractant, dissolved in a diluent impregnated inside the pores of the membrane, but instead consist of a separate organic solution which flows either between two flat sheet membranes or in a select set of hollow fibers. This facilitates a continuous removal of extracted compounds and is considered very applicable in the fermentation industry. In a typical fermentation process there is a continuous evolution of new products with the duration of

the process.

Kim (1984) conducted studies on the feasibility of membrane based solvent extraction for the selective removal and recovery of metals. He used a microporous membrane as an interface between an aqueous solution and organic solvents containing liquid ion exchangers. Metal ions were transported from the aqueous solution to the organic phase at the interface created in the pores of the membrane. The organic solution loaded with metal ions in the extraction module, is regenerated in contact with the stripping solution in a separate stripping module. One important gain from this system was improved process stability and flux. The disadvantage is the need for a separate stripping module.

Tompkins and Peretti (1992) did considerable research using NPOE as the SLM diluent. His research involved p-nitrophenol extraction and transport across a hollow fiber SLM. The overall mass transfer coefficient for the extraction was measured and analyzed in terms of the individual resistances to mass transfer. The resistance to mass transfer of the tube side boundary layer and membrane were found to be controlling, while the shell side boundary layer resistance was negligible. The tube side boundary layer resistance agreed well with the prediction based on the Sherwood number correlation for well developed laminar flows in tubes. The experimentally measured membrane overall MTC was substantially smaller than that predicted for solute diffusion through octanol occupying the membrane pores; flow maldistribution and channeling of

the solvent in the shell space was believed to be the most probable cause of this disparity.

Plucinski and Nitsch (1989) attempted to calculate the SLM permeability rates based on the already known kinetics of liquid-liquid extraction. They used the system zinc(aq)-dithizone-carbon tetrachloride because of its very well known mechanism and kinetics of extraction. They used general step model based on the summation of resistance in series model to describe SLM mass transport and used standard programs to numerically integrate the system of equations. A good fit between experimental and predicted data was obtained showing that SLM transport can be predicted on the basis of good knowledge of liquid-liquid extraction and hydrodynamics of the apparatus.

### **3.1.6 SLM Stability**

In spite of the success of the SLMs in the laboratory very few pilot scale studies have been undertaken. The primary reason for this low utilization are low flux rates and membrane instability. Hollow fiber technology which offers high surface area per unit volume and hence a compact unit can overcome the low flux limitation. Membrane instability generally occurs because of the gradual loss of the extractant-diluent in water. Such loss can occur because of:

1. The water solubility of the extractant and diluent (Danesi and Vandegrift, 1986 a,b).
2. Capillary displacement of pressure between the two sides of the SLM due to

aqueous solution pumping (Danesi, 1984-85; Pearson, 1983).

Such losses are not likely to be totally eliminated but may be reduced by improving the membrane porous structure or by improving the hydrophobic characteristics to reduce capillary pressures or by using highly lipophilic solvents. Another possibility is to continuously impregnate the membrane with the extractant solution by carrying it along with the stripping solution (Takahasi and Takeuchi, 1985; Pearson, 1983). The use of NPOE and NPPE as membrane diluents have offered very stable membranes even after 90 continuous days of operation (Stolwijk et al., 1987).

SLM instability defined as the gradual loss of the organic membrane solution due to aqueous solubility losses, is one the prime causes for relatively slow commercialization of the process. Significant research has been conducted at various institutions to determine the causes for this membrane instability however, a permanent remedial solution is still at large. Neplobreck et al. (1992), have studied in detail the SLM instability effects and have concluded that contrary to literature data this instability is not caused by osmotic pressure differences. They also found that Accurel membranes provide the most stable SLMs. They used a Laplace equation to model the maximum acceptable pressure difference across an SLM. They concluded that SLM instability resulted from lack of sufficient solvent-water interfacial tension and low critical surface tension of the polymer support.

SLM instability can be further subdivided into 1. Arising because of loss of

extractant from the membrane phase leading to a loss in permeability, and 2. A complete "break down" resulting in direct water transport between the two water phases. The complete "break down" effect can be explained with the help of the osmotic pressure gradients across the membrane. Water transport increases with this gradient and this transport induces a repulsion of the liquid membrane phase out of the pores of the support which causes the SLM to degrade (Fabani and Merigiole, 1987). Fabani (1987) concluded that osmotic pressure differences play a significant role in determining membrane stability. These osmotic pressure differences wash the organic solution from the pores of the membrane. However, Danesi (1987) concluded after a series of experiments that the "osmotic pressure model" was not responsible for membrane instability. He and Takeuchi and Takahasi (1987) found that this form of instability was due to the poor nature of the solvent and low solvent water interfacial tensions. The author of this dissertation also concludes that osmotic pressures do not play an important role in determining SLM stability as such high pressures are never realized. In the present study, a typical feed solution consisted of 1 M sodium nitrate and 0.1 mM sodium perrhenate dissolved in deionized (DI) water. The strip solution was pure DI water. As per Cussler (1984) Equation 3 defines the osmotic pressure across a membrane separating two solutions.

$$\Delta\Pi = nRT (C_{iF} - C_{iS}) \quad (3.3)$$

where:

$\Delta\Pi$  = The osmotic pressure, atm

$R$  = Gas constant,

$T$  = Temperature in  $^{\circ}\text{K}$ ,

$n$  = Number of ions per mole.

At  $25^{\circ}\text{C}$ , this osmotic pressure equals 48.9 atm. or 720 psi. It would take about 1" thick steel pipe to contain this pressure. This pressure is never realized unless the membrane has sheared and there is a water flow through the membrane from the strip to the feed solution. In such a case there would be a gradual decrease in strip solution and an increase in the feed solution volumes when operated in a recirculating mode. Since this change in volumes was never observed, it can be reasonably concluded that such osmotic pressures were never realized.

Takeuchi and Takahashi (1987) also found that membrane instability increased with aqueous feed velocity and also with increasing hydrostatic pressure gradient across the membrane. Neplebroeck et al. (1992) concluded that SLM instability can be accounted by studying the type of solvent used and the molecular structure of the extractant. There was no direct relation between viscosity of the organic solution and membrane instability but there was some connection with the interfacial tension. However these relations are not unambiguous. The overall consensus was that SLM instability was not caused by osmotic pressure differences. Neplebroeck et al. (1992) also suggested two ways to improve this process stability by:

1. Gelation of the matrix holding the extractant molecule

2. Application of a stabilization layer between the extractant phase and the feed phase.

Chirazia (1991) reported that use of amines as membrane solvent lead to maximum stability when compared to aliphatic diluents. Also, even among the amines the order of stability was tertiary > secondary > primary. This is the reverse of the order of the amine solubility in water and of the interfacial tension lowering at the water-organic solution interface. Use of polymers which can cross link the extractant to the support can increase SLM stability. Also, hollow fiber modules are more stable than the flat sheet module because the fibers have greater thickness and because of the compaction achieved by the packing of hollow fiber bundle.

Davis and Neukom (1992), conducted several studies with the main objective of comparing experiment and computation values relating to SLM stability. However, fundamental uncertainties in determining the critical transport coefficients made a purely predictive analysis of the transient stability data very difficult. Sinbo and Yamaguchi (1993) investigated the effect of membrane solvent on transport efficiency and membrane stability in a crown ether-mediated amino acid transport system. They found that NPOE was the most stable among over 50 organic solutions used in the study. NPOE-SLM systems were stable for over 90 days. They concluded that membrane solvent must have high dielectric constant and low solubility in water for the SLMs to be highly stable and permeable.

Takeuchi and Takahashi (1987) found that pore size had the greatest effect on membrane stability. Smaller the pore size, greater was the SLM stability. This is because the effect of capillary pressures on membrane lifetimes was significant for bigger pore size systems. He also concluded that the critical surface tension of the support as a measure of its surface energy is more sensitive to the variations in interfacial tension. The critical surface tension of the support must be higher than the organic aqueous interfacial tensions. Dozol et al. (1993) concluded that for enhanced membrane stability water solubility of the solvent must be less than 12 g/l and simultaneously the drop point of the SLM (as proportional to the interfacial tension) must be higher than 1.1 bar. The diluent must have surface tension lower than the critical surface tension of the support. The organic solution viscosity however, has no effect on membrane stability.

### **3.1.7 Anion Transport in SLMs**

Most of the research conducted has focused on the transport of cations across SLMs. Molnar W.J., and Cussler E.L., are some of the few researchers who have conducted studies on anion transport across an SLM. As per Molnar et al. (1978), facilitated diffusion can increase both the flux and selectivity of transport across membranes. Such diffusion is achieved by the use of a mobile carrier, a molecule which reacts selectively with the solute of interest and diffuses with it across the membrane. Their research was based on facilitated diffusion capable of concentrating anions with energy supplied by the diffusion of hydroxide ions. As such, the process is a mirror of

the other systems which concentrate cations by the diffusion of protons. However, experimental results are not completely analogous to cation transport and illustrate interesting complexities in the chemistry of facilitated diffusion. They found that the potential selectivity of the anion membrane was less than that of the cation membrane because for cation membranes there are a number of exotic chemicals like crown ethers capable of high selectivity. For anions such materials are less common and hence selectivity is less.

Sumi and Nakamura, (1994) studied the selective up hill transport of cyanide ion across bulk liquid membranes (BLMs) and SLMs. NPOE was used as the diluent and dichloromethane was used as the extractant. They found that the OH ligand was easily substitutable with the cyanide anion. The equilibrium constant of the reaction with cyanide ion was much higher than those with halide ions. From kinetic analysis of the transport experiments, the fluxes of cyanide ion were affected by the diffusion process of the extractant molecule in the membrane. This was especially true in the case of the SLM where the low flux was mainly caused by the small diffusion of the extractant molecule in NPOE.

### **3.1.8 Crown Ether based SLM systems**

Dr. Reinhoudt's group, University of Twente, The Netherlands have made a significant contribution towards the understanding of crown ether based SLM chemistry

and mass transport (Stolwijk, et al., 1987, 1989, 1990). They were the first to develop with a mathematical model which could determine whether the transport in the SLM was due to free ions or ion pairs. They also showed the procedure of estimating equilibrium constants, crown ether loadings, partition coefficients, diffusion coefficients from mass transfer flux experiments without the need for any batch experiments. They also found that for NPOE systems, free ion transport was predominant inside the membrane (a similar result was also obtained by the author of this dissertation), membrane diffusion was rate limiting and that the membrane stability can be significantly improved by increasing the lipophilicity of the crown ether without any drop in the diffusion coefficient. They also determined that by binding the crown ether with polysiloxane compounds significant membrane stability improvements can be made and there is no drop in mass transfer flux (Stolwijk et al., 1987, 1989, 1990). Equation 3.4 describes the MTF for an ion pair transport in an SLM. Equation 6.9 in Chapter 6 describes MTF for free ion transport.

$$J = \frac{k_m (K_{dl}) [A^+][B^-]}{1 + K_{dl} [A^+][B^-]} [E] \quad (3.4)$$

Another group at the Department of Chemical Technology, University of Twente, The Netherlands headed by Neplenbroek has done considerable research investigating nitrate transport in an SLM (1992). As per the group SLMs are ideal for separations involving low concentrations of ions in water (below some hundreds of mg/L) because

high enrichment factors can be obtained. They used counter transport of the chloride ions for transport of nitrate. They found that below 0.001 nitrate concentration in the feed there was a sharp decrease in mass transfer flux which was attributable to two factors:

1. A reduced complexation of nitrate ions due to the ion exchange equilibrium;
2. A delayed nitrate supply due to concentration polarization effects.

However, at the strip side they found that ion exchange equilibrium was responsible for the reduction in the flux value when lowering the chloride concentration in the stripping phase. The overall flux was again limited by the diffusion of the extractant molecules through the membrane phase. Boundary layer effects were significant on the feed side when nitrate concentrations were below 0.001 M.

Another group headed by R.A. Bartsch, Department of Chemistry, University of Texas, Lubbock, have also contributed significantly to crown ether based SLM research. Their main focus was on the transport of alkali metal cations across SLMs. Macrocyclic polyethers (crown ethers) with pendant acidic functions or acidic groups incorporated into the macrocyclic structure are novel reagents for the transport of metal cations across SLMs (Bartsch et al., 1984; Fyles, T.M., 1985; Strezlbicki and Bartsch, 1990;). For such extractants, the cation is complexed within the cavity of the anionic form of the crown ether during passage through the organic membrane thus eliminating the need for concomitant transport of an aqueous source phase anion. A pH gradient is used to facilitate the transport of the metal cation across the membrane by counter-transport of protons (Brown and Bartsch, 1991). Brown and Bartsch (1991) demonstrated that the

performance of NPPE as a plasticizer in liquid membrane ion-selective crown ether systems surpasses that of NPOE. In a different study (Brown and Bartsch, 1991) ten different alkyl nitrophenyl ethers were studied for cation removal efficiency, selectivity and stability using crown ether as the extractant. They found that in terms of efficiency and selectivity NPPE was the best membrane solvent but when stability was used as the criterion NPOE was the best membrane solvent.

In a different study, the same group investigated the effects of temperature, different levels of ionization of crown ethers, organic membrane solvent and pH on the transport of alkali metal cations across crown ether based SLMs (1990). The results showed that dibenzo-16-crown-5-oxyacetic acid gave the highest process selectivity, sodium cation was selectively transported by crown ether from an aqueous mixture of lithium, sodium, potassium and rubidium. Permeation rate increased with an increase in temperature, use of NPOE as the membrane diluent resulted in a lower flux than the use of NPPE as the membrane diluent and no remarkable influence of the pH of the source solution on sodium transport rate from basic solutions was found.

### **3.1.9 Cation Transport in SLMs**

Fyles (1985) investigated a number of parameters affecting the transport of cations across SLM containing crown ethers as the extractant and determined that rate limiting steps. Membrane transport in bulk liquid membrane systems (BLMs) generally

in U tubes were found to be dependent upon stirring of all the three phases. The systems examined were found to be rate limited by diffusion at some or all stirring speeds. In some cases the adsorption/desorption steps at the interface was rate limiting. Stirring was also found to be inefficient at above 300 rpm and this resulted in "slippage". In fact the Nernst layers achieved a constant thickness. The reactions generally followed first order kinetics.

Murai and Masai (1990) studied the membrane transport of alkali metals by crown ethers in an SLM. They found that smaller the enthalpy of hydration of the inorganic anion (counter ion required for the co-transport of a cation), the higher was the transport rate of the potassium cation. Thus, the results show that the hydrophobicity of the inorganic anion used as a counter ion is one of the factors governing the transport rate of the alkali cations. The relative size of alkali ions to the size of the crown ether cavity and the substituted groups on the crown ether also significantly controlled the cation transport rate.

Mohapatra and Kanungo (1992, 1995) have studied in detail the kinetics of manganese and zinc transport from aqueous sulfate solution across an SLM as a function of the hydrodynamic parameters, concentrations of Mn and  $H^+$  in the feed solution, extractant concentrations in the membrane and temperature. It was observed that as the manganese flux reached a plateau region, the rate of permeation was predominantly controlled by diffusion through the membrane. On the other hand at low manganese and

high  $H^+$  ion concentrations, the high diffusivity of the Mn-extractant complex causes the overall permeation rate to be controlled by the interfacial reaction. The rate of Mn permeation is first order with respect to dimer concentration up to 40 mM and half order above this concentration.

Juang and Huang (1987) studied the rate and transport of zinc across SLMs. A microporous PVDF film was used as the solid support. The measured rates were found to agree well with the mechanism proposed in the study which was based on the model proposed by Danesi. Juang (1993) also studied the transport of cobalt and nickel across SLMs. He found that higher selectivity for cobalt and nickel was obtained when the diffusional resistance in the membrane phase was the controlling resistance.

### **3.1.10 Transient Response In SLMs**

The group headed by Noble R.D. at the National Bureau of Standards, National Engineering Laboratory, Boulder, CO have conducted extensive research in the area of transient non-steady state behavior of SLMs. Folkner and Noble (1993) studied the transient flux for one dimensional facilitated transport in a flat plate, cylindrical and spherical geometries. The results were presented graphically and the flux was found as a function of four parameters namely extractant concentration, diluent, membrane thickness and aqueous velocity. The graphical results allow one to predict the permeate flux as a function of time for a given set of operating conditions, determine the steady state flux

and the time required to reach steady state.

Another group headed by Sashidhar V., at the Department of Chemical Engineering, State University of Buffalo have also conducted significant research in analyzing the transient behavior of SLMs. Sashidhar (1982) found that during the transient period of facilitated transport of a permeant across a thin liquid film, the ratio of the concentration of the extractant at the two ends of the film as a function of time has a shape which is sensitive to the values of the physicochemical parameters. In certain systems involving ionic extractants, the above concentration ratio can be related to a conveniently measurable potential difference,  $\delta V$ , across a pair of electrodes attached to the two faces of the liquid film. They also measured  $\delta V$  vs time for NO-FeCl<sub>2</sub>-formamide system and observed that this goes through a maximum before reaching the asymptotic value corresponding to the steady state,  $\delta V_s$ . Sashidhar (1982) solved numerically the species conservation equations for reversible reaction oriented facilitated transport. They found that the  $\delta V$  reached a maximum when the time scales of diffusion and backward reactions in the film are of comparable magnitude. They concluded that the measurement of  $\delta V$  vs time provided the most accurate method for determining the above parameters than those based on flux experiments.

### 3.1.11 Transport of Organics across SLMs

Uritiga et al., (1992) studied the application of a hollow fiber SLM for separation-concentration of phenol from waste solutions. Kerosene and a mixture of kerosene and methyl isobutyl ketone were immobilized in the porous walls of two different polypropylene membranes. They found that the hollow fiber membrane SLM was feasible in simultaneously separating and concentrating phenol from waste solutions. The use of kerosene resulted in systems with stabilities exceeding 2000 hours. The use of a stripping solution containing sodium hydroxide provided a significant enhancement on phenol separation rate compared to the use of water as a stripping agent. The value of the distribution coefficient had a significant effect on the mass transfer rate. The analysis of the process based on the film theory allowed the calculation of the membrane mass transfer coefficient. Zha (1994) also studied the transport of phenol across SLMs both in intact and in decayed systems. Zha also found results very similar to Uritiga.

Teramoto (1994), demonstrated for the first time the facilitated up-hill transport of eicosapentaenoic acid ethyl ester through BLMs and SLMs based on the use of solvent dependance of the distribution ratio of a permeant solute. An equilibrium model was formulated and the predicted equilibrium data matched well with the experimental results.

### 3.2 Rhenium Extraction

Crown ethers have found suitable for extracting oxo-anions namely perrhenate from aqueous solutions. Caletka et al., (1986) described the extraction of rhenium (VII) with di-cyclohexano-18-crown-6 (DC18C6) in 1,2-dichloroethane from hydrofluoric acid and potassium fluoride solutions. Yang and Cussler (1986) studied the extraction of rhenium with benzo-15-crown-5 in nitrobenzene from sulfuric acid solutions containing potassium ions. Koshima and Onishi, (1990) systematically investigated the extraction behavior of rhenium with crown ethers and developed useful methods for its separation and determination. They, i.e. Koshima et al. found that the distribution coefficient of perrhenate with DC18C6 increases with increase in the dielectric constant of the organic diluent. This observation convinced the author of this dissertation that NPOE and NPPE which are diluents with a high dielectric constants are very suitable for perrhenate extraction. Zhang and Shu, (1993) also studied the extraction of perrhenate with DB18C6. They found that the presence of either sodium or potassium ion was necessary for extraction. They also found that perrhenate was extracted as an ion pair in non polar diluents and as free ion in polar diluents. Thermodynamic data indicated that extraction of perrhenate was enthalpy driven

### 3.3 Technetium

Technetium is a radionuclide with a considerable mobility and it is this mobility which makes it a threatening chemical to the environment. Mobility tests conducted by researchers have demonstrated considerable technetium mobility even when placed at a considerable depth (Sheppard, M.I., et al., 1991). Technetium is present in all environmental compartments as the long lived isotope Tc-99 in the form of pertechnetate,  $\text{TcO}_4^-$ , which under oxic conditions is highly mobile in marine, freshwater and terrestrial ecosystems. However under anoxic conditions it can be reduced and immobilized. Low concentration factors and high elimination rates in most biota, and the high mobility are responsible for the fast recycling of technetium in the biosphere. It remains mobile and available for accumulation over long distances and times. The accumulation of considerable amounts of Tc-99 in high level radioactive wastes are of great concern with respect to potential biochemical and radiological effects (Schulte, E.H., 1984).

Knowledge of technetium in terms of its migration properties in groundwater, in rock structures, its sorption properties, redox states and reactive properties are important to understand its behavior in the environment. Researchers have conducted diffusion experiments with an artificial fracture between two pieces of granite to study technetium sorption mechanisms and its diffusion into the granite. This knowledge is useful for determining the migration of Tc-99 in groundwater and granite rock structures. Sorption on granite, gneiss, basalt, andesite, and rhyolite was measured and expressed as a

function of interstitial water. An excellent correlation was determined between the sorption of Tc and the amount of interstitial water (Shimooka, 1985). Another study has shown that under environmental conditions, Tc predominantly exists in the oxidation states +vii (pertechnetate) and +iv, as insoluble technetium dioxide or in organic complexes with di or tri carboxylic acids. Slight retardation is observed in aerobic soils, whereas substantial immobilization can occur in anaerobic soils (Nilsson, 1985). A different study has shown little sorption of Tc under oxic conditions and low to moderate sorption under anoxic conditions. The extent of sorption was highly dependent on groundwater composition and the method of basalt pretreatment (Meyer, R.E., 1984). Studies conducted on the rate of adsorption and geochemical partitioning of long-lived radio nuclides in sediments showed that technetium adsorption was relatively low and slow as compared to transuranics (Gastaud, M.J., et al., 1984). Another study showed that Tc was susceptible to reduction under suitable sedimentary conditions with consequent marked changes in their affinity for solid and liquid phases. These results were obtained by studying the interstitial water chemistry of sediments from the Irish sea and with emphasis on its effect on Tc.

### **3.4 Summary of Literature Data and Comparison of Results**

It was quite evident from the preceding discussion of SLM literature that several studies on the transport of metal ions, radio nuclides, organics and anions across SLMs, involving a number of mass transport models, have been conducted by numerous

researchers all over the world namely Cussler, Danesi, Stolwijk, Teramoto, Sirkar etc.

Some of their results are summarized here:

Babcock et al., (1980) successfully transported Uranium across an SLM and obtained a MTF of  $5 \text{ E-06 moles/cm}^2/\text{hr}$ . The corresponding fluxes calculated from the Stokes-Einstein equation were over 5 times larger. This discrepancy was due to the hindered diffusion of the uranium complex in the small pores of the membrane. Baker et al., (1977) used counter-ion transport for copper separation across an SLM. They obtained a pH dependent flux which averaged  $4 \text{ E-06 moles/cm}^2/\text{hr}$ . Mohapatra and Kanungo, (1995) obtained a zinc flux of  $2 \text{ E-05 moles/cm}^2/\text{hr}$ . Their flux rates varied linearly with initial zinc concentration in the feed solution. Danesi and Chirizia, (1983) obtained a cadmium MTC of  $3 \text{ E-03 cm/s}$  and a zinc MTC of  $1.0 \text{ E-04 cm/s}$  across an SLM for a feed containing 0.5 mM initial cadmium and zinc concentrations. Danesi obtained a MTC of  $4.0 \text{ E-03 cm/s}$  for americium transport across an SLM. Juang, (1993) obtained a MTC of  $2.6 \text{ E-04 cm/s}$  for 0.001 M nickel transport across an SLM.

Stolwijk et al., (1987) obtained a mass transfer flux of  $1 \text{ E-07} - 1 \text{ E-08 moles/cm}^2/\text{hr}$  for 0.1 M potassium perchlorate transport across an SLM. They also obtained an effective diffusion coefficient of  $1.5 \text{ E-07 cm}^2/\text{s}$ . They used crown ethers as the extractant. Brown and Bartsch, (1991) obtained a sodium MTF of  $2.4 \text{ E-07 moles/cm}^2/\text{hr}$  using crown ether as the extractant and NPOE as the diluent. Also for

similar conditions, Strzelbicki and Bartsch, (1990) obtained a sodium MTF of  $5 \text{ E-}07$  moles/cm<sup>2</sup>/hr.

Summi Nakamure, (1994) obtained a cyanide MTF and MTC of  $1 \text{ E-}07$  moles/cm<sup>2</sup>/hr and  $1.24 \text{ E-}03$  cm/s respectively for  $0.1 \text{ mM}$  initial cyanide concentration. Neplenbroek and Bargeman, (1992) obtained a nitrate MTF of  $7 \text{ E-}06$  moles/cm<sup>2</sup>/hr and a  $D_{\text{eff}}$  of  $3 \text{ E-}07$  cm/s for an initial nitrate concentration of  $0.4 \text{ mM}$ . Chirazia (1991) obtained nitrate, pertechnetate, and uranium MTCs of  $6 \text{ E-}03$ ,  $1.75 \text{ E-}03$  and  $5 \text{ E-}04$  cm/s respectively. He also used a simulant of DOE Hanford waste and the concentrations were similar to the ones used in this study. Molnar et al., (1978) obtained a MTF of  $2.0 \text{ E-}05$  moles/cm<sup>2</sup>/hr for chloride concentration across an SLM. The feed solution contained an initial chloride concentration of  $0.2 \text{ M}$ .

In comparison, this study produced sodium nitrate and Re MTFs of  $1 \text{ E-}06$  -  $\text{E-}07$  and  $1 \text{ E-}07$  -  $\text{E-}08$  moles/cm<sup>2</sup>/hr respectively, Na, NO<sub>3</sub>, Re MTCs of  $1 \text{ E-}03$ ,  $1 \text{ E-}03$ ,  $2.36 \text{ E-}04$  cm/s respectively and a  $D_{\text{eff}}$  of  $1.6 \text{ E-}07$  cm<sup>2</sup>/s. These results compare favorably to results published in literature.

# **CHAPTER 4**

## **MATERIALS AND METHODS**

### **4.1 Materials**

Crown ether (dtb-CH18C6), NPOE and NPPE were obtained from Fluka Chemicals; Sodium perrhenate and sodium nitrate from Sigma Chemicals. All other chemicals required for the preparation of the Melton Valley waste simulant were supplied by Fluka Chemicals. Flat sheet Celgard 2500 membrane was supplied by Hoechst Celanese Inc. The SLM module was fabricated in the machine shop of ORNL based on the design supplied by the authors. The Melton Valley Waste Simulant (MVWS) used in this set of experiments was made in the laboratory based on the composition listed in Table 4.1. MVWS is a form of alkaline tank waste and has its origins from nuclear processing operations in Oak Ridge, TN.

#### **4.1.1 Analytical Measurement of Metal Cations and Anions**

Sodium metal ion concentrations and perrhenate anion concentrations were measured by Inductively Coupled Argon Plasma (ICAP) spectrometry. Nitrate ion concentrations were not measured.

Table 4.1: Melton Valley Waste Simulant (MVWS) Composition

| Component         | Concentration |
|-------------------|---------------|
|                   | M             |
| Sodium Nitrate    | 4.23          |
| Cesium Nitrate    | 0.0000043     |
| Potassium Nitrate | 0.29          |
| Strontium Nitrate | 0.000011      |
| Calcium Nitrate   | 0.000087      |
| Sodium Hydroxide  | 0.158         |
| Aluminum Nitrate  | 0.000016      |
| Sodium Perrhenate | 0.00006       |
| Sodium Bromide    | 0.0006        |
| Sodium Chloride   | 0.085         |
| Sodium Chromate   | 0.000042      |
| Sodium Carbonate  | 0.1           |
| Sodium Sulfate    | 0.007         |

## **4.2 Methods**

### **4.2.1 Experimental Protocol**

The Separations group at the Oak Ridge National Laboratory (ORNL) has done extensive research on metal specific extractants. Their research involves the design and synthesis of novel ligands for selective metal binding, separation and structural analysis of ligands and complexes. The ORNL team has developed advanced extractants capable of removing technetium with favorable selectivity and extraction efficiencies. The experimental work for this project was performed in collaboration with this team in their laboratory.

### **4.2.2 Experimental Procedure**

Figure 4.1 shows a schematic of the experimental apparatus used in this study.

1. The first step involves the preparation of the membrane phase solution. Peter Bonnesen, Staff Scientist, ORNL has supplied the initial solutions of Crown Ether in the diluent while the author has made up the various dilutions.
2. The membrane was then cut into a membrane sheet 6 cm x 4 cm and soaked in at least 2 mL of CE + diluent for 48 hours. Care was taken to see that the entire membrane was completely immersed in the liquid.

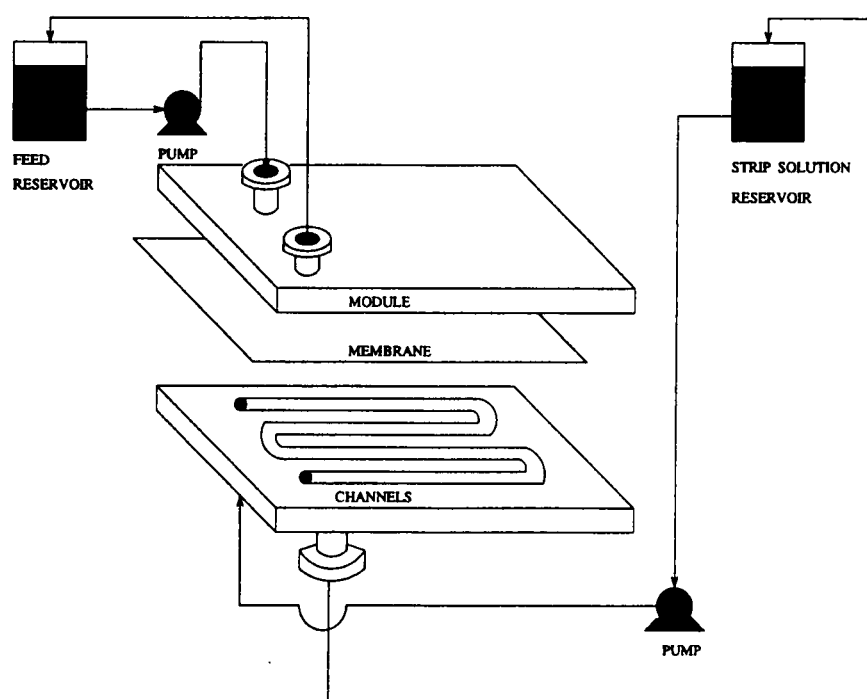


Figure 4.1: Schematic of the SLM Experimental Apparatus

3. After 48 hours the SLM was removed from the glass plate and was held over the plate for 1-2 minutes in order to allow excess solvent to drip off. The SLM was transparent due to the saturation of pores with solvent.
4. The SLM was placed on one end of the steel module in such a way as to cover the serpentine channels and the entry and exit ports. It was visible that at this stage the SLM sticks to the module surface. The module's symmetrical other half was then placed on top of the SLM. Care was taken to align the channels on both sides of the membrane. The entire module with the SLM was fastened with a set of 6 bolts. Care was taken to provide almost equal torque to all the bolts.
5. The feed solution was first prepared by dissolving the desired amount of sodium perrhenate and sodium nitrate in separate 500 mL volumetric flasks. A sample was withdrawn from both the flasks for ICP analysis. The ICP data divided by two gave the feed sodium and perrhenate concentrations.
6. The feed solution was then prepared in an 1 L flask by mixing the two 500 mL solutions and 500 mL was poured into a cleaned feed tank. 500 mL of deionized (DI) water was poured into a cleaned strip tank. The feed and strip tanks were cleaned before the start of every experiment with distilled water. At this stage a sample (6-7 mL) of the strip solution was withdrawn from the strip tank into a

sample vial. This represents the control or strip sample at 0 hour.

7. Next the feed and strip pumps were set at a flow rate of 400 mL/hour and were turned on to initiate the beginning of the experiment. The module was operated in a cocurrent manner as countercurrent operations produced high pressure differences across the membranes leading to bulges and hence very low flow rates. Samples of the strip solution were taken every half hour for the first 3 hours and then hourly for the next 2 hours in polyethylene (PE) vials. At this stage the pump was turned off. Flow rate was monitored at the beginning and at the end of each experimental run. Feed samples were not taken as high nitrate concentration in the feed resulted in erroneous rhenium concentrations during ICP analysis due to matrix effects. 8 mL of sample was required for ICP analysis and a total of 10 samples are taken during an experimental run. Duplicate samples were not taken because this would lead to a large change in tank volumes and hence erroneous results. Total change in tank volume was restricted to less than 10% for better accuracy.
8. Samples were placed in ICP vials, sealed and analyzed for Na and Re once a week (3 data sets per ICP analysis). The results were recorded in the note book and saved on the hard disk. The average value as given by the ICP was recorded.
9. Flux was calculated by taking the slope of concentration,  $C$ , vs time and

multiplying it with (strip tank volume/membrane area/molecular weight).

10. This procedure was repeated every time.

### **4.3 List of Tasks**

#### **4.3.1 Task 1: Mass Transfer Model**

The mass transport model developed in this research study ( Chapter 5.2) was used to predict the MTCs in closed and open loop experiments.

#### **4.3.2 Task 2: Statistical Analysis**

The MTF data were compiled in a data file and was entered into a SAS program. The SAS program was written with the intention of obtaining a multiple regression of MTF (dependent variable) on all the variables which help in predicting MTF. Specific interaction terms were also incorporated along with test statements to test their significance at a 95% confidence interval level. The program would empirically link MTF to over 10 variables and 5 interaction terms. This would enable readers to interpolate and obtain MTF data without the need for experiments.

### **4.3.3 Task 3 EDM Experiments**

The objective of this set of experiments was to determine the optimum extractant-diluent-modifier (EDM) combination for an SLM. Experiments were performed in a flat sheet membrane system consisting of two blocks of stainless steel with identical machined grooves having dimensions 0.2 x 2.5 x 50 mm formulating six channels with a nominal volume of 25 microliters each. Figure 4.2 shows the schematic of the serpentine arrangement of the channels in the membrane module and the flow path of the aqueous streams in the channels. The membrane (60 x 30 mm) was placed between the blocks which were clamped together with 6 bolts.

Experiments were conducted with dilute rhenium feed concentrations ( $10^{-4}$  M). A number of extractants, diluents and modifiers were tried in various combinations as the membrane solution. The combination which resulted in the highest overall MTC and selectivity across the membrane was used for the remainder experiments.

### **4.3.4 Batch Experiments**

Batch experiments involving solvent extraction studies were conducted at the Oak Ridge National Laboratory by the research team. A typical batch experiment involved the following steps:

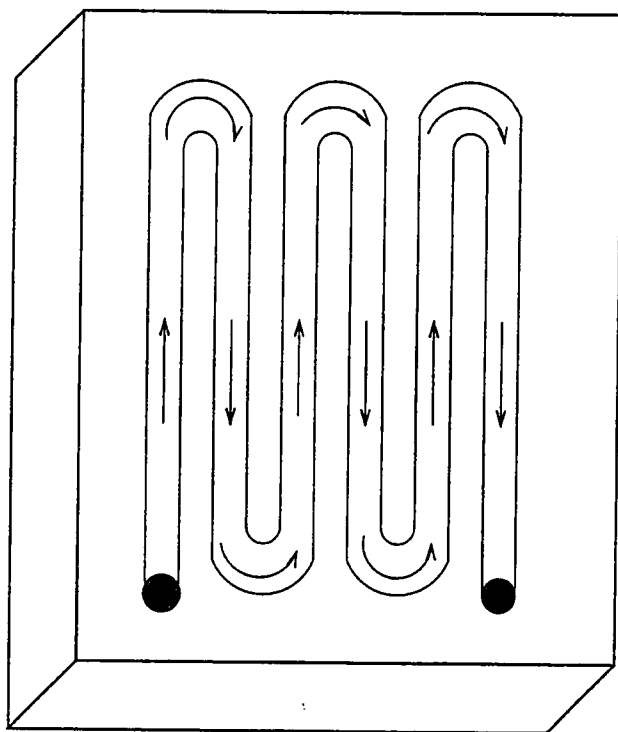


Figure 4.2: Schematic of the Serpentine Channel Arrangement in the SLM Module

1. Contact of 1.5 mL organic solution (extract + diluent) with 1.5 mL DI water at a high 300 rpm for 1 hour.
2. Centrifugation of the vials and separation of 1 mL each of the organic and aqueous phases into separate vials.
3. Back extraction of the organic phase with 10 mL of DI water.

Batch solvent extraction experiments were conducted on the optimum EDM combination determined from phase one experiments to obtain the distribution coefficients. Task 15 was partially accomplished through these set of experiments.

#### **4.3.5 Task 4: Optimal Extractant Concentration Experiments**

Experiments were conducted with 0.0, 0.01, 0.04, 0.07, 0.1, 0.2 M concentration of the crown ether selected from the phase one experiments. Experiments were performed in a closed loop and as per the procedure outlined in 4.2.2.1. The effect of varying crown ether concentrations on sodium and rhenium fluxes, mass transfer coefficients (MTC) and selectivity were quantified and plotted. The concentration which yielded the highest selectivity and a reasonably high MTC and rhenium flux were used in the scale-up experiments. A kinetic analysis was done to determine the average crown ether loading inside the membrane.

#### **4.3.6 Task 5: Feed and Strip Flow Rates Experiments**

Experiments were conducted at varying feed and strip flow rates and velocities.

An increase in flow rate increases the Reynolds number and causes a corresponding increase in the MTC due to a decrease in the boundary layer thickness and resistance. At a certain flow rate the boundary layer thickness reaches its minimum value and there is no further decrease in the boundary layer thickness and resistance when operated beyond this flow rate. This flow rate beyond which there is no appreciable increase in MTC and mass transfer flux (MTF) and decrease in boundary layer thickness was considered as the optimal flow rate and should be used in the scale-up design.

#### **4.3.7 Task 6: Permeability vs Feed Molar Activity Experiments**

Another set of experiments were conducted to determine the effect of increasing feed molar activity in terms of perhenate or sodium ion concentrations on rhenium extraction efficiency in an SLM. Experiments were conducted with  $10^{-1}$ , 0.5, 1, 2.5 and 5 M concentrations of sodium added as sodium nitrate. Every other parameter was maintained at a constant value throughout this experimental run. Another set of experiments were performed this time by varying the sodium perhenate concentration and keeping the sodium nitrate concentration constant. The effect of varying sodium and

perrhenate concentrations on sodium and rhenium MTFs, selectivities and MTCs were studied and plotted.

#### 4.3.8 Task 7: MTC Experiments

Experiments were conducted to determine the overall mass transfer coefficient,  $K$ , and through  $K$  the aqueous and membrane mass transfer coefficients. Experimental apparatus as shown in Figure 4.1 was also used for this study. The first set of experiments were conducted to determine the effect of feed and strip flow rates on membrane permeability. The next set of experiments were conducted at the feed and strip rates determined from the first set of experiments with the intention of minimizing the feed and strip side boundary layer resistances. The controlling mass transfer resistance in this case could be the membrane diffusion resistance. Interfacial reaction resistances on the feed and strip sides are negligible assuming extractant solute reactions are fast reactions. The Damkohler number,  $D$ , defined as the ratio of diffusion to reaction resistance provides a measure of the relative rates of diffusion and reaction in a system. This  $D$  is equal to  $l^2/D_{\text{eff}}/t_{1/2}$  where  $l^2$  is the square of the membrane thickness ( $\text{cm}^2$ ),  $D_{\text{eff}}$  is the effective membrane diffusion coefficient ( $\text{cm}^2/\text{sec}$ ), and  $t_{1/2}$  is the reaction half life (sec). In the present case  $D$  is equal to  $6.25\text{E-}06/6.0\text{E-}07/1\text{E-}06$  (Danesi, 1985) which is approximately equal to  $1\text{E}+07$ . If  $D$  is greater than 10 then diffusion is the controlling process (Cussler, 1972). Since in the present case  $D \gg 10$  interfacial reaction resistance is negligible. The aqueous feed and strip MTCs can be computed from the Sherwood

Equation.

#### **4.3.9 Task 8: Steady State Simulations**

Simulations were conducted on the steady state open loop mass transfer model. These simulations help in predicting the steady state strip pertechnetate concentrations under any experimental conditions. Steady state experiments were performed on a predetermined set of experimental conditions (feed composition, etc) and the steady state experimental strip pertechnetate concentration was compared against the concentration as predicted by the computer simulation. A favorable comparison within 95% accuracy could result in the usage of the model for predicting the steady state pertechnetate concentrations in the feed solution without the need for any further experiments. This would help in the design of an SLM system for actual wastes.

#### **4.3.10 Task 9: Steady State Experiments**

Steady state open loop experiments were conducted on pre-selected sets of experimental conditions to determine the steady state exit concentrations from the membrane module, steady state MTF, steady state MTC and process selectivities. A correlation was also developed between closed and open loop MTCs which would be useful in predicting open loop MTCs from closed loop MTCs especially when open loop

experiments yield steady state values very close to instrument detection limits. These experiments will prove useful during process scale-up.

#### **4.3.11 Task 10: Membrane Thickness Experiments**

Experiments were conducted with varying membrane thickness in order to determine the effect of membrane thickness on MTF and MTCs. Multiple membranes, pre soaked in the solvent-diluent solution, placed on top of each other between the channels were used to simulate variable membrane thicknesses. An increase in membrane thickness will result in a decrease in membrane MTC and will not effect the aqueous MTCs. Hence the difference between the inverse of the overall MTC between 2 and 3 membranes will equal the inverse of the product of extraction side distribution coefficient and membrane MTC ( $1/(K_{dl}k_m)$ ). Also, a linear relationship between membrane thickness and MTF will mean that membrane mass transport is the rate limiting step (Stolwijk, 1991).

#### **4.3.12 Task 11: NPPE Experiments**

Experiments were conducted with nitrophenylpentylether (NPPE) as the membrane diluent. NPPE is more polar (higher dielectric constant) than NPOE and a correlation/comparison would provide an important understanding on the effect of membrane solution polarity on MTF, MTC, selectivity and stability. Experiments were

conducted at 0.04 M crown ether concentration on a single membrane, multiple membranes (to determine the membrane MTC), waste simulants, and at different flow rates.

#### **4.3.13 Task 12: "Up-Hill SLM Transport Experiments**

Experiments were performed to determine whether perrhenate can be transported against its own concentration gradient by varying the strip solution composition. From the flux equation 6.12 in chapter 6 it is evident that strip concentration can be greater than the feed concentration as long as  $K_{d2}/K_{d1}$  is  $< C_F/C_S$ . The distribution coefficient ratio is dependent on the feed and strip side activity and equilibrium constants. Hence by keeping the feed activity a constant and varying the strip activity the ratio can be changed. In the first set of experiments, strip solution was spiked with varying Re concentrations ranging from 10 to 40 mg/L. Since the feed had only 18 mg/L Re and a large excess of sodium (the driving force) a steady build-up of Re must take place in the strip solution in a closed loop SLM. Any build-up beyond 20 mg/L strip Re concentration will show that Re can be transported against its gradient.

#### **4.3.14 Task 13: Melton Valley Simulant Experiments**

Experiments were conducted on a simulant of the Melton Valley, Oak Ridge tank waste. Rhenium was used as the Tc surrogate. MTFs for open and closed loop NPOE and NPPE

systems were determined and compared to the MTF data obtained earlier with the simple simulant.

#### **4.3.15 Strip Composition Experiments**

The strip solution for this set of experiments was spiked with sodium nitrate ranging from 0.0001 M to 0.1 M. This should result in an increase in the strip side distribution coefficient,  $K_{ds}$ , and a drop in MTF. The nitrate concentration at which there is a sharp fall in the MTF, would be considered as the "bleed off" concentration and a portion of the stripping solution would be bled off to maintain the nitrate concentration lower than the "bleed off" concentration in the strip solution.

#### **4.3.16 Task 14: Equilibrium Composition Experiments**

Experiments were conducted continuously for a period of 10 days using the same feed and strip solutions and on the same membrane. The feed and strip solutions were operated in a recycle mode and samples were withdrawn daily. The equilibrium/"Quasi Steady State (QSS)" feed and strip concentrations were compared with the concentrations predicted by the model.

#### **4.3.17            Tasks 15, 16, 17: Kinetic Analysis and Equilibrium Constants**

Kinetic analysis on the MTF data obtained by varying the feed molar activity can determine the apparent equilibrium constant and the effective diffusion coefficient for nitrate and perrhenate transport in an SLM. Apparent equilibrium constant is defined as the ratio of the actual equilibrium constant over the anion distribution coefficient which is a constant (Stolwijk et al., 1987).

Kinetic analysis on the flux data also helped in determining whether the predominant means of transport inside the membrane is because of free ions or ion pairs. If the dependence is linear with the inverse of the square of the molar activity in the feed solution then ion pair is the predominant means of transport. However, if the dependence is linear with the inverse of feed molar activity then free ion transport is predominant inside the membrane. Kinetic analysis also provided information on complexation constants, equilibrium constants and effective membrane diffusion coefficients. Task 3 was accomplished through this set of experiments.

#### **4.3.18            Task 18: Stability Experiments**

Experiments were conducted to determine the long term stability of the SLMs. Gradual loss of extractant and diluent into the aqueous streams because of aqueous solubility is the root cause of membrane instability. It is desirable to select an extractant

diluent combination which is very stable or where the aqueous loss is negligible. There is a sudden change in the MTC when the membrane loses its stability. Experiments were conducted for 10 days of continuous operation in a closed loop and since even after 10 days there was no change in the MTF, the SLM was considered as stable.

## **CHAPTER 5**

### **MASS TRANSPORT MODEL**

#### **5.0 Theory**

Solvent extraction processes across a microporous membrane are based on either counter-ion coupled transport or co-ion coupled transport processes. In counter-ion transport process an exchange of an ion from the extractant of the same charge as the solute ion takes place across the membrane interface, while in co-ion transport process an ion of the opposite charge is co-transported along with the solute ion into the extractant-diluent solution at the membrane interface. Perrhenate ( $\text{ReO}_4^-$ ) is extracted through the co-ion transport process and is transported along with a cation i.e sodium or potassium in order to maintain electroneutrality. Figure 5.1 shows a schematic of sodium perrhenate (co-ion) transport across an SLM.

#### **5.1 Mass Transport Model**

The basic approach to the derivation of the mass transfer model has been adapted from the literature (Danesi, 1985) with suitable modifications by the author to account for the strip side mass transfer resistance and overall mass transfer kinetics. Cussler (1972)

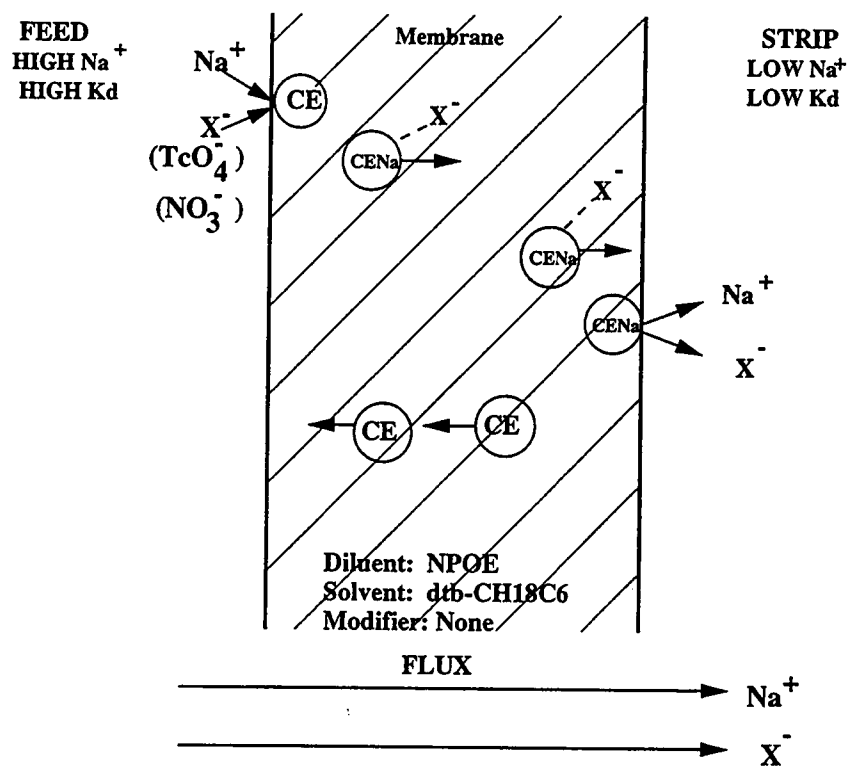


Figure 5.1: Schematic of Coupled Co-Transport of Sodium Cation and Monovalent Anions Across SLMs

was probably the first researcher to model facilitated transport. His approach utilized the distributed parameter model which involved the set-up of differential equations describing ion and ion pair complex inside the pores of the membrane. Cussler's approach though thorough in its analysis produced a form of flux equation which can not be analytically integrated. This limited its application as any mass balance would involve integration. Danesi (1985) was the first researcher to follow the lumped parameter approach where all the effects of the co- or counter-ion diffusion are lumped into a single experimentally determinable overall MTC,  $K$ . This allowed the representation of the model basically as a single ion system, but in reality it was not as the overall MTC and the distribution coefficients accounted for the multi-ion effects. It may be noted that the value of the overall MTC would change when the concentration of any ion in the system is changed since the overall MTC was dependent on the distribution coefficients and in turn the distribution coefficients were dependent on all the ion concentrations in the systems. Untill this study, to the best of the author's knowledge, the overall MTC was always determined experimentally. The author has in this chapter attempted to relate the distribution coefficients to the chemistry and to all the components/ions in the system both for free ions and ion-pair transport. Thus, in summary Equation 5.7 and similar equations used by Danesi and others represent multi-ion transport with the effects of all the other ions lumped into an experimentally determinable parameter, the overall MTC. This approach was successfully used by a number of researchers to explain the behavior of a number of single, two and multi ion systems. Some of them include: Danesi for

transport of Am, Eu, Nitrate (3 components) from radioactive wastes (1984-85), copper, zinc, chloride from electroplating wastes (1986), nickel, cadmium, sulfate from plating wastes (1987); Chirazia (1991) for transport of nitrate, technetium, uranium from DOE wastes (3 components), cobalt, nickel and sulfate from plating baths (1987); Yinger for transport of cobalt and nickel from plating solutions (1987); Nishiki for transport of platinum, palladium and chloride from precious metal wastes (1985); Harada (1984) for transport of iron, zinc, magnesium (3 components); and Pearson (1983) for transport of copper, chromium and hydrogen (3 components). The author has also used a similar approach but has attempted to relate the overall MTC to the distribution coefficients through Equation 5.9 and the distribution coefficients to all the ions in the system through Equations 5.50 And 5.54 for ion-pair and free ion transport respectively. Hence Equations 5.8 and 5.9 represent multi-component systems.

#### **5.1.1 Assumptions**

1. Chemical reactions between the perrhenate ion and the extractant are fast (no interfacial mass transfer resistances).
2. The system is at steady state.
3. Perrhenate concentration gradient throughout the membrane and aqueous phases is linear.
4. Diluent associated transport is negligible.

### 5.1.1.1 Terminology

- a) Feed: A solution of sodium perrhenate and sodium nitrate in DI water.
- b) Strip: DI water
- c) Extractant: dtbCH18C6 a type of crown ether (CE).
- d) Diluent: An organic solution (NPOE, NPPE) into which the extractant is dissolved.
- e) Modifier: An organic functional group added to the extractant to make it more lipophilic. In this study no modifier was used.
- f) Raffinate: This is the exit feed stream coming out of the membrane module.
- g) Extract: Sometimes used for exit strip stream.

Figure 5.2 illustrates the concentration profile of perrhenate across an SLM.

The mass transfer flux equations are:

1. Aqueous feed side mass transfer flux:

$$J_a = k_a (C_F - C_I) \quad (5.1)$$

where:

$J_a$  = Aqueous mass transfer flux (moles/hr.cm<sup>2</sup>)

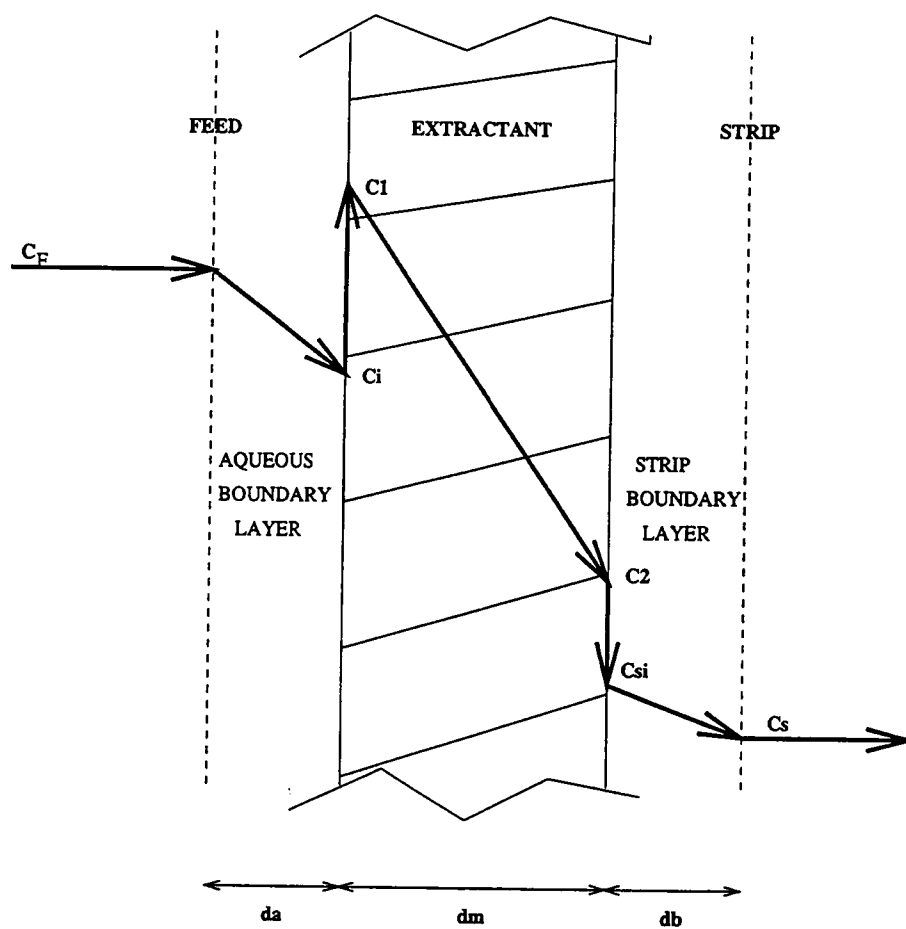


Figure 5.2: Schematic of the Concentration Profile across an SLM

$k_a$  = Aqueous mass transfer coefficient, cm/s

$C_f$  = Bulk feed perrhenate concentration, M

$C_i$  = Interface perrhenate concentration, M

2. Membrane mass transfer flux:

$$k_m (C_1 - C_2) = J_m \quad (5.2)$$

where:

$C_1, C_2$  = Bound perrhenate concentration at the feed and strip interfaces respectively, M

$J_m$  = Membrane mass transfer flux, moles/hr/cm<sup>2</sup>

$k_m$  = Membrane mass transfer coefficient, cm/s and is equal to  $D_{eff}/d_m$  (membrane diffusivity constant/membrane thickness).  $D_{eff}$  is the

effective membrane diffusivity and is equal to  $(D_o e/t)$  where  $D_o$  is perrhenate diffusivity in bulk extractant-diluent solution,  $e$  is the membrane porosity and  $t$  is membrane tortuosity.

3. Strip mass transfer flux:

$$C_{si} - C_s = \frac{J_s}{k_b} \quad (5.3)$$

where:

$C_{si}$  and  $C_s$  = Strip side interfacial and bulk perhenate concentrations respectively,

$M$

$J_s$  = Strip mass transfer flux, moles/hr.cm<sup>2</sup>

$k_b$  = Strip side mass transfer coefficient, cm/s

$K_{d1}$  and  $K_{d2}$  are the extraction and strip side distribution constants respectively and are defined as:

$$K_{d1} = \frac{C_1}{C_i} \quad (5.4)$$

$$K_{d2} = \frac{C_2}{C_{si}} \quad (5.5)$$

At steady state all mass transfer fluxes are equal to  $J$ .

Researchers have so far only concentrated on the extraction side MTC and have more or less ignored the stripping side MTC. The author recognizes the fact the SLM process is a composite of extraction and stripping processes unlike the solvent extraction process where stripping is done in a separate operation. Hence, to model the complete

SLM process it is necessary to consider strip side boundary layer resistance. The section on overall mass transfer flux looks at the SLM in total and accounts for the contribution of strip side MTC to the overall MTC.

### 5.1.2 Overall mass transfer flux with finite strip concentration

The overall mass transfer flux and coefficients when  $C_s$  is not neglected are determined by taking into account the resistances encountered due to the feed side boundary layer, membrane film thickness or membrane diffusion and strip side boundary layer. Equation 5.6 relates  $C_2$  to  $C_s$ .

$$C_2 = \left( \frac{J}{k_b} + C_s \right) K_{d2} \quad (5.6)$$

Equation 5.7 describes the relationship between mass transfer flux and the feed and strip side bulk concentrations. Rearranging Equations 5.1, 5.2 and 5.4 yields  $C_1 = C_2 + J/k_m$ , and  $C_F = C_1/K_{d1} + J/k_a$ . Substituting Equation 5.6 for  $C_2$  in  $C_1 = C_2 + J/k_m$  above and the resulting  $C_1$  for  $C_F = C_1/K_{d1} + J/k_a$  above leads to Equation 5.7

$$C_F - \frac{K_{d2}}{K_{d1}} C_s = J \left[ \frac{1}{k_a} + \frac{1}{k_m K_{d1}} + \frac{K_{d2}}{k_b K_{d1}} \right] \quad (5.7)$$

or

$$J = K \left( C_F - \frac{K_{d2}}{K_{d1}} C_S \right) = K (C_F - C^*) \quad (5.8)$$

where:

$C^*$  = Concentration in the strip which is in equilibrium with the feed  
concentration, mg/L

It is assumed that the initial concentration of perrhenate in the strip solution is equal to zero and that the rate of disappearance of perrhenate in the feed tank (moles/time) is equal to the rate of appearance of perrhenate (moles/time) in the strip tank (conservation of mass) as there is neither any accumulation nor disappearance of perrhenate in the membrane system.

It may be noted that the feed and strip side mass transfer coefficients  $k_a$  and  $k_b$  are dependent only on the flow rates and are proportional to the feed and strip side flow velocities raised to the one third power (for laminar flow only, Cussler, 1972; Tompkins and Perreti, 1992).

### 5.1.3. Overall Mass Transfer Coefficient, K

The overall mass transfer coefficient is the sum of the three resistances in series namely the aqueous feed boundary layer resistance, membrane resistance and the aqueous strip boundary layer resistance. Equation 5.9 describes the overall mass transfer resistance, K.

$$\frac{1}{K} = \frac{1}{k_a} + \frac{1}{K_{d1}k_m} + \frac{K_{d2}}{K_{d1}k_b} \quad (5.9)$$

#### 5.1.4 Simplified Model for Reynolds Number > 200

Based on the experiments conducted in this study it has been determined that for feed and strip side Reynolds numbers greater than 200, the feed and strip side mass transfer resistances are negligible (the overall MTC is independent of  $N_{Re} > 200$ ). Hence the overall MTC  $K$  is now equal to:

$$K = K_{d1} \frac{D_{io} \epsilon}{d \tau} = K_{d1} \frac{D_{eff}}{d} = K_{d1} k_m \quad (5.10)$$

and the MTF is then equal to:

$$J = k_m (K_{d1} C_F - K_{d2} C_S) \quad (5.11)$$

where:

$$k_m = D_{eff}/d$$

The term in the parenthesis of Equation 5.11 provides the driving force for mass transport.

## 5.2 Two- and Multi-Component Transport

It is important to note that there is a separate "Quasi-Steady State (QSS)" condition for both the anions. This QSS condition where there is no net transport of the concerned anion across the membrane, is attained when the product of the activities of the cation and the anion in question in the feed equals to the product of their activities in the strip solution. Activity coefficients would play a significant role in the feed solution as the feed has a high ionic strength. On the contrary, activity coefficients in the strip solution would be close to unity because the strip is a very dilute solution. Also, while one anion transport is at a QSS, the other anion could be very far from its QSS. At overall "Equilibrium", the activity of each ion in the feed is equal to its activity in the strip.

This model also predicts that it is possible for sodium perrhenate to be back transported from the strip solution to the feed solution while sodium nitrate is being forward transported from the feed to the strip solution. Indeed the results of the concentration study experiments (section 6.1.4.1, chapter # 6) have corroborated this hypothesis and  $\text{NaReO}_4$  was back transported during simultaneous forward transport of  $\text{NaNO}_3$ .

### 5.3 Mass Balances

#### 5.3.1 Closed Loop System

If  $V_1$  and  $V_2$  represent the volumes of the feed and strip tank respectively,  $C_0$  and  $C(t)$  represent the initial and at time  $t$  perhenate concentrations in the feed tank, then perhenate concentration in the strip tank  $C_s$  is equal to:

$$C_s(t) = \frac{V_1}{V_2} [C_0 - C(t)] \quad (5.12)$$

##### 5.3.1.1 Feed Side

###### 5.3.1.1.1 Module Mass Balance

Mass balance around a thin section of the membrane having a thickness  $\delta x$  yields:

Accumulation = Input - Output - Disappearance (due to diffusion) which in a mathematical form is:

$$b\delta x \frac{\delta C_{F,m}}{\delta t} = U_F b\delta x (C_{F,m/x} - C_{F,m/x+\delta x}) - AK(C_{F,m} - SC_{S,m}) \quad (5.13)$$

where:

$U_F$  = Feed velocity, cm/s

$C_{F,m}$  and  $C_{S,m}$  = Feed and strip solution concentrations at any point in the

membrane module, M

$A/V$  = Membrane area to total channel volume ratio

$s$  = Ratio of the strip side to feed side distribution constants

$b$  = Membrane width, cm

$t$  = Membrane thickness, cm

The partial differential equation (PDE) representing the mass balance across an SLM module is obtained by dividing Equation 5.13 with the membrane sectional volume  $bt\delta x$ :

$$-\frac{\partial C_{F,m}}{\partial t} = -U_F \frac{\partial C_{F,m}}{\partial x} - \frac{AK}{V} (C_{F,m} - sC_{S,m}) \quad (5.14)$$

#### 5.3.1.1.2 Tank Mass Balance

Mass balance of the transporting solute or component around the feed tank yields:

Accumulation = Input - Output

The PDE representing the mass balance of perrenate in the feed tank is given by

Equation 5.15:

$$\frac{\partial C_{F,t}}{\partial t} = - \frac{Q_F}{V_F} (C_{Fm, x=L} - C_{Fm, x=0}) \quad (5.15)$$

where:

$Q_F$  and  $V_F$  = Feed flow rates, mL/hr, and feed tank volumes respectively, mL

$x$  = Any point in space in the membrane module along the  $x$  axis

$L$  = Length of the channel or membrane, cm

$L$  = Length of the channel, cm

$C_{Ft}$  = Concentration of perrhenate in the feed tank at any time  $t$ , M

It is assumed that the feed and the strip tanks are totally mixed and that the concentration exiting the feed tank is the same as the feed concentration entering the SLM module. A similar set of equations will also hold for the strip side mass balances. These equations can be numerically calculated with the appropriate initial and boundary conditions. However, if the flow rate is fast enough to produce only a very small concentration difference during any single pass through the membrane then, the mass balance may be simplified to the following form (here  $dC/dx$  is approximately equal to zero):

$$-\frac{V_F}{A} \frac{dC}{dt} = K (C_F - SC_S) \quad (5.16)$$

Indeed, subsequent steady state experiments outlined in section 6.1.2.2. have shown that only 1% of the feed concentration was transferred to the strip solution in a single pass thereby vindicating the assumption.

Substituting Equation 5.12 for strip side concentration in Equation 5.16 and integrating yields:

$$\ln \frac{C_0}{(1+R) C - C_0 R} = (1+R) \frac{KA}{V_F} t \quad (5.17)$$

where:

$$R = sV_F/V_S$$

This Equation could be used to determine the overall Mass Transfer Coefficient, K, by plotting the Left Hand Side of the equation against time. If Y is defined as the degree of extraction then Y is equal to:

$$Y = (1 - X_F) = \left(1 - \frac{C_F}{C_{F0}}\right) \quad (5.18)$$

where:

$X_A$  = Fraction of perrhenate remaining in the feed solution at any time t.

Substituting Equation 5.18 in Equation 5.17 yields:

$$\ln \frac{1}{(1+R) Y-R} = (1+R) \frac{K}{M} t \quad (5.19)$$

where:

$$M = V_F/A$$

#### 5.4 Open Loop System

Let  $Q_F$  and  $Q_S$  represent the feed and strip side volumetric flow rates respectively then, the average perhenate mass transfer flux,  $J$ , is equal to :

$$\frac{Q_F (C_o - C)}{A} = J = \frac{Q_S C_S}{A} \quad (5.20)$$

The steady state strip side perhenate concentration,  $C_S$ , can also be expressed as:

$$C_S = \frac{Q_F (C_o - C)}{Q_S} \quad (5.21)$$

To obtain the actual mass transfer flux across the membrane consider a thin section of the membrane with width  $b$  and length  $dL$ . Let the perhenate concentrations at the feed side and raffinate side of this section be equal to  $C$  and  $C-dC$  (moles/L) respectively. Then, the steady state mass transfer equation for the feed side is equal to:

$$\frac{dC_F}{dz} = -\frac{1}{U_F} \frac{A}{V} K (C_F - sC_S) \quad (5.22)$$

A similar equation for the strip side is:

$$\frac{dC_S}{dz} = \frac{1}{U_S} \frac{A}{V} K (C_F - sC_S) \quad (5.23)$$

where:

$U_S$  = Strip solution velocity, cm/s

These set of ordinary differential equations (ODEs) can be solved by obtaining the respective Eigen values and vectors. The final solutions for cocurrent flow are:

$$C_F = \frac{C_{F0}}{\left(s + \frac{K_1}{L}\right)} \exp - \left( (K_1 + sL) z \right) \quad (5.24)$$

$$C_S = \frac{C_{F0}}{s + \frac{K_1}{L}} (1 - \exp - \left( (K_1 + sL) z \right)) \quad (5.25)$$

where  $L$  is equal to  $nwK/Q_S$ ,  $K_1$  is equal to  $nwK/Q_F$ ,  $n$  is equal to the number of loops in the module, and  $w$  is the width of each loop. Similar set of equations can also be derived for counter-current operations.

## 5.5

### N versus J Flux

N flux which happens to be the total flux of the transporting species across the membrane is the sum of the convective flux and the diffusive flux, J. Convective flux is associated with the bulk motion of the fluid while the diffusive flux is related relative to this bulk fluid velocity and is governed by Fick's law. The following equation represents the relationship between the total flux, convective and diffusive flux:

$$N_{Re} = N \frac{C_{Re}}{C} + J \quad (5.26)$$

where:

$N_{Re}$  = Total Flux, moles/cm<sup>2</sup>/hr

$NC_{Re}/C$  = Convective flux, moles/cm<sup>2</sup>/hr

J = Diffusive flux, moles/cm<sup>2</sup>/hr

$C_{Re}$  = Concentration of rhenium in the membrane, M

C = Concentration of all species in the membrane, M

In a typical SLM experimental run the concentration of the rhenium in the membrane is around 0.18 mg/L or 9.68 E-07 M, while the concentrations of crown ether and NPOE are 0.04 M and 0.4 M respectively. Thus the ratio of the concentration of perrhenate over all species in the membrane is 2.2 E-06 and hence it can be concluded

that the contribution of convective bulk flow to overall MTF is negligible and  $N_A = J$ .

## 5.6 Equilibrium/Quasi Steady State (QSS) Condition

At overall equilibrium there is no net mass transfer flux or mass transport of any species across the SLM. In the present case at equilibrium the activities of sodium, nitrate and perrhenate ions in the feed will be equal to their respective activities in the strip. The feed and the strip solutions would then become identical and the distribution coefficients of all the ions would be the same for both feed and the strip side.

At equilibrium the following relationship would hold true:

$$J_{Na} = J_{NO_3} = J_{Re} = 0 \quad (5.27)$$

Equations 5.28 represents the sodium perrhenate QSS situation for the present system.

$$J = 0 \Rightarrow C_{Re, F} = \frac{K_{d2}}{K_{d1}} C_{Re, S} \quad (5.28)$$

As per Cussler (1984), QSS is a condition which supports the maximum concentration difference between the feed and the strip solutions. In the case of dilute systems used by Cussler, the distribution coefficients of the salt in the feed is approximately equal to its value in the strip and hence the product of the activities of the

$$V_F[Re]^0 = V_F[Re]_F + V_S[Re]_S + V_M[Re]_M \quad (5.30)$$

$$K_{d1} = \frac{[Re]_{M, Feed}}{[Re]_F} \quad (5.31)$$

$$K_{d2} = \frac{[Re]_{M, Strip}}{[Re]_S} \quad (5.32)$$

$$\frac{[Re]_F}{[Re]_F^0} = \frac{1}{1 + \frac{K_{d1}}{K_{d2}}} = \frac{1}{1 + \frac{20}{6}} = \frac{3}{13} \quad (5.33)$$

$$\frac{[Re]_S}{[Re]_F^0} = \frac{1}{1 + \frac{K_{d2}}{K_{d1}}} = \frac{10}{13} \quad (5.34)$$

This means that the strip gets more concentrated than the feed solution at equilibrium.

## 5.7 Model Applications

Current coupled facilitated transport models in literature (Danesi, 1986; Stolwijk et al., 1987) give importance to the extraction half of the SLM process. They consider the ion concentrations in the stripping solution to be negligible. This is true only when, either the volume of the feed solution is much lower than the volume of the strip solution for a closed loop system or when the stripping solution is not recycled. Both of these situations are undesirable as they lead to an increase in waste volume. Also, as per the current models in literature, transport of an ion against its concentration gradient is predicted to be impossible in co-transport.

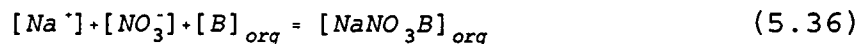
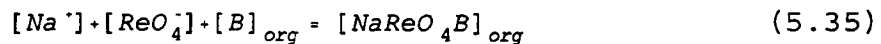
One of the primary objectives of this research was to explore the possibility of transport of an ion against its concentration gradient in co transport. This model shows that such a transport is possible when  $C_F/C_S$  is greater than  $K_{d2}/K_{d1}$ , due to a continuous removal of the other components from the stripping solution either by ion exchange, precipitation, adsorption etc. In the present case, to maximize the concentration of perrhenate in the strip, continuous removal of sodium and/or nitrate ion is required.

From the SLM experiments the feed, membrane and strip side mass transfer coefficients,  $k_a$ ,  $k_m$ , and  $k_b$  respectively can be determined. The distribution coefficients  $K_{d1}$  and  $K_{d2}$  can be predetermined from batch experiments. Hence, the overall mass transfer coefficient,  $K$ , can be determined from Equation 5.9. The mass transfer flux can also be determined from Equation 5.8 for both closed and open loop systems. Conversely, Equations 5.17 and 5.25 can predict the area required to achieve a desired strip side concentration for open and closed loop systems and from this area, the membrane contactor can be designed. This model can also predict the performance when a different membrane is used under particular conditions. The only mass transfer coefficient that would change is the membrane mass transfer coefficient,  $k_m$ . The membrane MTC,  $k_m$ , is directly proportional to the effective membrane diffusivity,  $D_{eff}$ .  $D_{eff}$  varies for each membrane due to their different membrane porosity and tortuosity. In contrast, the diffusivity in bulk organic-diluent solution,  $D_{io}$ , is a constant for any membrane and is only dependent on the composition of extractant-diluent solution. This value of  $D_{io}$  can be directly obtained from the experiments. Hence, the effective

diffusivity  $D_{\text{eff}}$  in a different membrane can be predicted if membrane porosity and tortuosity parameters are known. Even if these parameters are not known, a single experiment at high feed and strip flow rates would be sufficient to predict membrane performance as under these conditions the overall mass transfer coefficient is equal to the membrane mass transfer coefficient. The overall mass transfer coefficient can be determined from equations 5.17 and 5.25.

## 5.8 Ion Pair/Free Ion Chemistry Model

The above model projects the ratio of feed and strip side distribution coefficients to be the all important SLM design parameter. Hence, it is imperative to have a model which could quantify this ratio as a function of process chemistry. In this model it is assumed that the feed consists of nitrate, sodium and perhenate ions. In order to formulate a multi-ion transport model, a thorough understanding of the process is essential. The following equations represent the chemistry of the process for low dielectric constant diluents where ion pair is the predominant means of transport within the membrane at the respective feed and strip interfaces.



where:

[B] = Extractant concentration, M

Let  $K_x$  and  $K_y$  be the equilibrium constants for Equations 5.35 and 5.36 respectively then,

$$\frac{[NaBRe]_{org}}{[Re]} = K_{dl} = K_x [Na^+] [B]_{org} \gamma_{\pm}^2 \frac{\gamma_B}{\gamma_{NaBRe}} \quad (5.37)$$

where:

$\gamma$  = activity coefficient

[Re] has been used to represent perrhenate concentration for simplicity sake.

Also,

$$[NaBNO_3]_{org} = K_y [Na^+] [B]_{org} [NO_3^-] \gamma_{\pm}^2 \quad (5.38)$$

Let  $B_T$  represents the total moles of extractant available. Then,  $B_T$  is equal to:

$$\frac{B_T}{V_{org}} = C_b = ([B] + [NaBRe] + [NaBNO_3])_{org} \quad (5.39)$$

where:

$V_{org}$  = Volume of the organic phase in the SLM, mL

In the present system, concentration of perrhenate complexed by the extractant [NaBRe] is much smaller than the concentration of nitrate complexed by the extractant as initial nitrate concentration is greater than perrhenate concentration by over 4 orders of

$$[B]_{org} = C_b - [NaBNO_3]_{org} \quad (5.40)$$

$$[B]_{org} = \frac{C_b}{1 + K_y [Na^+] [NO_3^-] Y_{\pm}^2} \quad (5.41)$$

$$\frac{Y_B}{Y_{NaBRe}} = 1 \quad (5.42)$$

$$R = K_x [Na^+] Y_{\pm}^2 \quad (5.43)$$

Substituting Equation 5.43 in Equation 5.37 yields,

$$K_{d1} = R_{feed} [B]_{feed} \quad (5.44)$$

$$K_{d2} = R_{strip} [B]_{strip} \quad (5.45)$$

It may be noted that the strip side equations are just the reverse of feed side equations and the equilibrium constants are the reciprocal of  $K_x$  and  $K_y$  for perrhenate and nitrate respectively.  $K_{d2}$  is identical to  $K_{d1}$  except that in  $R$  and  $[B]$  the sodium and nitrate concentrations would be the desired strip side concentrations. These could be made constant by bleeding the strip solution at any desired sodium and nitrate concentrations and by adding an equal amount of fresh water to the strip solution.

The constant  $R$  for feed and strip sides can be represented by Equations 5.46 and 5.47 respectively.

$$R_{feed} = K_x [Na^+]_{feed} Y_{\pm, feed}^2 \quad (5.46)$$

$$R_{strip} = K_x [Na^+]_{strip} \gamma_{\pm}^2_{strip} \quad (5.47)$$

and similarly

$$[B]_{feed} = \frac{C_b}{1 + K_{y1} [Na^+]_{feed} [NO_3^-]_{feed}} \quad (5.48)$$

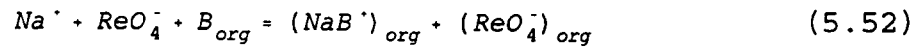
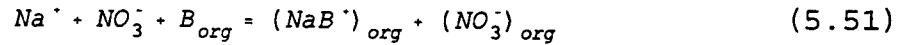
$$[B]_{strip} = \frac{C_b}{1 + K_{y1} [Na^+]_{strip} [NO_3^-]_{strip}} \quad (5.49)$$

where  $K_{y1}$  is the original nitrate equilibrium constant,  $K_y$ , multiplied by the activity coefficient correction factor gamma square.

The ratio  $K_{d2}/K_{d1}$  is equal to:

$$\frac{K_{d2}}{K_{d1}} = \frac{[Na^+]_s \gamma_{\pm}^2_s (1 + K_{y1} [Na^+]_f [NO_3^-]_f)}{[Na^+]_f \gamma_{\pm}^2_f (1 + K_{y2} [Na^+]_s [NO_3^-]_s)} \quad (5.50)$$

For a free ions system as in the case of transport in a polar diluent (NPOE), the corresponding chemistry is:



Using a similar set of equations and relationships as in the case of the ion pair model results in:

$$\frac{K_{d2}}{K_{d1}} = \frac{D_{Na, strip}}{D_{Na, feed}} \quad (5.53)$$

where:

$D_{Na}$  = Sodium ion distribution coefficient.

Also,  $D_{Na}$  is equal to:

$$D_{Na} = -K_y Y \pm [Na^+]_f \pm \frac{\sqrt{K_y^2 Y^4 [NO_3^-]_f^2 - 4 C_B Y^2 K_y}}{2} \quad (5.54)$$

Substituting the terms for  $K_{d1}$  and  $K_{d2}$  and Equations 5.50 and 5.53 for the ratio  $K_{d2}/K_{d1}$  in Equations 5.7, 5.8 and 5.9 yields the design equation for a multi-ion system. The flux depends upon initial and final perhenate concentrations, total moles of extractant, volume of the organic phase, feed, strip and membrane mass transfer coefficients, feed and strip sodium ion concentration and complexed nitrate ion concentration. This ratio plays the all important role in determining whether the strip side technetium concentration can be higher than the feed side concentration because, in Equation 5.7 a positive mass transfer flux,  $J$ , is possible as long as  $C_F$  is greater than  $(K_{d2}/K_{d1})x C_s$ , even if

$C_s$  is greater than  $C_F$ . This is possible when, either the transport of sodium nitrate is very small due to the enhanced process selectivity of perrhenate over nitrate or when the concentrations of sodium and nitrate ions in the strip solutions are made negligible by passing the strip solution through an ion exchange system.

For example, in the case with isopar as the diluent, and with the feed and strip side sodium and nitrate concentrations are 5 M and 0.001 M respectively,  $\gamma$ s in feed and strip sides are approximately 0.3 and 1.0, respectively. The nitrate equilibrium constant from Equation 5.38 is equal to  $(1/5 \times 5)$  0.04. The feed side perrhenate concentration is 0.0001 M. From Equation 5.50  $K_{d2}/K_{d1}$  is  $(0.001 \times 1 \times (1 + 0.04 \times 5 \times 5)) / (1 \times 0.09(1 + 0.04 \times 0.001 \times 0.001))$  which is approximately equal to 0.02 which means that the strip side perrhenate concentration can be 50 times greater than the feed side concentration. The  $K_d$ s are a function of nitrate, sodium and perrhenate concentrations in the feed and strip solutions. Therefore, by suitably varying these concentrations a favorable ratio can be achieved and indeed batch experiments done at ORNL have produced distribution coefficient ratios lesser than 0.01. Hence, this model also helps in the achievement of one of the main goals of environmental restoration which is waste minimization. However, despite favorable equilibrium properties, isopar failed produce any significant rhenium transport across the SLM as the mass transport was very slow due to the bulk of the ion pair and hence low diffusivity coefficients. This resulted in the substitution of isopar with NPOE and NPPE where, despite a high  $K_{d2}/K_{d1}$  ratio of 0.3 transport was possible due to the formation of free ions in the membrane solution. In

fact, as explained in Chapter 6, uphill transport was successfully demonstrated with NPOE as the membrane diluent.

## CHAPTER 6

### QA/QC AND RESULTS & DISCUSSION

#### 6.0 Quality Assurance and Quality Control (QA/QC) Procedures

The first step in any QA/QC procedure involves the determination of the precision of the experiments and the percent errors. Absolute precision error is defined as one standard deviation around the mean while relative precision error is the ratio of the standard deviation over the mean (Ott, 1993). Percent precision error is relative error multiplied by 100%. In the present experimental set-up, errors are possible in the ICP measurements, sample collection and analysis, determination of the exact feed and strip flow rates and preparation of solutions. The overall error is the combination of all these individual errors.

Experiments with 0.04 M crown ether (CE) as the solvent, nitrophenyloctylether (NPOE) as the membrane diluent, 1 M NaNO<sub>3</sub> and 0.1 mM NaReO<sub>4</sub> as the feed were repeated 6 times over a period of 6 months in order to determine the relative and absolute precision error of the experiments. The Rhenium (Re) mass transfer flux ( MTF) obtained for the set of 6 experiments were 4.18 E-08, 4.21 E-08, 4.02 E-08, 4.00 E-08, 4.05 E-08, and 4.39 E-08 moles/cm<sup>2</sup>/hr. This results in an absolute precision error of 1.36

E-09 around a mean of  $4.14 \times 10^{-8}$  and a relative precision error of 3.29 %. It is assumed that since the experiments were conducted during different time periods, the precision error for all the experiments would approximately be the same and would be equal to 3.29%, the precision error for the above experiments. Similarly the relative precision error for Na MTF was 3.6%.

All data were measured using the Inductively Coupled Argon Plasma (ICAP). Sodium and rhenium calibration studies were conducted during every analysis and ICAP data were adjusted as per the calibration curves for sodium and rhenium. Figures 6.1 and 6.2 show a typical sodium and rhenium calibration curves respectively. The concentration of either sodium or rhenium was determined in the following manner. The ICP reading was first marked along the Y-axis and a horizontal line was drawn parallel to the X- axis. Next the point where this line intersected the ICP calibration line (marked as ICP in Figures 6.1 and 6.2) was determined and finally the projection of this point on the X-axis was used to determine the concentration. Such a calibration was necessary as the ICP used a 2 point calibration which resulted in erroneous data.

During the course of the experimental study some samples were fed into the ICP as triplicates and as quadruplicates to determine the precision of the ICP. The ICP analysis data has an absolute precision error of 0.49 mg/L around the mean value and a percent relative precision error of 0.62%.

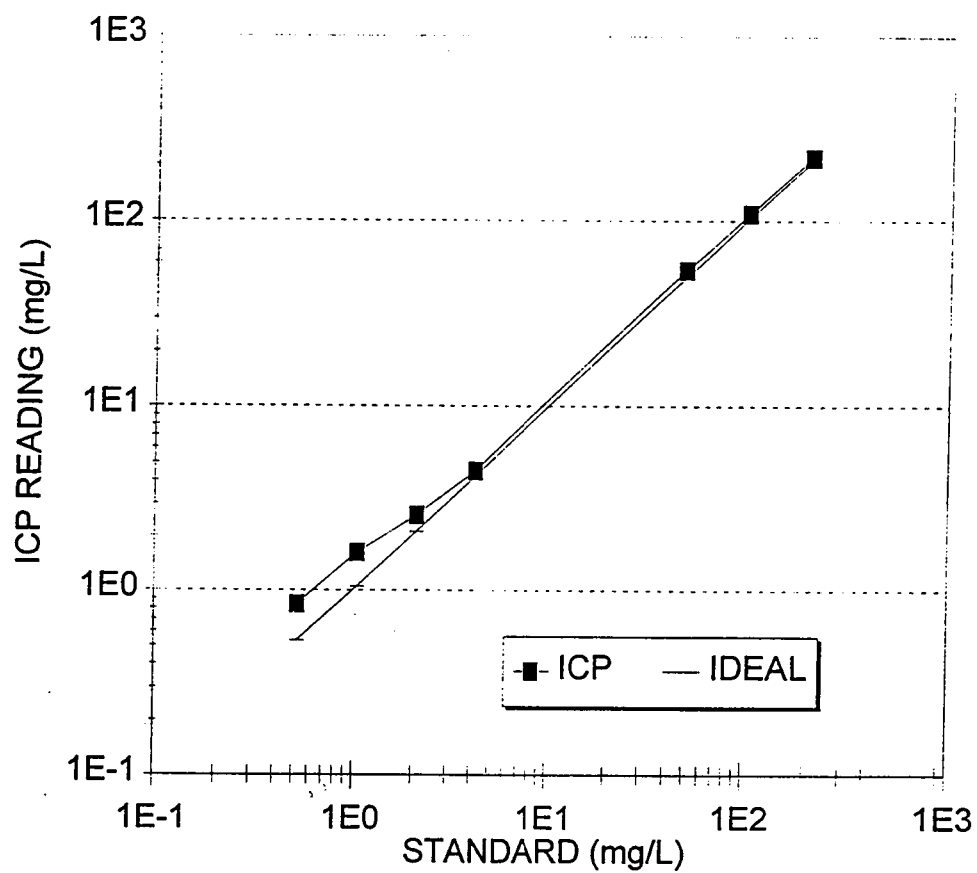


Figure 6.1: ICP Sodium Calibration Plot

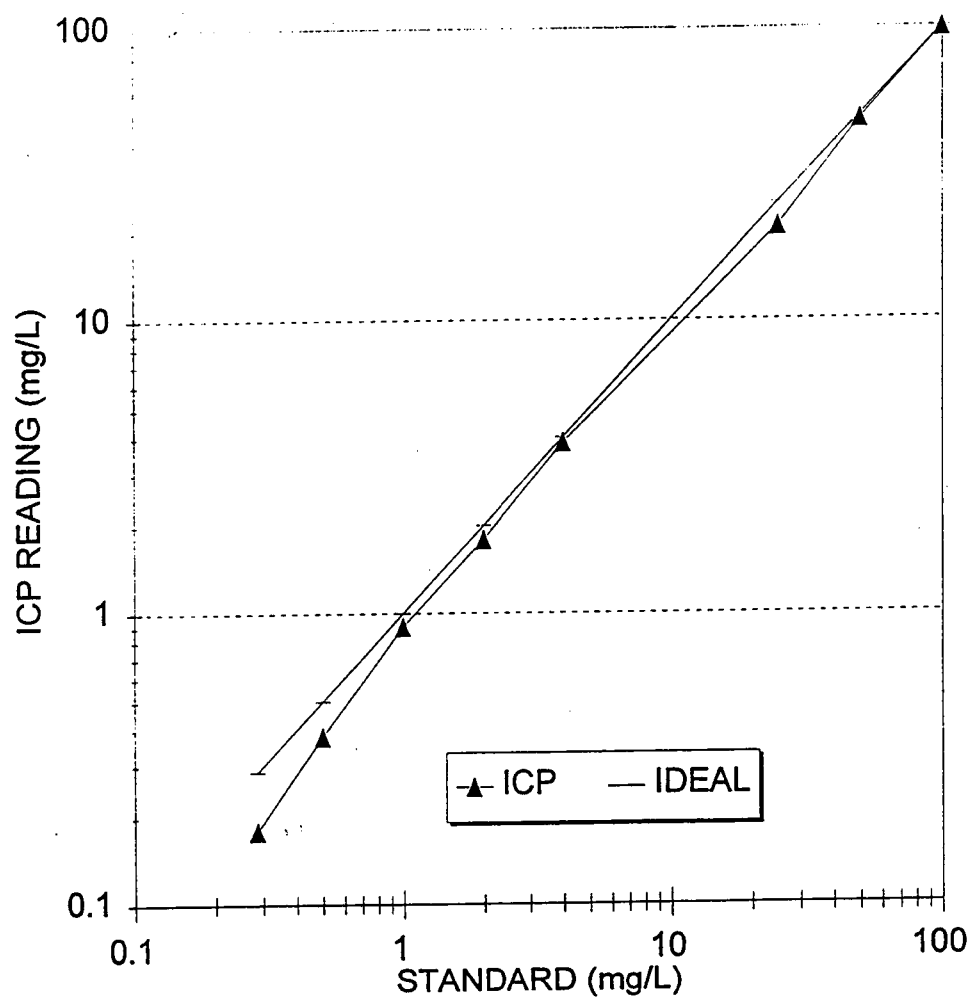


Figure 6.2: ICP Rhenium Calibration Plot

Also, both the feed and the strip flow rates were measured at the start and the end of each experiments for consistency and precision estimation. The mean feed and strip flow rates were 406 mL/hr and 338.2 mL/hr and the standard deviations were 12.54 and 9.69 mL/hr respectively. From these data the feed flow rate and strip flow rate relative precision errors were 3.08% and 2.87 % respectively. The overall percent relative errors for Re and Na MTFs were 5.38% and 5.57% respectively (based on the propagation of errors formula, Ott, 1993).

## **6.1 Results & Discussion**

This section has been divided into 4 subchapters namely, Mass transfer flux experiments, Mass transfer coefficient experiments, Model verification & Kinetic analysis, and Equilibrium/QSS analysis. The objective of the mass transfer flux experiments was to determine the feasibility of extracting and transporting sodium perrhenate across an SLM from a simple waste simulant and from a simulant of an actual DOE waste. The objective of the mass transfer coefficient experiments was to individually determine the aqueous feed and strip and membrane MTCs and the overall MTC. The objective of the model verification and kinetic analysis section was to compare the experimental MTF and MTC data with the predicted results obtained from the Stoke's-Einstein's equation, Stolwijk et al. (1987) and Cussler (1984) models. Finally the objectives of the equilibrium/QSS analysis section were 1) to determine if sodium perrhenate could be transported against its concentration gradient and 2) to make the

readers familiar with the concentrations at QSS in a typical SLM experiment/run.

### **6.1.1 Mass Transfer Flux (MTF) Experiments (Tasks 3,4,5,6,10,11,18)**

#### **6.1.1.1 Optimum Extractant-Diluent-Modifier (EDM) Combination Experiments**

**Note: All feed, strip, membrane concentrations and operating conditions used in this research were same as those specified in the footnote of Table 6.1 unless otherwise stated.**

The objective of this set of experiments was to evaluate the efficacy of several crown ethers (as extractants), diluents and modifiers in extracting perrhenate across an supported liquid membrane (SLM). The separations research group in the division of Chemical and Analytical Sciences at the Oak Ridge National Laboratory had previously identified a set of crown ethers, diluents and modifiers for use in the conventional solvent extraction process. A modifier is typically an organic functional group which is added to either the extractant or diluent in order to make the resultant solution more lipophilic. The chemicals identified, were used as the starting point in the SLM experiments. The feed solution consisted of 1 M sodium nitrate and 0.1 mM sodium perrhenate while the strip solution used was deionized water. Experiments were performed in a closed loop as per the procedure outlined in Chapter 4

Table 6.1: Results of the Optimum EDM Experiments

| Crown Ether | Conc. | Diluent  | Modifier       | Na MTF*                   | Re MTF*                   |
|-------------|-------|----------|----------------|---------------------------|---------------------------|
|             | M     |          |                | moles/cm <sup>2</sup> /hr | moles/cm <sup>2</sup> /hr |
| dtbCH18C6   | 0.04  | Isopar V | 4-1-BPP        | NT                        | LDTL                      |
| dtbCH18C6   | 0.1   | Isopar M | 4-1-BPP        | NT                        | LDTL                      |
| dtbCH18C6   | 0.04  | Isopar M | 4-1-BPP        | NT                        | LDTL                      |
| dtbCH18C6   | 0.04  | Isopar M | 2-Octanone     | NT                        | 9.50e-09                  |
| dtbCH18C6   | 0.04  | NPOE     | none           | 5.40e-07                  | 6.10e-08                  |
| dtbCH18C6   | 0.04  | NPPE     | none           | 1.80e-06                  | 1.60e-07                  |
| DCH18C6     | 0.04  | Isopar M | 2-Octanone     | 1.00e-04                  | 1.50e-08                  |
| DCH18C6     | 0.04  | Isopar M | 1:1-2-Octanone | 3.20e-07                  | LTDL                      |

LDTL = Less than detection limit = 1.09 E-09 moles/cm<sup>2</sup>/hr

NT = Not tested

**\*System Conditions**

Closed Loop

Feed:

1 M Sodium Nitrate, 0.1 mM Sodium Perrhenate

Strip:

DI Water

Flow Rates:

Feed and Strip = 400 mL/hr

Membrane Area = 7 cm<sup>2</sup>

Membrane Tortuosity = 3.4

Membrane Porosity = 45%

Temperature 25 °C

Volume:

Feed and Strip = 500 mL

Fresh Membrane Used Each Run

Table 6.1 lists the results of all the chemicals tried in this study in transporting perrhenate across an SLM. Only the diluents, nitrophenyloctylether (NPOE) and nitrophenylpentylether (NPPE) were successful in extracting perrhenate across the SLM. Mass Transfer Fluxes (MTFs) ranged in the order of  $10^{-6}$  -  $10^{-7}$  (moles/cm<sup>2</sup>/hr) for nitrate and  $10^{-7}$  -  $10^{-8}$  (moles/cm<sup>2</sup>/hr) for perrhenate. None of the EDM combinations, successful in the conventional solvent extraction process, proved successful in extracting rhenium across an SLM. This could be attributed to a number of factors such as the high polarity and dielectric constant of NPOE and NPPE as compared to Isopar V and M, viscosity of the membrane solution, molecular size of the crown ether-diluent-modifier-cation-anion-complex, and effective membrane diffusion coefficient.

Polar diluents transport solutes predominantly as free ions and non-polar diluents transport as ion pairs (Stolwijk et al., 1987). Free ions generally tend to diffuse much faster than ion pairs across SLMs. Also, ion pairs which consist of both the cation and the anion bound to the crown ether molecule, have a larger molecular size than free ions. Larger sized molecules have a much lower effective diffusion coefficient than smaller sized molecules during transport along a very tortuous path as in the Celgard membrane which has a tortuosity factor of over 3.0. Tortuosity factor is defined as the ratio of the actual distance traveled by a solute over the shortest distance (linear distance) between its starting point where it gets complexed and its ending point where it gets decomplexed. Finally, diluents with a lower viscosity, larger dielectric constant and larger effective

diffusion coefficients transport faster than highly viscous diluents. NPPE systems which have a 40% less viscosity and 20% higher dielectric constant than NPOE, transported faster than NPOE systems. Also, Isopar V and M and 2-Octanone which have considerably less polarity failed to transport sodium perrhenate across an SLM. Based on the results, NPPE is the best membrane diluent of all the tested diluents followed by NPOE. However, it should also be noted that generally polar diluents are more water soluble and hence could lead to membrane instability.

#### **6.1.1.2 Batch Experiments**

Batch experiments were conducted on the optimum EDM system identified from the task 3 experiments and on the same set of feed and strip conditions as used in the continuous SLM experiments. The objective of these experiments was to determine the feed and strip side distribution coefficients. These distribution coefficients are essential for computation of the MTCs. NPOE by itself extracted no detectable rhenium in batch experiments. This indicates that NPOE doesn't by itself solvate  $\text{TcO}_4^-$  and  $\text{ReO}_4^-$  and hence there would be no stripping constraints in an SLM operation as no additional energy would be required to break any solvation bonds.  $K_{d1}$  and  $K_{d2}$  values determined by batch experiments for the EDM system and used for the MTC calculations were 20 and 6 respectively for 0.04 M dtbCH18C6 in NPOE, 1 M  $\text{NaNO}_3$ , 0.1 mM  $\text{NaReO}_4$  feed, and DI water as the strip solution.

### 6.1.1.3 Optimum Extractant Concentration Experiments

The objective of this set of experiments was to determine the optimum extractant concentration to be used in the membrane in terms of MTF, MTC, and selectivity. It is desirable to determine this optimum condition because any concentration below this optimum concentration would result in lower mass transfer flux and selectivity, while any higher concentration would result in increased cost and/or decreased selectivity and MTF. The concentration which results in a high process selectivity for perrhenate over nitrate at a fairly high MTF, would be considered as the optimum concentration. It is not necessary for the optimum concentration to yield the largest MTF but it should yield close to the largest selectivity.

Figure 6.3 shows a plot of sodium and rhenium fluxes as a function of initial crown ether concentration (dtbCH18C6),  $[CE]^0$ . Error bars represent the total experimental error as discussed before. As is evident from the graph, MTF does not vary linearly with  $[CE]^0$  which is an indication of free ion transport (Stolwijk et al., 1987). Statistical analysis of the MTF data presented in Chapter 7, indicates a nonlinear quadratic relationship between MTF and initial crown ether concentration in the membrane. The sum of the nitrate and perrhenate flux is equal to the sodium flux as sodium is the common cation co-transported along with both the anions. This is true on

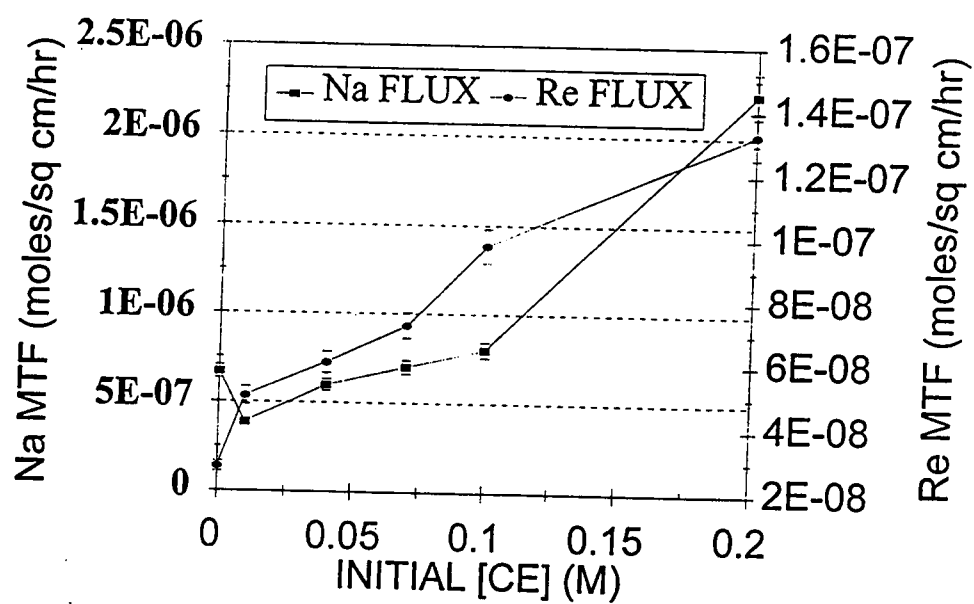


Figure 6.3: Effect of Initial Crown Ether Concentration on MTF

the basis of ion balance and electroneutrality. For nitrate transport, mass transfer flux for the NPOE (diluent) only system with no crown ether was 80% more than the MTF for the system with an initial crown ether concentration,  $[CE]^0$ , of 0.01 M and was 11% more than the MTF when  $[CE]^0$  was 0.04 M. But this observation is driven by the higher MTF value obtained in the absence of the crown ether. This data point could itself be erroneous and hence not much attention should be paid to this drop in MTF between  $[CE]^0$  of 0.0 and 0.01 concentrations. But when the  $[CE]^0$  was increased to 0.07 M and 0.1 M, MTF over the diluent, MTF increased by 5 and 20% respectively. Between 0.1 and 0.2 M  $[CE]^0$ , MTF increased by nearly 3 times. Unlike as in the case of batch experiments (solvent extraction), there was some transport of sodium perrhenate in an NPOE only system.

Perrhenate flux initially increased rapidly by a factor of 280% till a  $[CE]^0$  of 0.04 M and then gradually increased to 478% at a  $[CE]^0$  concentration of 0.2 M. This means that at lower  $[CE]^0$  concentrations of up to 0.1 M, perrhenate transport is highly favored over nitrate transport resulting in higher selectivity. At  $[CE]^0$  beyond 0.1 M perrhenate is still preferred over nitrate but not as much as before as is evident from the sharp drop in rhenium selectivity beyond  $[CE]^0$  of 0.1 M. Hence it is prudent to operate the SLM at  $[CE]^0$  values of less than 0.1 M.

Figure 6.4 shows a plot of selectivity as a function of  $[CE]^0$ . Selectivity is

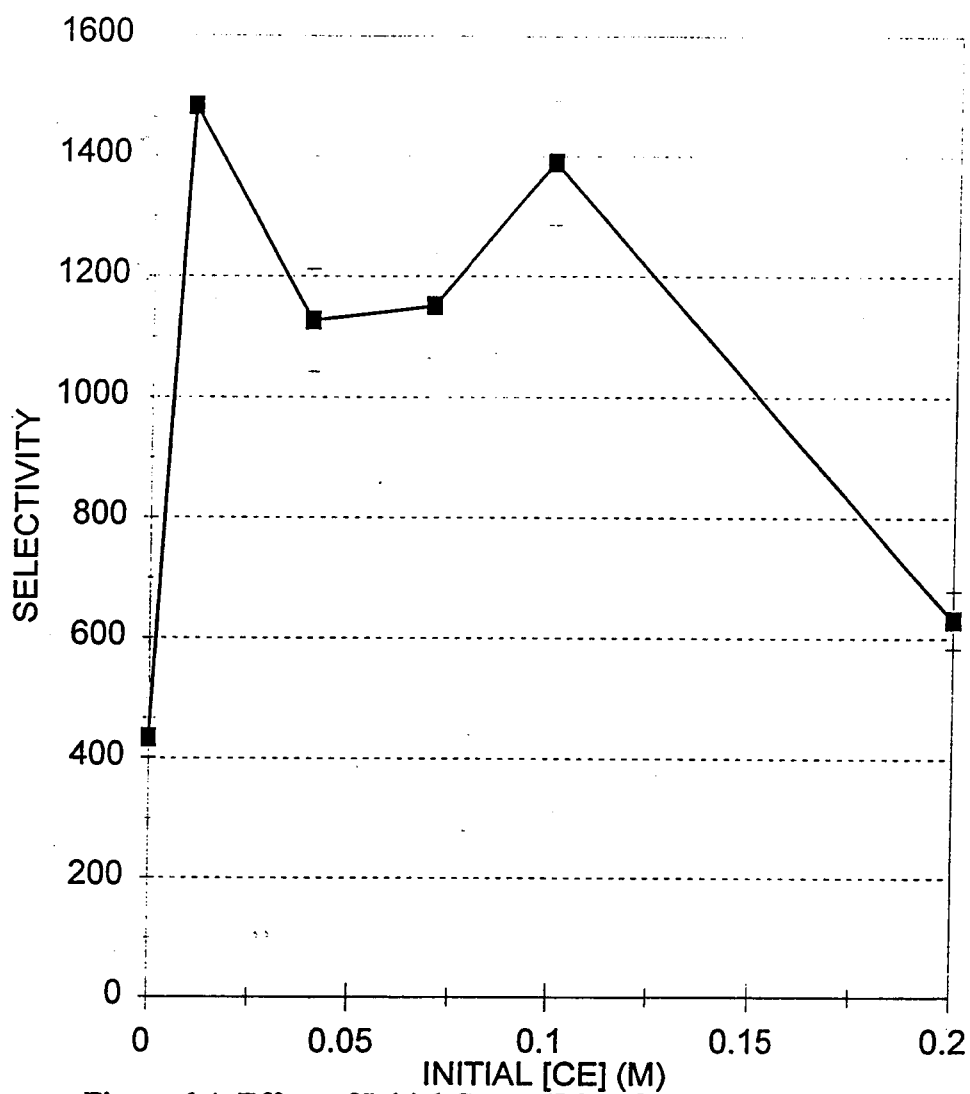


Figure 6.4: Effect of Initial Crown Ether Concentration on Perrhenate Process Selectivity.

defined as the ratio of rhenium flux over nitrate flux times the ratio of initial nitrate concentration over initial perhenate concentration. Selectivity was low at a value of 400 for the NPOE only system and reached a maximum of 1500 between  $[CE]^0$  of 0.01 to 0.1 M before decreasing to 620 at  $[CE]^0$  of 0.2 M. Selectivity data has shown considerable scatter and has an error of 7.5%. Incorporation of the error bars shows that selectivity was a near constant around 1350 between  $[CE]^0$  of 0.01 and 0.1 M. Based on the results of this set of experiments 0.04 M  $[CE]^0$  was chosen as the optimum initial CE (extractant) concentration.

Even if the overall experimental precision error of  $\pm 5.5\%$  is included in the analysis, there are no significant deviations in the overall conclusions. The only exception would be the Re MTF dependence plot wherein, a positive error correction to the MTF (Actual value + 5.5%) would make the curve appear much smoother.

#### **6.1.1.4 Feed and Strip Velocity Experiments**

The objective of this experiment was to determine the optimum feed and strip flow velocity to be used in an SLM operation. Operation beyond the optimum flow rates results in higher power costs while operation below the optimum flow rates results in lower flux, and lower MTC and higher costs due to a larger module. Figures 6.5 and 6.6 show plots of MTF and MTC as a function of feed and strip velocity. The MTCs were

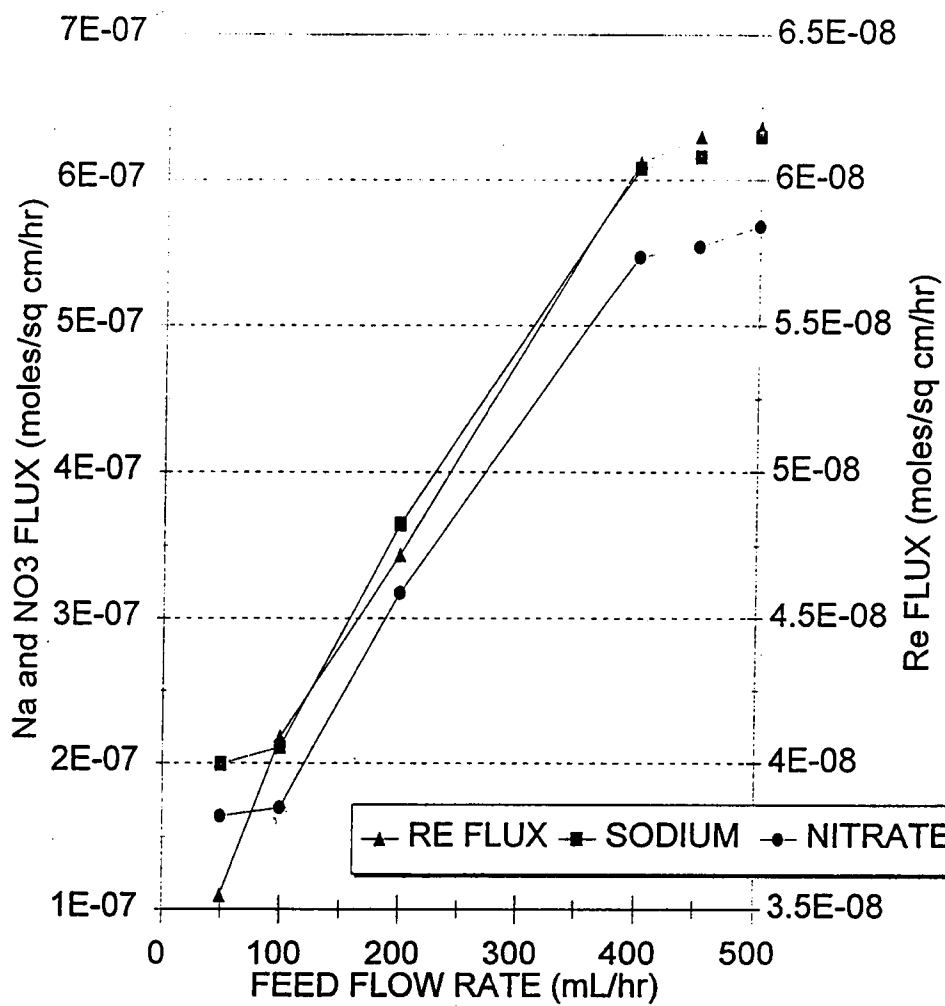


Figure 6.5: Effect of Feed Flow Rate on MTF

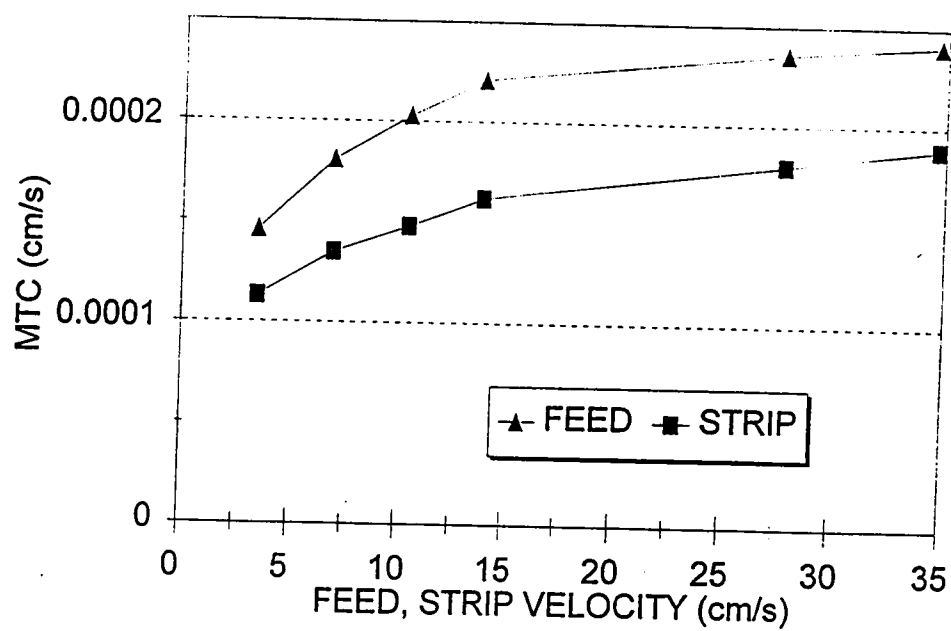


Figure 6.6: Dependence of mass transfer coefficient on feed and strip velocity.

determined from Equation 5.17 (Chapter 5). Feed and strip  $K_d$  values used for determining the MTCs were 20 and 6 respectively. Nitrate MTF rose to  $5.32 \times 10^{-7}$  moles/cm<sup>2</sup>/hr at 400 mL/hr and then rose more slowly to its maximum value of  $5.70 \times 10^{-7}$  moles/cm<sup>2</sup>/hr at a flow rate of 500 mL/hr. However, perrhenate MTF rose from  $3.5 \times 10^{-8}$  to  $6.2 \times 10^{-8}$  moles/cm<sup>2</sup>/hr respectively, when the flow rate was increased from 50 to 400 mL/hr before rising slowly to its maximum value of  $6.4 \times 10^{-8}$  moles/cm<sup>2</sup>/hr. The MTF and MTCs reached a maximum, for the range tested, for both nitrate and perrhenate at the highest flow rate tested of 500 mL/hr. Both the feed and strip velocity profiles are nearly parallel to one another throughout the entire range of the experiment. The optimum feed and strip velocity also are identical and equal to 27 cm/s corresponding to a flow rate of 400 mL/hr. This flow rate is considered optimum because beyond this flow rate there was no appreciable increase in MTF and MTC.

Figure 6.7 shows a plot of selectivity as a function of feed velocity. Not much statistical significance is attached to the increase in selectivity when the flow rate was increased from 50 to 100 mL/hr as there is nearly  $\pm 7.3\%$  analytical error in selectivity data. Hence, it is possible that both the values could have been nearly identical. Selectivity decreased from 2400 to 1100 when feed flow rate was increased from 100 to 500 mL/hr, suggesting a preference for nitrate transport at higher flow rates. This could be because at lower flow rates there is a larger concentration difference between the bulk solution and the interface due to the presence of a relatively large boundary layer. This

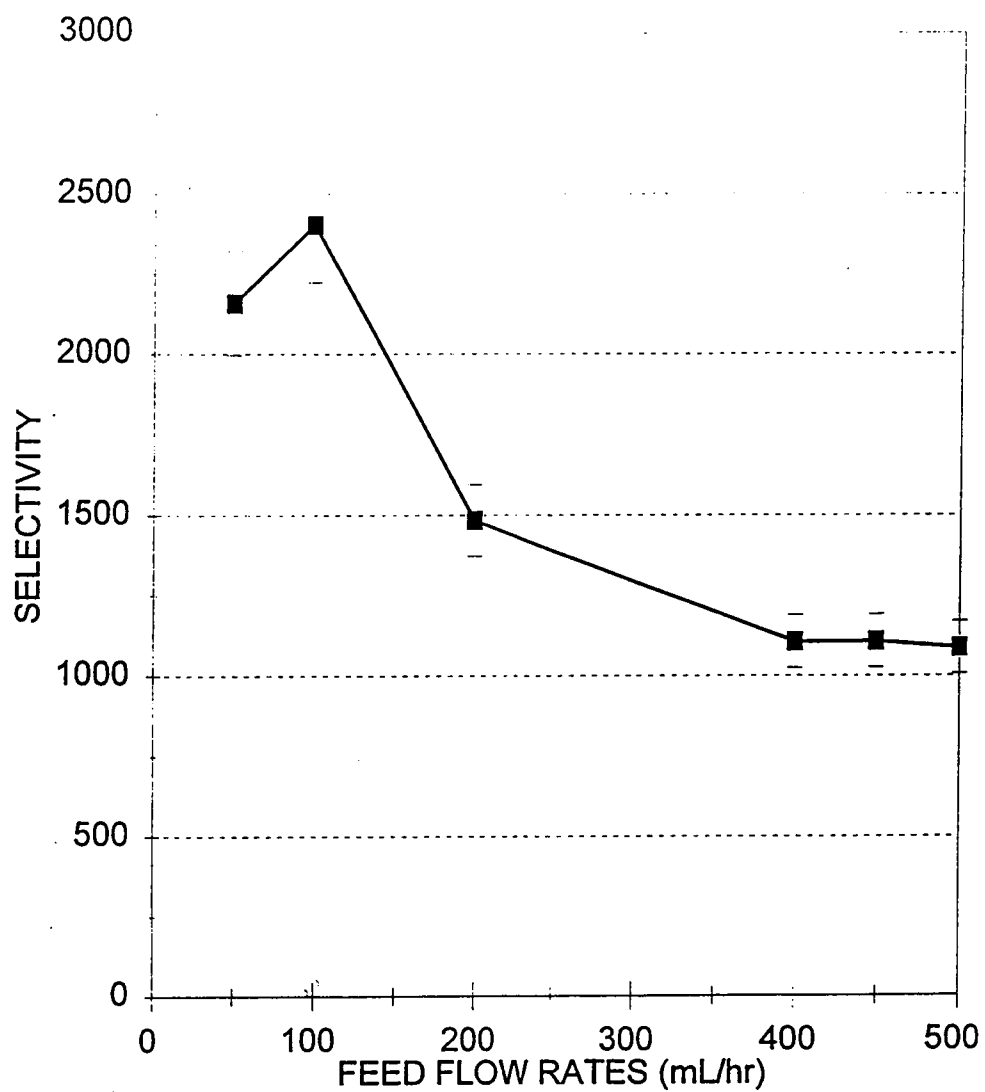


Figure 6.7: Effect of Feed Flow Rate on Process Selectivity

concentration drop would actually result in lower nitrate concentration at the interface, lower distribution coefficients and hence lower MTF. At higher flow rates boundary layer thickness decreases leading to an increase in the interfacial nitrate concentration and transport. This effect of aqueous flow rates and boundary layer thickness on aqueous concentration profile is very pronounced when the aqueous feed concentrations are greater than 0.001 M (Cussler et al., 1986). Since rhenium was always kept at a concentration lower than 0.001 M, the effect of aqueous velocity on perrhenate concentration can be considered negligible. Hence, Re aqueous concentration profile and transport is nearly a constant and this resulted in a drop in selectivity. As per the propagation of errors formula the overall error in selectivity estimation would be the root of the sum of the variance of Re and Na MTF estimation errors and is equal to 7.3%.

An interesting point to be noted in this set of experiments is that unlike the previous research (Danesi, 1985), strip velocity MTC profile parallels the feed velocity profile suggesting that strip velocity and strip side concentrations and distribution coefficients cannot be neglected in the mass transport model. In Danesi's experiments the MTF curve was horizontal and parallel to the X axis which indicates no relationship with the aqueous strip velocity.

#### 6.1.1.5 MTF versus Feed Molar Activity Experiments

The objective of this set of experiments was to determine the effect of a change in feed composition on mass transport. The concentration of sodium perrhenate was changed from 0.01 to 0.5 mM in the first set of experiments, while the sodium nitrate concentration was kept fixed at 1 M. Figure 6.8 shows the effect of changes in perrhenate concentration on the sodium and rhenium MTFs. Both sodium and rhenium MTF increased linearly with an increase in feed perrhenate concentration. Nitrate MTF, which is the difference of sodium and rhenium MTFs, also increased linearly with feed perrhenate concentration. Surprisingly however, the percent increase in sodium and nitrate flux was over 6 times more than the percent increase in rhenium MTF over the same range. Since different and separate  $K_d$  values are required for each different feed rhenium and nitrate concentrations, MTCs were not computed for this set of experiments.

Figure 6.9 shows a plot of selectivity as a function feed perrhenate concentration. Selectivity drops from over 3600 to 240, or over an order of magnitude, when the feed perrhenate concentration was increased from 0.01 to 0.5 mM. This is because of an increase in the rhenium MTF due to an increase in the feed perrhenate concentration is more than offset by a corresponding decrease in the ratio of feed nitrate over perrhenate concentrations.

Figure 6.10 shows the effect of change in feed sodium concentration on Na and

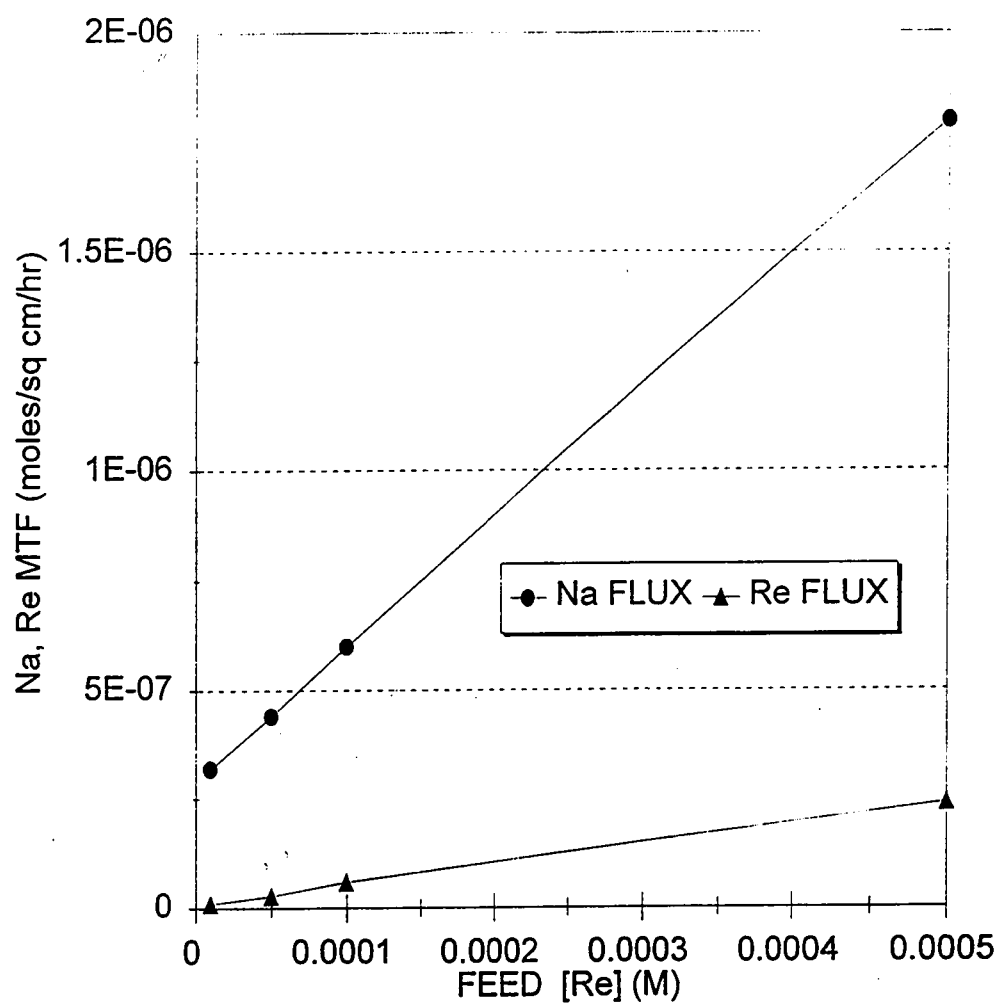


Figure 6.8: Effect of Feed Rhenium Concentration on Sodium and Rhenium MTF

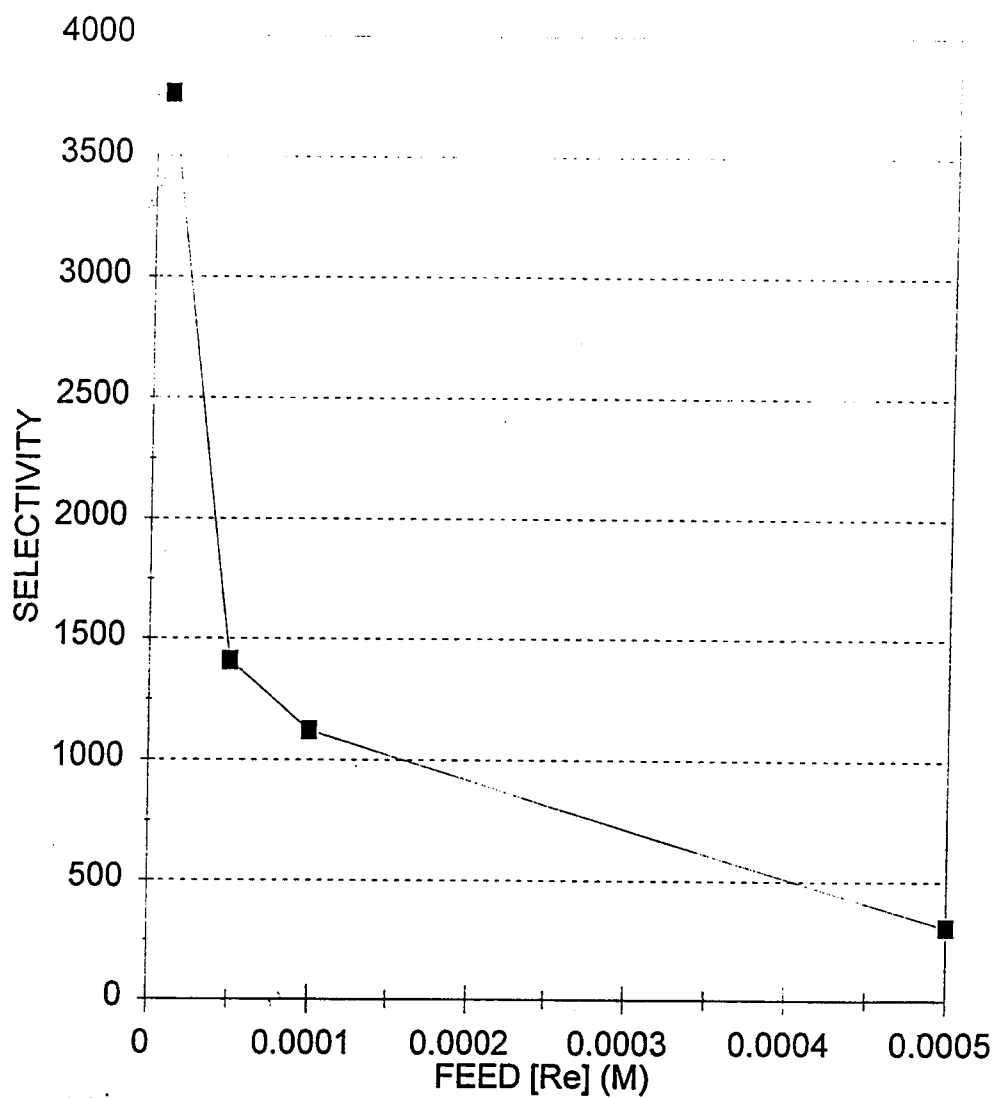


Figure 6.9: Effect of Feed Rhenium Concentration on Rhenium Process Selectivity

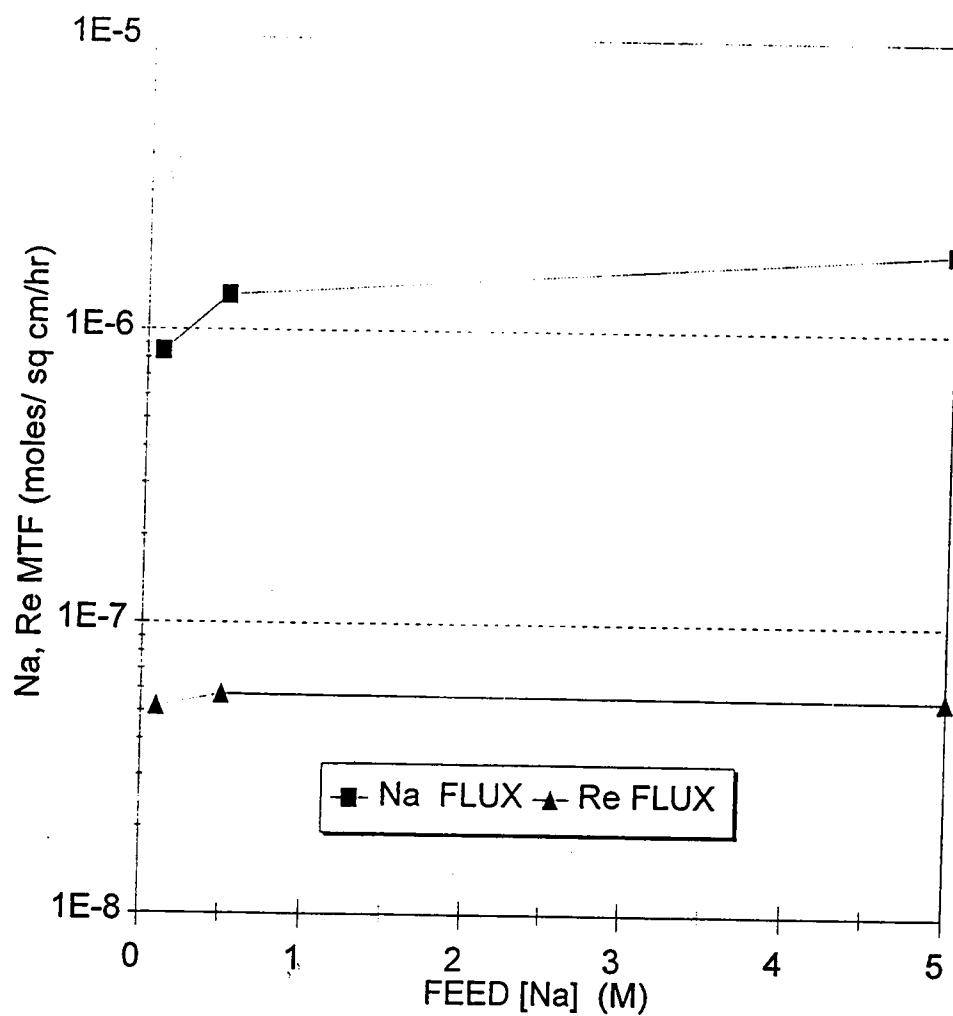


Figure 6.10: Effect of Feed Sodium Concentration on MTF

Re MTF. When the sodium nitrate feed concentration increases from 0.1 to 5 M with sodium perrhenate concentration fixed at 0.1 mM, there was only a slight increase in sodium and rhenium MTFs and that to only till 0.5 M sodium nitrate feed concentration. An increase in sodium nitrate feed concentration beyond 0.5 M, resulted in no appreciable increase in the MTFs for both sodium and rhenium. This could be because 0.5 M sodium ion concentration gradient between the feed and strip solution, which is the driving force behind this mass transport, could be the saturation concentration gradient and any further increase in the feed sodium concentration would lead to no further appreciable increase in either nitrate or perrhenate MTF. Subsequent steady state and strip composition experiments provide the corroborating evidence to this postulation. This information is very important for designing the stripping cycle as in an actual field operation, the strip solution would be operated in a closed loop to concentrate the waste while the feed would be operated in an open loop once through mode. This 0.5 M sodium ion concentration gradient between the feed and strip solution provides the "break through point" or the point at which the strip solution should be bled off for further treatment. Any further build-up in the strip sodium ion concentration would result in a decrease in the concentration gradient between the feed and strip solution and a decrease in the MTF.

Figure 6.11 shows the effect of feed sodium concentration on selectivity.

Selectivity increased from 72 to 1700 when feed sodium concentration was increased

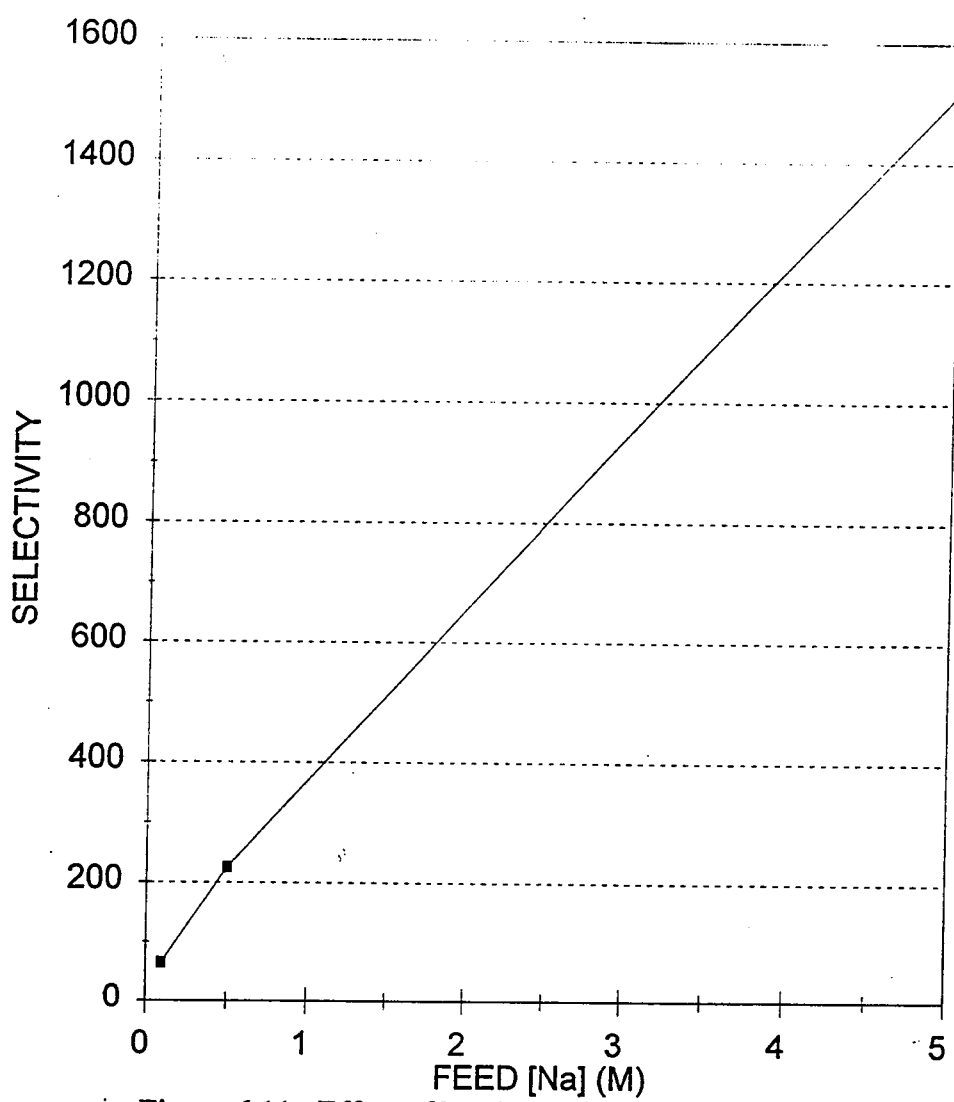


Figure 6.11: Effect of Feed Sodium Concentration on Rhenium Selectivity

from 0.1 to 5 M because of an increase in the ratio of feed sodium nitrate to feed sodium perhenate concentrations.

#### **6.1.1.6 Membrane Thickness Experiments**

The objective of these experiments was to determine whether MTF varied linearly with the inverse of the membrane thickness. If it varies linearly then membrane mass transfer resistance is the controlling resistance (Stolwijk et al., 1987). Experiments were conducted with multiple membranes sandwiched between the channels. Figure 6.12 shows the relationship between MTF and membrane thickness. As can be seen from the plot and the regression analysis ( $R^2 > 0.99$ ), the relationship is linear suggesting that the membrane mass transfer resistance is the controlling resistance to mass transport.

#### **6.1.1.7 Membrane Stability Experiments**

The objective of these experiments were to determine the long term stability of the SLM. Membrane instability is caused by gradual loss of the membrane solution due to aqueous solubility. Figure 6.13 shows the plot of MTF over a period of 10 days of continuous membrane operation. As can be seen from the plot, MTF is very stable over the period and varied from  $4.04 \times 10^{-8}$  to  $4.2 \times 10^{-8}$  /cm<sup>2</sup>/hr (a variation of only 5%).

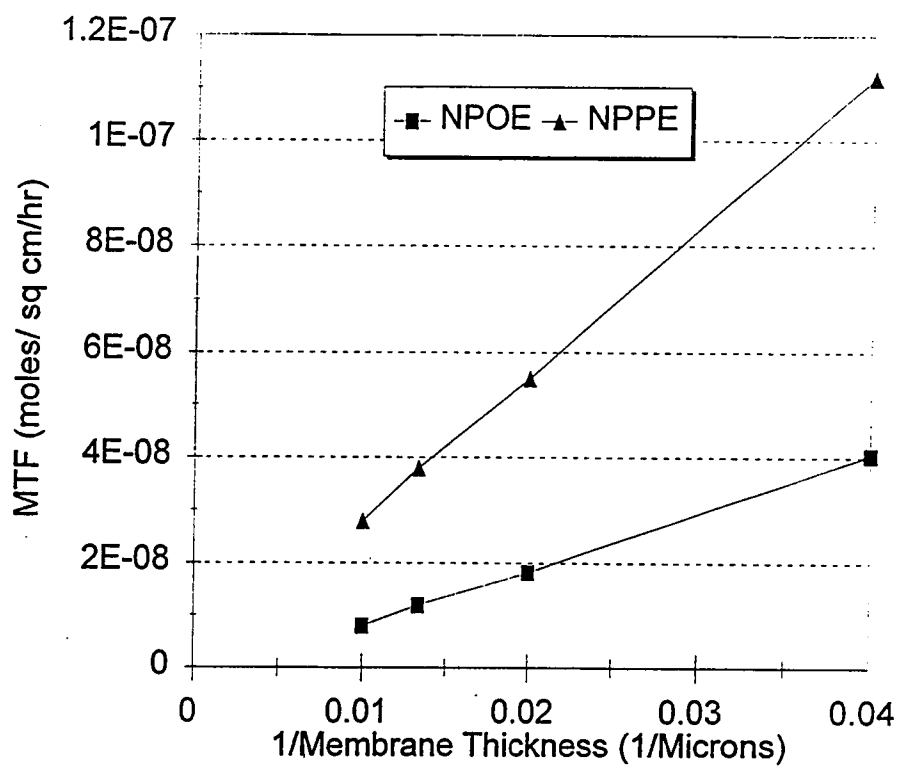


Figure 6.12: Dependence of MTF on Membrane Thickness. A Linear Relationship Indicates that Membrane Resistance was the Limiting Resistance.

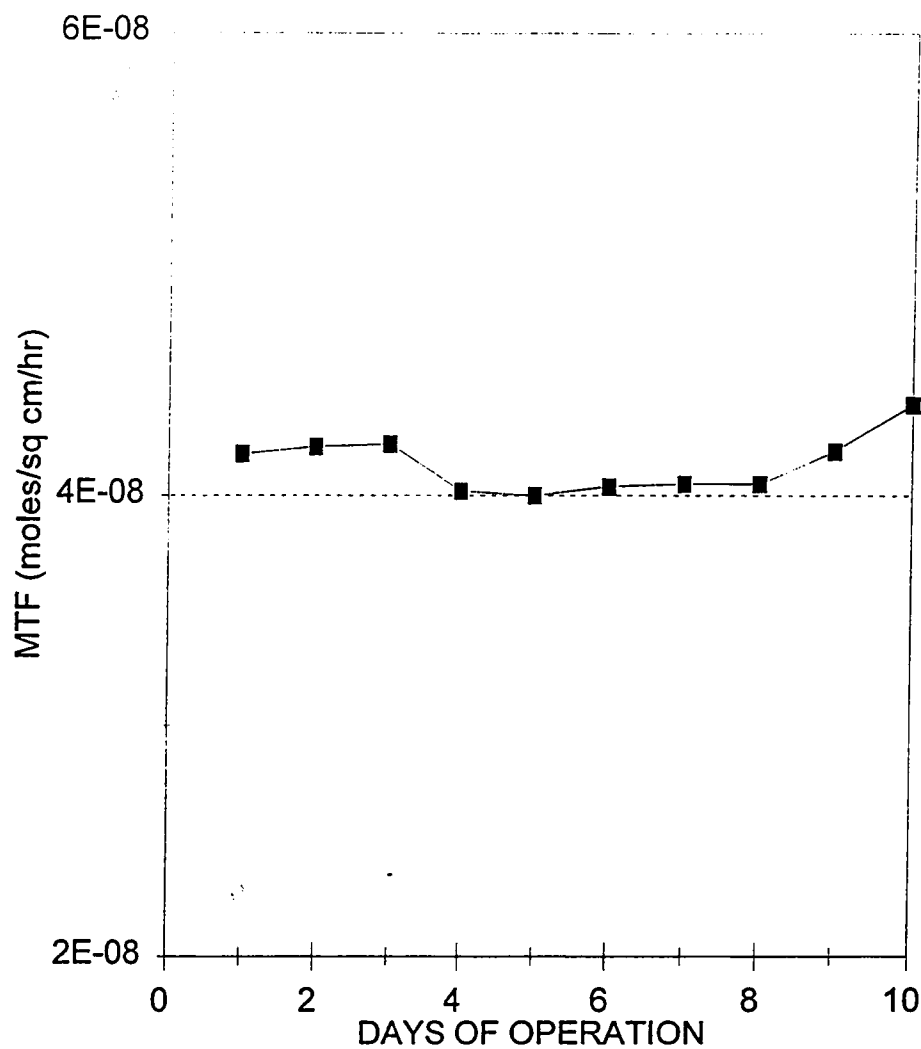


Figure 6.13: Dependence of MTF on Number of Days of Continuous Operation. A Near Constant MTF Indicates Stable SLM

Hence the dtbCH18C6 (CE)-NPOE membrane system can be considered as long term stable.

#### **6.1.1.8 NPPE Experiments**

The objective of this set of experiments was to determine the mass transport of rhenium across an SLM with a higher dielectric constant and lower viscosity diluent. All experimental conditions were similar to the NPOE experiments. Figure 6.12 also shows a linear relationship between MTF for a NPPE system and the inverse of the membrane thickness suggesting that membrane mass transfer resistance is the controlling resistance to mass transport. MTF for NPPE system was about 3.26 times more than NPOE systems. MTCs were not computed for NPPE systems as batch tests are required to determine the ratio  $K_{d2}/K_{d1}$  for NPPE. However, the product of  $K_{d1}$  times the membrane mass transfer coefficient,  $k_m$ , for NPPE is  $4.73 \times 10^{-4}$  cm/s as compared  $1.45 \times 10^{-4}$  cm/s for NPOE. Membrane MTF decreased from  $1.12 \times 10^{-7}$  to  $2.8 \times 10^{-8}$  cm<sup>2</sup>/hr when membrane thickness was increased from 25-100 microns. MTC decreased by 50% when membrane thickness was doubled from 25 to 50 microns. These results show that MTCs and MTFs increase with the dielectric constant of the diluent. Viscosity of the diluent is also inversely proportional to MTF and MTCs.

#### 6.1.1.9 Melton Valley Waste Simulant (MVWS) Experiments

The objective of this set of experiments was to determine the MTF for MVWS waste in a closed and open loop SLM and compare it to the MTF with the simple waste system used in the study so far. This was the first time when knowledge gained from previous transport experiments was used on an actual DOE tank waste simulant. Both NPOE and NPPE were used as diluents in separate experiments. Table 4.1 lists the composition of the MVWS used for this set of experiments. Rhenium MTF was  $7.15 \text{ E-}08 \text{ moles/cm}^2/\text{hr}$  when NPPE was used as the diluent. Corresponding value with NPOE as the diluent was  $2.64 \text{ E-}08 \text{ moles/cm}^2/\text{hr}$ . Similar to the simple waste experiments, NPPE MTF was about 2.7 times more than NPOE MTF in both open and closed loop SLM. Rhenium MTF for MVWS system was 73% of its corresponding simple waste value for both NPOE and NPPE systems. This could be partly attributed to the presence of only  $6 \times 10^{-5} \text{ M}$  rhenium in the MVWS waste as compared to  $1 \times 10^{-4} \text{ M}$  Re in the simple waste used earlier. The NPPE MTF for the MVWS system was around  $8 \times 10^{-8} \text{ moles/cm}^2/\text{hr}$ , while the NPOE MTF was  $3 \times 10^{-8} \text{ moles/cm}^2/\text{hr}$ .

Open loop SLM results mirrored the results of the closed loop experiments. Steady state (S.S.) exit strip Re concentrations with NPOE as the diluent were between 0.17 and 0.18 mg/L ( $1.0 \text{ E-}06 \text{ M}$ ) while in NPPE the corresponding values were 0.49 mg/L ( $2.72 \text{ E-}06 \text{ M}$ ).

## 6.1.2 Mass Transfer Coefficient (MTC) Experiments (tasks 8,9)

It is quite evident from the previous section on MTF experiments that it is technically feasible to transport sodium perhenate across an SLM, using crown ether as the extractant and NPOE as the diluent, from both a simple waste simulant and from an actual DOE waste simulants. The next step involves the determination of the individual and overall MTCs and the steady state open loop exit strip concentrations. These data are especially useful for process scale-up.

### 6.1.2.1 Individual MTC Experiments

The objective of this set of experiments was to individually determine the overall, membrane and aqueous MTCs from the same data presented earlier in section 6.1.1.4. This would aid in determining the effect of feed and strip velocities on aqueous MTCs without the need for any further experiments during process scale-up. Also, from the membrane MTC an accurate estimate of  $D_{io}$  can be obtained which could be used to determine the  $D_{eff}$  for a different membrane with different porosity and tortuosity:

$$D_{eff} = D_{io} \frac{\epsilon}{T} \quad (6.1)$$

where:

$D_{eff}$  = Effective diffusion coefficient, (cm<sup>2</sup>/sec)

$D_{io}$  = Diffusion coefficient of an ion  $i$  in an organic solvent/diluent,  $o$ , ( $\text{cm}^2/\text{sec}$ )

$\epsilon$  = Porosity

$T$  = Tortuosity

$D_{io}$  is, in theory, only dependent on the membrane solution (in this case CE-NPOE) and is independent of the membrane support porosity and tortuosity. Hence  $D_{io}$  would be the same irrespective of any support, and  $D_{\text{eff}}$  for a different membrane can be calculated from Equation 6.1 above.

For a well defined laminar flow in an SLM, Tomkins (1992) and Cussler (1984) found that the empirically determined Sherwood number and the aqueous phase mass transfer coefficients is proportional to the  $N_{\text{Re}}^{1/3}$  (Tomkins C.J., 1992). The aqueous MTCs in the present study are also proportional to  $N_{\text{Re}}^{1/3}$ , thereby indicating that the flow in the channels was also laminar. As per Cussler, the flow is laminar if  $N_{\text{Re}}$  is  $< 400$ . Figure 6.14 shows the relationship of aqueous feed and strip mass transfer coefficients on the Reynolds number. The feed MTC and the strip MTC obtained based on a regression on mass transport data are:

$$k_a = 5.50 \times 10^{-5} N_{\text{Re}}^{1/3} \quad (6.2)$$

$$k_b = 4.86 \times 10^{-5} N_{\text{Re}}^{1/3} \quad (6.3)$$

where:

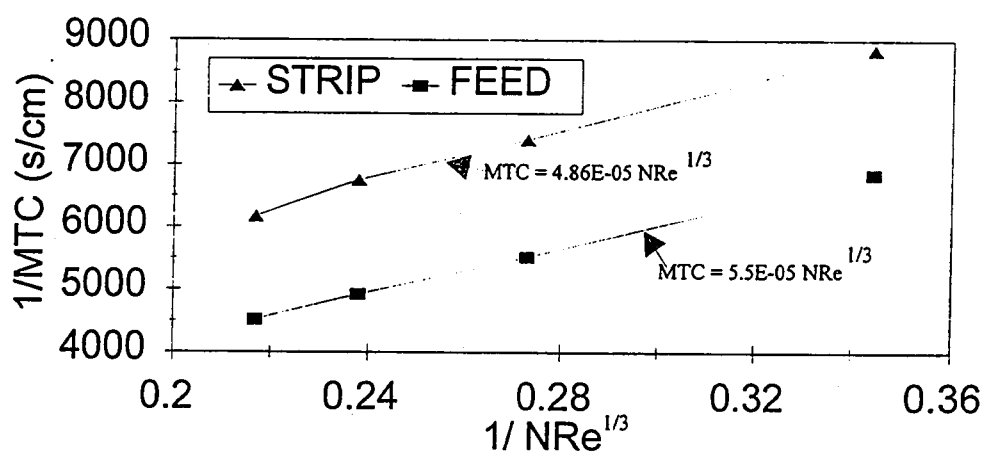


Figure 6.14: A Plot of Aqueous Feed and Strip MTCs as a Function of Reynolds Number

$k_a$  = Aqueous feed MTC, (cm/s)

$k_b$  = Aqueous strip MTC, (cm/s)

$N_{Re}$  = Reynolds number

Tomkins obtained the aqueous phase MTC to be equal to  $7.0 \times 10^{-4} N_{Re}^{1/3}$  which is an order of magnitude more than the corresponding values in this study. However Tomkins's system consisted of a hollow fiber SLM and transported p-nitrophenol and hence is not expected to give the same MTCs as in the case of the present study.

Having obtained the individual aqueous MTCs as a function of the Reynolds number, the author conducted a new set of experiments to determine the membrane MTC for NPOE-dtbCH18C6 system. Unlike the aqueous MTCs, membrane MTC is an unique value for a given system and is only dependent on the nature and properties of the organic membrane solution and membrane support. The membrane MTC can be calculated from the resistance in series model proposed by Sirkar (1984). According to the theory, a transporting solute faces resistances due to the aqueous feed and strip boundary layers and due to the membrane support. The overall resistance, the inverse of the overall MTC, is equal to the sum of the individual resistances. Equation 6.4 shows the relationship between the overall resistance and MTC and the membrane resistance and MTC. This equation is derived from Equation 5.9 presented in Chapter 5.

$$\frac{1}{K} = \frac{1}{k_a} + \frac{K_{d2}}{K_{d1}} \frac{1}{k_b} = \frac{1}{K_{d1} k_m} \quad (6.4)$$

where:

$K$  = Overall MTC, (cm/s)

$K_{d1}$ ,  $K_{d2}$  = Extraction and strip side organic distribution coefficients respectively

$k_a$ ,  $k_b$  = Aqueous feed and strip side MTCs respectively (cm/s)

$k_m$  = Membrane MTC (cm/s)

If the flow rates are kept identical and the thickness of the membrane is varied by sandwiching multiple membranes between the steel modules, then the overall MTC will vary because of the change in the membrane MTC. Membrane MTC which is defined as  $D_{\text{eff}}/d_m$  will reduce by half when the membrane thickness,  $d_m$ , is doubled as the  $D_{\text{eff}}$  remains the same since it is not a function of membrane thickness. So, the difference between the overall MTC for 25 and 50 micron thickness experiments is equal to:

$$k_{m,25} = \frac{\frac{1}{K_{d1}}}{\frac{1}{K_{50}} - \frac{1}{K_{25}}} = \frac{\frac{1}{20}}{\frac{1}{9 \times 10^{-5}} - \frac{1}{2.36 \times 10^{-4}}} = 7.3 \times 10^{-5} \text{ cm/s} \quad (6.5)$$

Membrane MTC for 0.04 M CE-NPOE was determined from Equations 6.4 and 6.5 to be  $7.3 \times 10^{-6}$  cm/s. Equation 6.5 is obtained from Equation 6.4.

### 6.1.2.2 Steady State (S.S.) Experiments

The objectives of these experiments were 1) to determine the steady state open loop perhenate concentration in the strip solution, 2) to obtain a correlation between open and closed loop MTCs, and 3) compare the open loop experimental results with results predicted by the model developed in Chapter 5. Figure 6.15 shows the open and closed loop MTCs correlation plot. The corresponding open and closed loop MTC values shown in the Figure 6.15 were for identical experimental conditions namely identical feed and strip concentrations, flow rates, membrane thickness, membrane composition and crown ether concentrations. Equations 5.25 and 5.17 were used to calculate the open and closed loop MTCs respectively. Equation 6.5b shows a sample calculation for open loop MTC. Equation 6.5b is obtained after rearranging Equation 5.25 and taking the log of both the sides of the equation to solve for K. Also,  $Q_F = Q_S$ ,  $s = 0.3$ ,  $w = 0.25$  cm,  $n = 6$  and  $z = 5$  cm. Closed loop MTC were calculated from the slope of the plot of Equation 5.17

$$K = - \frac{\left[ \ln \left[ 1 - \frac{C_S}{C_{F,0}} \left( s + \frac{Q_S}{Q_F} \right) \right] \right]}{\frac{nwz (s+1)}{Q_F}}$$

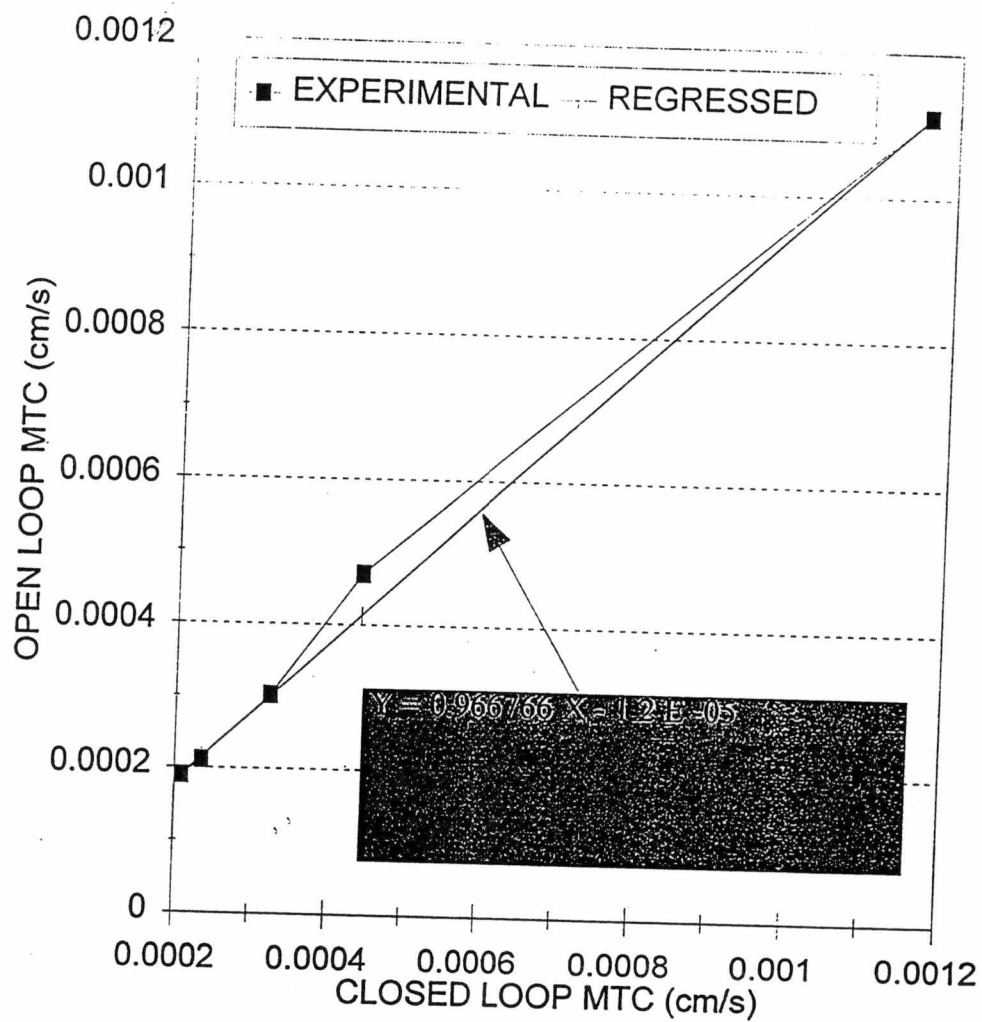


Figure 6.15: Open versus Closed Loop Overall MTC Correlation Plot

$$\begin{aligned}
& \ln \left( 1 - \frac{0.245 \frac{\text{mg}}{\text{L}}}{18 \frac{\text{mg}}{\text{L}}} \right) 1.3 \\
= - & \left[ \frac{18 \frac{\text{mg}}{\text{L}}}{6 \times 5 \times 0.25 \times 1.3 \times \frac{3600}{400}} \right] = 2.36 \exp -04 \text{ cm/s}
\end{aligned} \tag{6.5b}$$

The open loop steady state exit strip perrhenate concentrations for 5 M and 1 M initial sodium concentration and 18 mg/L feed perrhenate concentration were experimentally determined to be 0.248 and 0.245 mg/L respectively for experimental conditions listed in the foot note of Table 6.1, while for 11 mg/L initial perrhenate concentration were 0.156 and 0.154 mg/L respectively. These near identical values for both initial perrhenate concentrations confirms the theory earlier proposed in section 6.1.1.5, that beyond 0.5 M sodium ion concentration gradient across an SLM no significant increase in MTF or MTC or exit strip S.S. concentration is expected. Hence, the strip solution needs to be bled off for further treatment prior to the point when the sodium ion concentration differential across the SLM is greater than or equal to 0.5 M.

An excellent correlation with a  $R^2$  of over 0.9999 was obtained between open and closed loop MTCs (Figure 6.15). Open loop MTC was about 96.67% of the closed loop MTC. This correlation suggests that open loop MTCs can be computed from closed loop MTCs, and can circumvent problems when open loop operations produce exit strip side

concentrations close to the ICP detection limits.

Equation 6.6 shows a sample calculation for the computation of the steady state exit strip perrhenate concentration when the initial feed perrhenate concentrations was 18 mg/L. Equation 6.6 is obtained from Equation 5.25 by incorporating all parameter values such as the overall MTC, channel dimensions, flow rates,  $K_d$ s and the initial perrhenate concentration. Since the experiments were performed at a  $N_{Re} > 200$ , aqueous boundary layer resistances were neglected. The overall MTC used in Equation 6.6 was  $1.46 \text{ E-}04 \text{ cm/s}$  and was obtained from the closed loop experiments for identical experimental conditions namely feed initial sodium nitrate concentration of 1 M, feed initial sodium perrhenate concentration of 0.1 mM, DI water strip, 0.04 M CE-NPOE membrane solution, 25 micron thick Celgard membrane and 400 mL/hr feed and strip flow rates.

$$C_s = \frac{18}{1.3} [1 - \exp \left[ - \left[ \frac{1.46 \text{E-} 04 \times 6 \times 5 \times 0.25 \times 3600 \times 1.3}{400} \right] \right] ] = 0.178 \text{ mg/L} \quad (6.6)$$

The corresponding value for initial perrhenate concentration of 11 mg/L was 0.11 mg/L. Corresponding experimental values of exit S.S strip perrhenate concentrations were 0.248 and 0.156 mg/L respectively. This shows that the model has an error of 23.35% in predicting the experimental S.S data.

Figures 6.16, 6.17 and 6.17b show a comparison of the experimental and

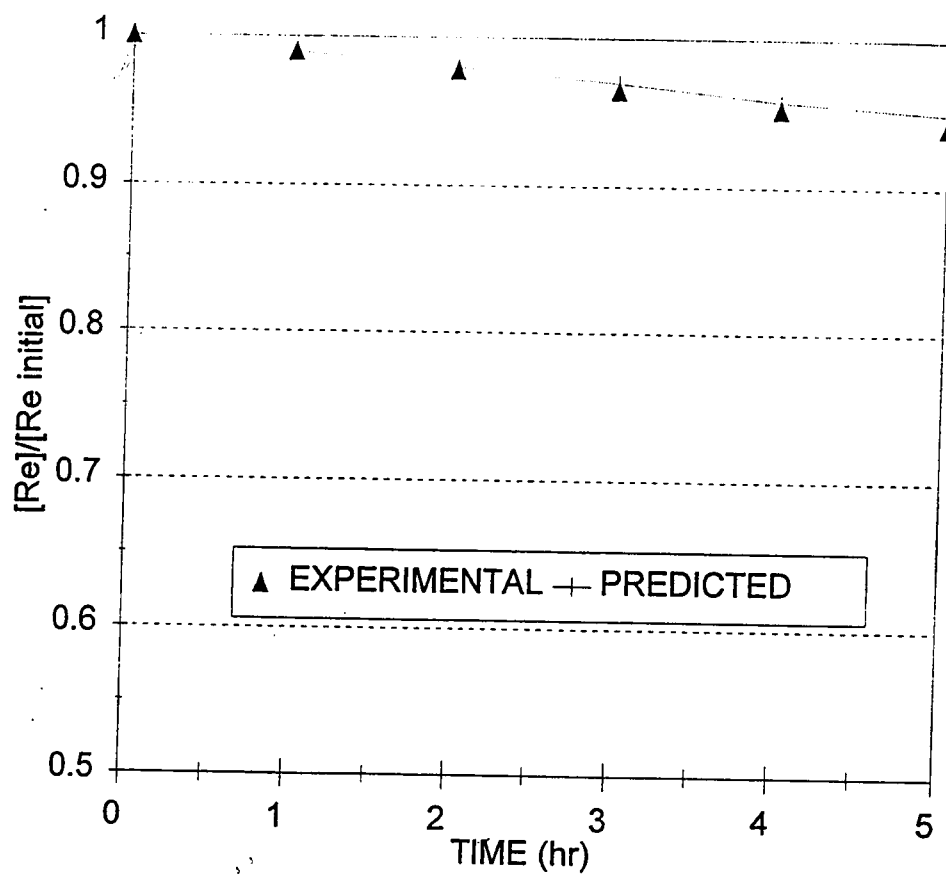


Figure 6.16: Comparison of Experimental Results with Predicted Results: Conditions: 1 M Nitrate, 0.1 mM Re, 25 Micron Thick Membrane

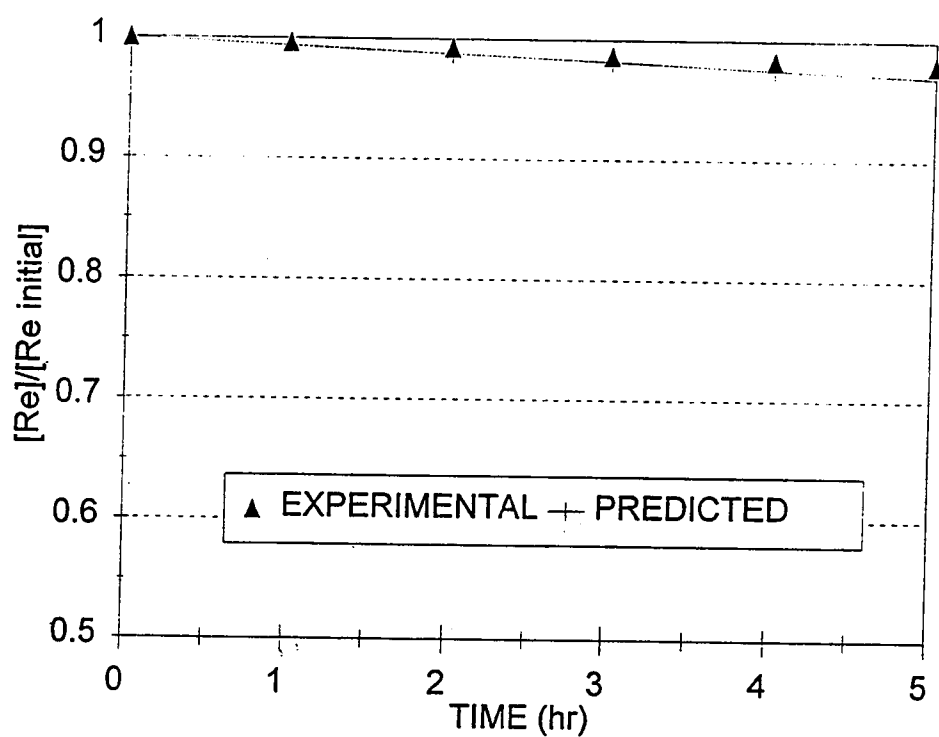


Figure 6.17: Comparison of Experimental Results with Predicted Results: Conditions: 1 M Nitrate, 0.1 mM Re, 50 Micron Thick Membrane.

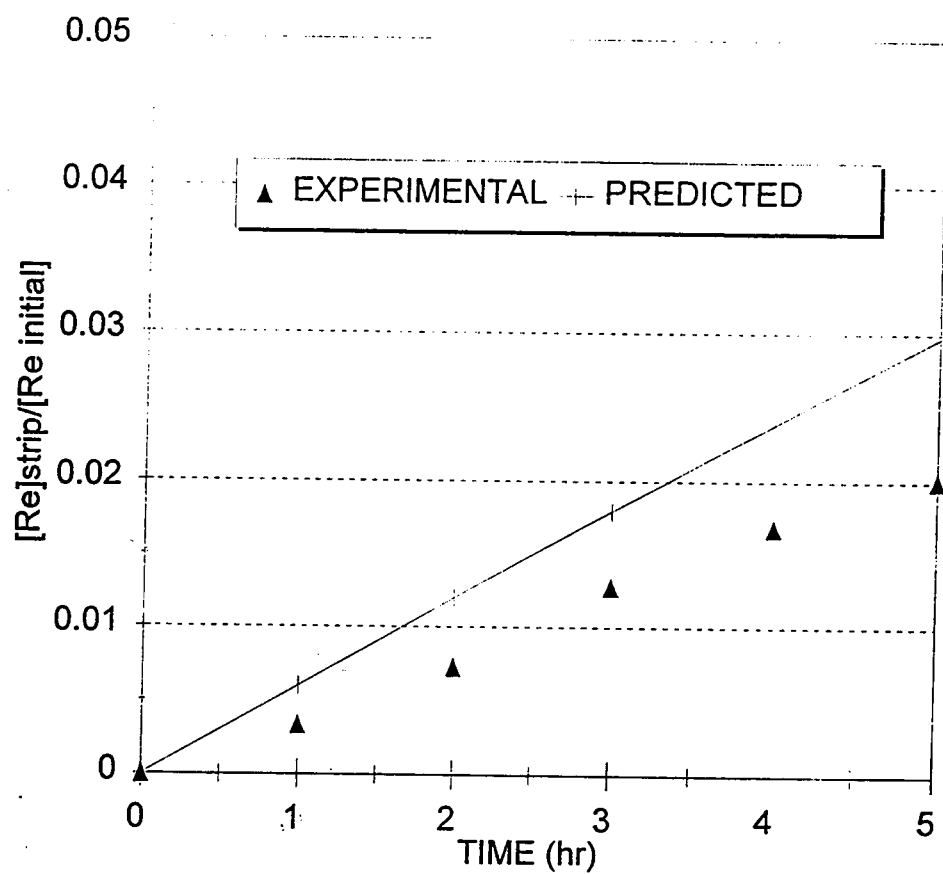


Figure 6.17B: Predicted Strip Composition vs Experimental Data.  
Conditions: 1M Nitrate, 0.1 mM Re, 25 Micron Thick Membrane

predicted  $[Re]/[Re, \text{ initial}]$  data, the ratio of the concentration of Re in the feed solution over the initial Re concentration in the feed solution versus time  $t$ . The predicted data were computed by incorporating  $K$ , as determined from the model developed in Chapter 5, Equation 5.17, into Equation 5.7. As a sample calculation, Equation 5.7 gives,  $(C/C_o)$

$$= \exp\{-(A/V)Kt\} = \exp\{-(7 \times 1.46 \text{ E-}04 \times 1 \times 3600/500) = 0.992$$

where:

$V$  = Aqueous volume, mL

$t$  = Time, s

$C$  = Concentration at any time  $t$ , M

$C_o$  = Initial Concentration, M

$A$  = Membrane area,  $\text{cm}^2$

$K$  = Overall MTC,  $\text{cm/s}$

The experimental conditions used were similar to the conditions listed in the footnote of Table 6.1. In both the cases there was a very close fit indicating the applicability of the model developed to describe multi-ion transport.

### 6.1.3 Model Verification (tasks 7,15,16,17)

This section compares the individual and overall MTCs and the effective diffusion coefficients determined in the previous section with the values predicted by the Stoke's-Einstein's equation and also with the values predicted by models developed by Stolwijk's

(1987) and Cussler (1984). The MTCs were determined based on the model developed by the author in Chapter 5.

### 6.1.3.1 Stoke's-Einstein Equation

The first step in the comparison between the actual versus the predicted MTC data involves the determination of the membrane MTC based on the Stoke's-Einstein equation. Equation 6.6b describes the Stoke's-Einstein relationship between diffusivity and the properties of the organic solution:

$$D_{io} = \frac{kT}{6\pi\eta R} = \frac{1.38 \exp -16 \times 293}{6\pi \times 12.63 \exp -02 \times 6.4 \exp -08} = 2.65 \exp -07 \frac{cm^2}{s} \quad (6.6b)$$

where:

$D_{io}$  = Organic diffusion coefficient,  $cm^2/sec$

$\eta$  = Viscosity of the solvent, cp

$k$  = Boltzman constant,  $g/cm^2/s^2$

$R$  = Atomic radius, cm

$T$  = Temperature in  $^{\circ}K$

Predicted  $D_{io}$  and  $D_{eff}$  were calculated from Equations 6.6 and 6.1 to be  $2.65 \text{ E-}07 \text{ cm}^2/sec$  and  $3.5 \text{ E-}08 \text{ cm}^2/sec$  respectively at  $20^{\circ}C$ . The corresponding predicted membrane MTC,  $k_m$ , defined as the ratio of  $D_{eff}$  over the membrane thickness,  $d$ , was 1.4

E-05 cm/s. The predicted membrane MTC, and the predicted effective diffusion coefficient,  $1.4 \text{ E-}05 \text{ cm/s}$  and  $3.5 \text{ E-}08 \text{ cm}^2/\text{sec}$  respectively, were nearly double their corresponding actual values which were  $7.3 \text{ E-}06 \text{ cm/s}$  and  $1.81 \text{ E-}08 \text{ cm}^2/\text{sec}$  respectively. This could be attributed to the over prediction of the diffusion coefficient using the Stokes Einstein equation. Also, the Stoke's Einstein equation is only 20-50% accurate for most systems (Cussler, 1984).

The overall predicted MTC,  $K_{pre}$ , is equal to  $D_{eff} K_{dl}/d_m$ . Substituting values obtained from the Stoke's-Einstein's equation for  $D_{io}$  into Equation 6.1 for  $D_{eff}$  gives  $K_{pre} = 3.5\text{E-}08 \times 20/25 \text{ E-}04 = 2.8 \text{ E-}04 \text{ cm/s}$  for  $N_{Re}$  greater than 200. Table 6.2 shows a comparison of the MTCs calculated from Equation 5.17 using experimental closed loop data and predicted MTCs from Stoke's-Einstein's Equation. Based on a statistical analysis on the data it can be inferred that for a 95% confidence interval:

$$\frac{K_{pre}}{K_{actual}} = 1 : 45 \quad (6.7)$$

This relationship has a relative precision error of 16.84%.

### 6.1.3.2 Kinetic Analysis

The objectives of the kinetic analysis were:

1. To compare the experimental MTCs and diffusion coefficients with the data predicted by Stolwijk and Cussler models.

Table 6.2: Predicted vs Actual Mass Transfer Coefficients

| Experimental Conditions |                           |                           |                      |                       |                       |                                  |                                   |                                    |
|-------------------------|---------------------------|---------------------------|----------------------|-----------------------|-----------------------|----------------------------------|-----------------------------------|------------------------------------|
| Exp. #                  | Feed NaN O <sub>3</sub> M | Feed NaReO <sub>4</sub> M | Feed Flow Rate mL/hr | Membrane Thk. Microns | Strip Flow Rate mL/hr | Pred. MTC cm/s, K <sub>pre</sub> | Actual* MTC cm/s K <sub>act</sub> | K <sub>pre</sub> /K <sub>act</sub> |
| 1                       | 0.5                       | 0.0001                    | 400                  | 25                    | 400                   | 2.80e-04                         | 2.20e-04                          | 1.3                                |
| 2                       | 5                         | 0.0001                    | 400                  | 25                    | 400                   | 2.80e-04                         | 2.10e-04                          | 1.3                                |
| 3                       | 1                         | 0.0001                    | 400                  | 25                    | 400                   | 2.80e-04                         | 2.40e-04                          | 1.2                                |
| 4                       | 1                         | 0.0001                    | 400                  | 50                    | 400                   | 1.40e-04                         | 8.20e-05                          | 1.7                                |
| 5                       | 1                         | 0.0001                    | 400                  | 75                    | 400                   | 9.30e-05                         | 5.30e-05                          | 1.8                                |
| 6                       | 1                         | 0.0001                    | 400                  | 100                   | 400                   | 7.00e-05                         | 4.20e-05                          | 1.7                                |
| 7                       | 1                         | 0.0001                    | 500                  | 25                    | 400                   | 2.80e-04                         | 2.40e-04                          | 1.2                                |
| Mean                    |                           |                           |                      |                       |                       |                                  |                                   | 1.45                               |
| Std. Dev                |                           |                           |                      |                       |                       |                                  |                                   | 0.24                               |
| Upper CI                |                           |                           |                      |                       |                       |                                  |                                   | 2.06                               |
| Lower CI                |                           |                           |                      |                       |                       |                                  |                                   | 0.82                               |

\*From the model presented in Chapter 5

2. To determine whether transport in an SLM was due to free ions or ion pairs.
3. To determine the apparent equilibrium constant, and the effective membrane diffusion coefficient without the need for any batch experiments.

**Definition:**

In Stolwijk's kinetic analysis (1987), apparent equilibrium constant is defined as the ratio of the actual reaction equilibrium constant over the anion partition coefficient (one separate for nitrate and another for perrhenate reactions with crown ether). According to D. Namoor (1984), anion partition coefficient is essentially a constant (Stolwijk et al., 1987). Hence, an estimate of the apparent equilibrium constant would also yield an estimate of the actual equilibrium constant. Besides, it is also possible to exactly determine the anion partition coefficient using batch solvent extraction tests.

All the equations for the kinetic analysis have been borrowed from Stolwijk et al. (1987). Equation 6.9, describes the relationship between MTF and feed Molar activity when the membrane transport is because of free ions (polar diluents).

$$\frac{[CE]^0 - [CE]_{aq} \frac{V_{aq}}{V_{memb}}}{dJ} = \frac{1}{D_{eff}} + \frac{1}{D_{eff} K_{app}} \frac{1}{[Na^+]} \quad (6.9)$$

where:

$[CE]^0$  = Initial crown ether concentration in the membrane, M

$[CE]_{aq}$  = Aqueous crown ether concentration due to partitioning, M

$d$  = Thickness of the membrane, cm

$J$  = MTF, moles/cm<sup>2</sup>/hr

$D_{eff}$  = Effective membrane diffusivity, cm<sup>2</sup>/sec

$V_{aq}$  = Aqueous feed and strip volumes, cm<sup>3</sup>

$V_{eb}$  = membrane volume, cm<sup>3</sup>

$[Na^+]$  = Initial concentration of sodium in feed, M

$K_{app}$  = Apparent equilibrium constant

Equation 3.4 in Chapter 3 describes the same relationship for non polar diluents where membrane transport is predominantly due to ion-pairs. The effective crown ether concentration in the membrane is the initial crown ether concentration minus the product of the aqueous crown ether concentration times the ratio of aqueous volume over membrane volume,  $[CE]^0 - [CE]_{aq} V_{aq}/V$ . Aqueous crown ether concentration would depend on its partitioning coefficient between the organic and aqueous phases. It is very difficult to actually measure the partition coefficient but as per literature it is greater than  $10^6$  for db18C6 crown ethers (Stolwijk et al., 1987). The aqueous and membrane pore volumes are 1000 mL and 0.175 mL respectively. Hence the effective crown ether concentration in the membrane for a  $[CE]^0$  of 0.04 M is 0.0376 M.

Regression of data was carried out based on Equations 6.9 and 3.4 for free ion and

ion pair transport respectively. Free ion regression coefficient was 0.99 while the ion pair regression coefficient was 0.78. This supports that free ion transport was the predominant means of membrane transport. The intercept and the slope had a value of  $6.28 \times 10^6$  and  $5.73 \times 10^6$  respectively. The standard deviation on the slope was  $4.19 \times 10^5$ . The effective membrane diffusion coefficient and apparent equilibrium constant for the sodium nitrate transport can be obtained from the free ion transport regression data (Stolwijk et al., 1991). The inverse of the intercept value gives the effective diffusion coefficient  $D_{\text{eff}}$  while the inverse of the slope gives the product of the apparent equilibrium constant ( $K_{\text{app}}$ ) and  $D_{\text{eff}}$ . For the sodium nitrate transport  $D_{\text{eff}}$  was  $1.6 \times 10^{-7}$  cm<sup>2</sup>/sec while  $K_{\text{app}}$  was  $1.1 \text{ M}^{-1}$ . Stolwijk et al. had also arrived at a similar conclusion for CE-NPOE systems. Figures 6.18 and 6.19 show the plots of the ion pair and free ion transport dependence data. The figures are consistent with the conclusion that, free ion transport was predominant over ion pair transport because as per Equation 6.1 the MTF varied nearly linearly with the feed Molar activity (as defined in Equation 6.9) and not with the square of the feed Molar activity. Stolwijk obtained  $D_{\text{eff}}$  for Accurel membrane with half the tortuosity and nearly identical porosity to be  $3.2 \times 10^{-7}$  cm<sup>2</sup>/sec. The corresponding organic diffusivity,  $D_{\text{io}}$ , values are  $8 \times 10^{-7}$  and  $8.2 \times 10^{-7}$  cm<sup>2</sup>/sec for the current system and Stolwijk's system respectively. As per Wilke-Chang's and Stoke's equations, the calculated value of  $D_{\text{io}}$  for the present system is  $5.5\text{--}7.2 \times 10^{-7}$  and  $2.6\text{--}3.0 \times 10^{-7}$  cm<sup>2</sup>/sec respectively. Hence, similar to Stolwijk's conclusion, the Wilke-Chang equation gives a better estimate of the membrane organic diffusion coefficient.

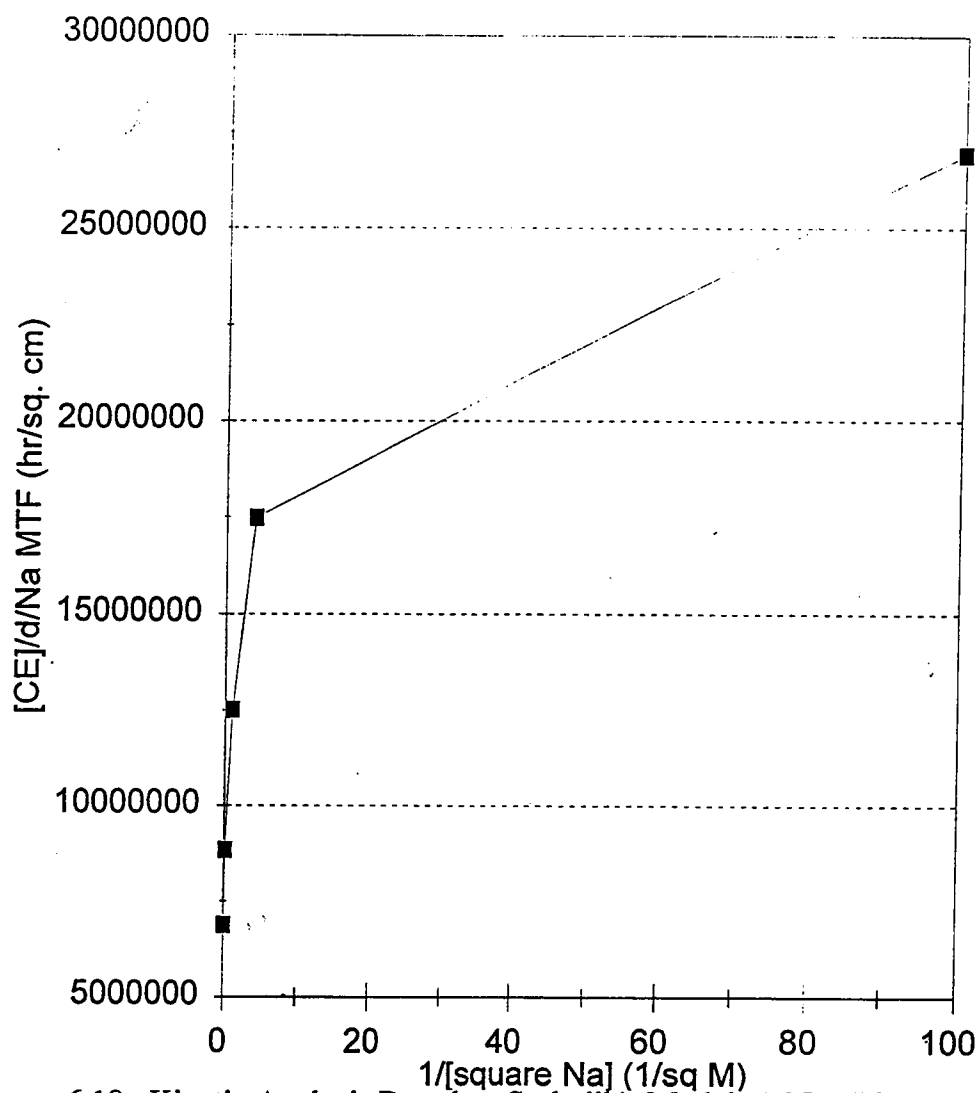


Figure 6.18: Kinetic Analysis Based on Stolwijk's Model: A Non Linear Relationship Between MTF and Square of Feed Na Concentration Indicates Free Ion and Not Ion Pair Transport in SLM

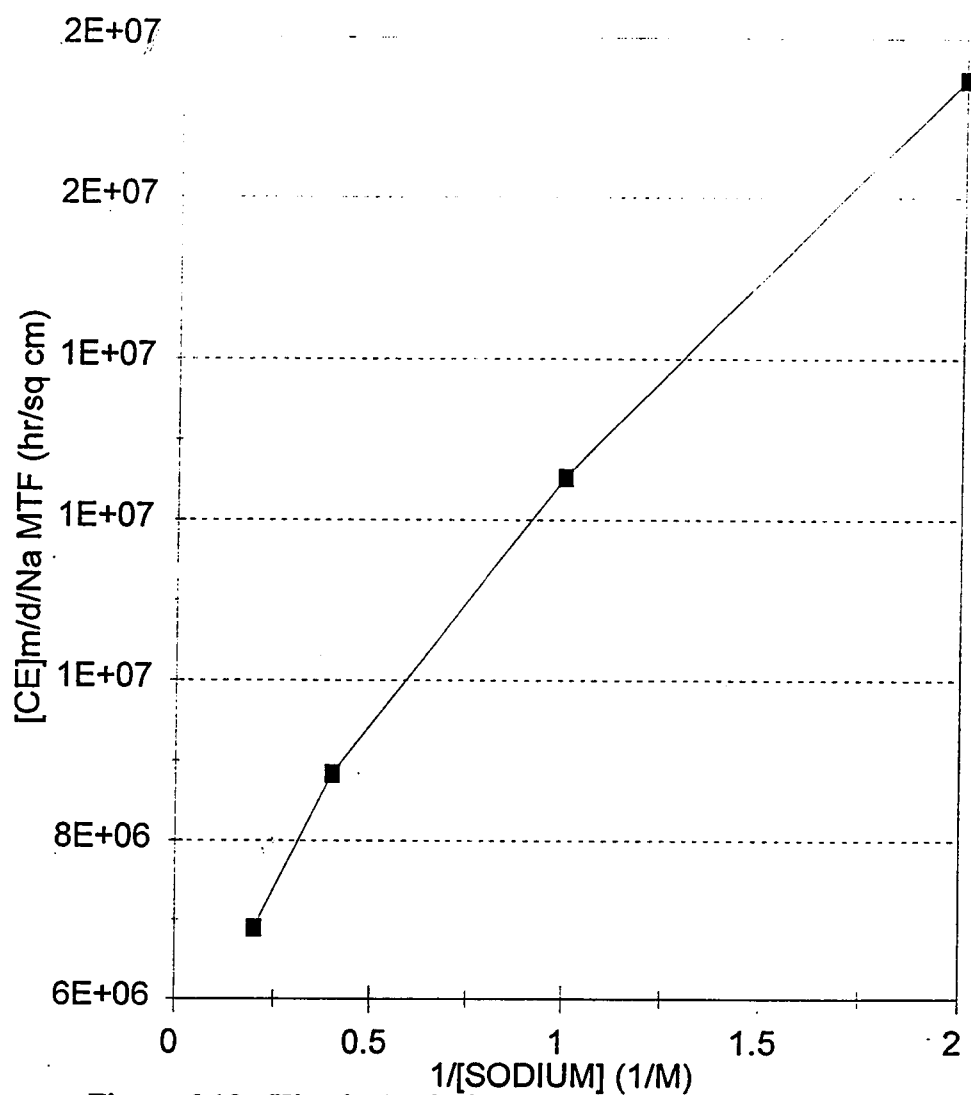


Figure 6.19: Kinetic Analysis Based on Stolwijk's Model: A Linear Relationship Between Na MTF and Feed Concentration Indicates Free Ion Transport in the SLM

A similar set of kinetic analysis when applied on rhenium MTF data provides an estimate of the transport parameters. Regression was again carried out based on Equations 3.4 and 6.9. Again for sodium perrhenate transport, free ions were the predominant means of membrane transport ( $R^2$  of 0.95 over an  $R^2$  of 0.91 for ion pair transport). The apparent equilibrium constant was  $2.77 \times 10^{-4} \text{ M}^{-1}$  and the membrane MTC was  $1.41 \times 10^{-6} \text{ cm/s}$ . The experimental membrane MTC was  $7.3 \text{ E-06 cm/s}$  which shows that the Stolwijk's model underpredicted the MTC by a factor of 5. Figures 6.20 and 6.21 respectively show the plots of ion pair and free ion transport for rhenium based on kinetic analysis.

Finally, the model developed by Cussler (1984) was used to compare the experimental data with the predicted data. Equation 6.10 shows the relationship between MTF and the initial concentration of the transporting solute.

$$\frac{1}{J} = \frac{d_m}{D_{eff} c} + \frac{d_m}{D_{eff} c K_{eq}} \frac{1}{C_0} \quad (6.10)$$

where:

$C_0$  = Initial concentration of the ion of interest, M

$K_{eq}$  = Equilibrium constant, for the transporting ion at water/membrane interface

$c$  = Average extractant concentration in the membrane, M

A plot of  $1/J$  vs  $1/C_0$  for perrhenate MTF data as presented in section 6.1.1.5 is shown in Figure 6.22. Based on regression analysis on perrhenate MTF data, the

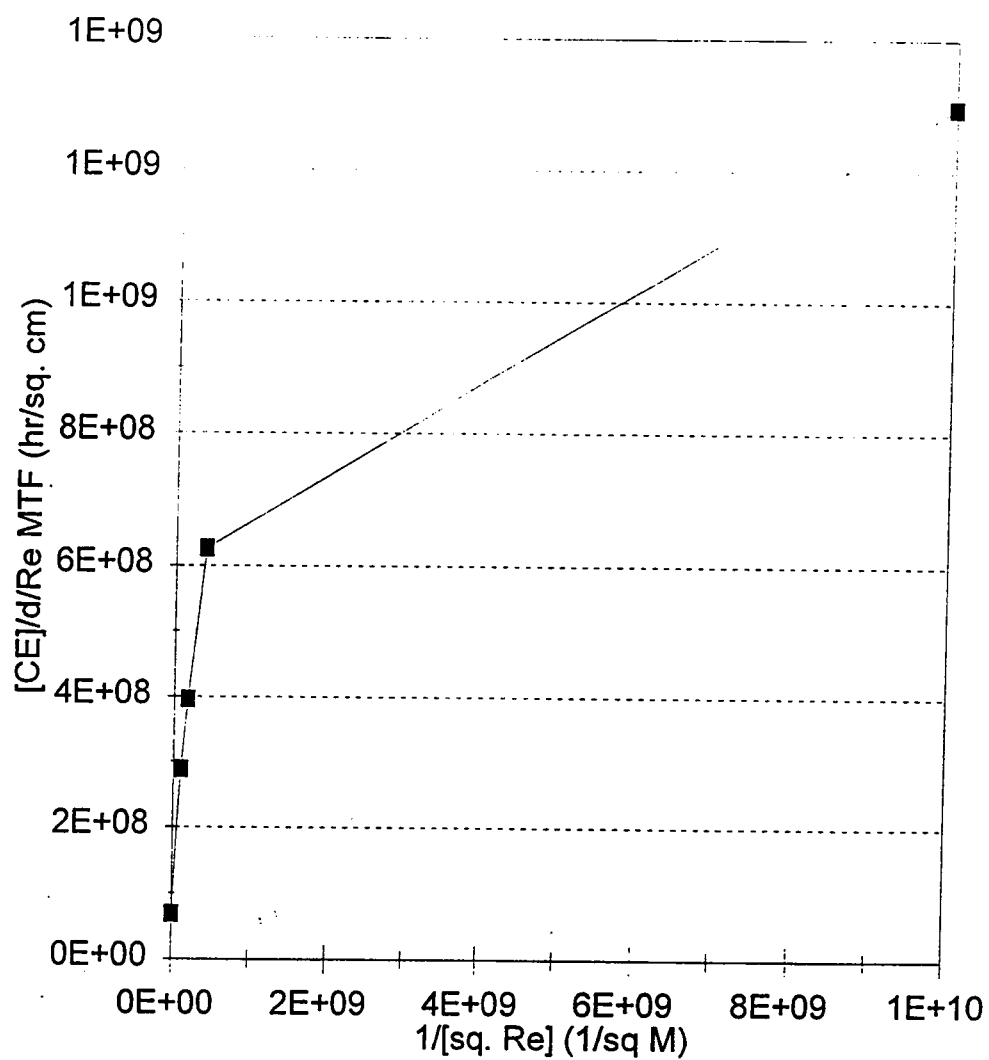


Figure 6.20: Kinetic Analysis Based on Stolwijk's Model:  
Non-Linear Relationship Between MTF and Square of Feed Re  
Conc. Indicates Free Ion and not Ion Pair Transport in SLM

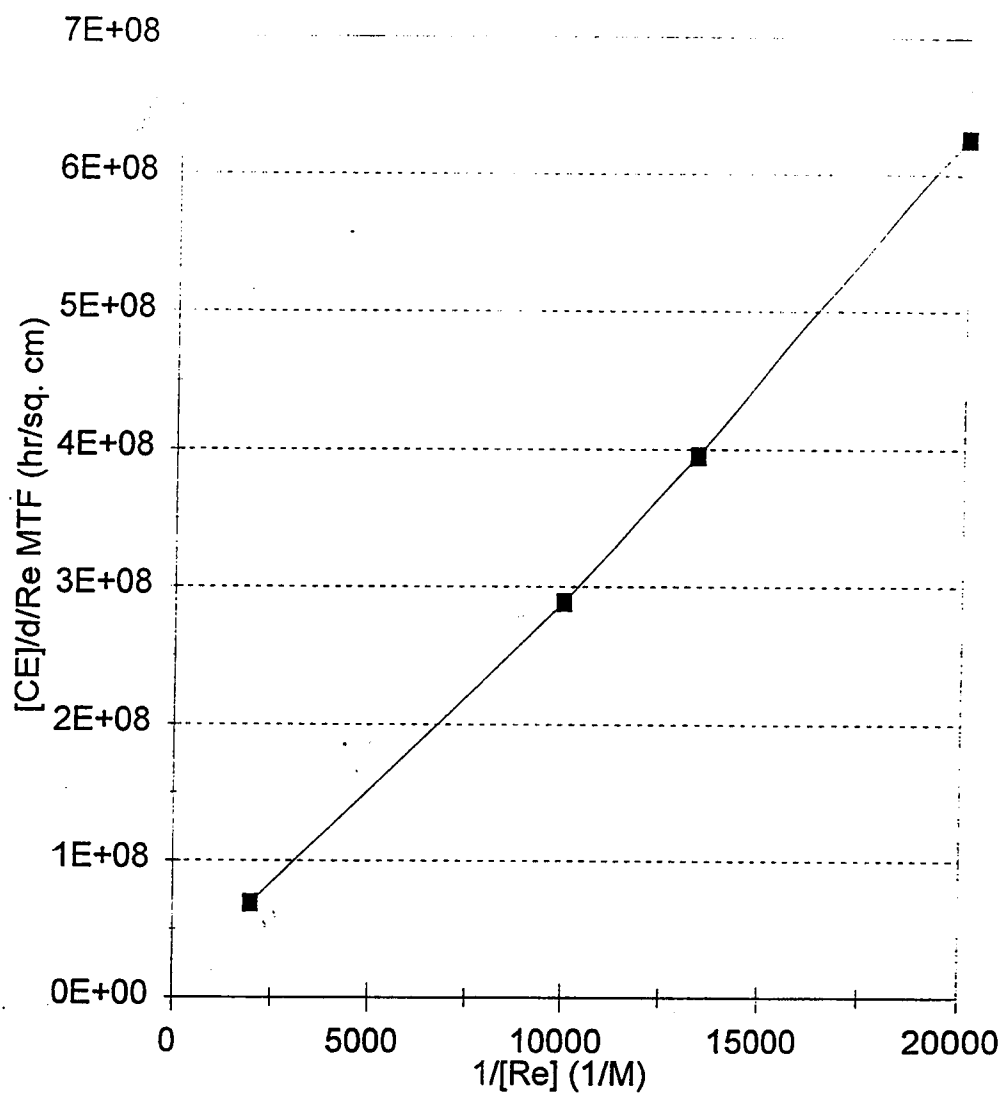


Figure 6.21: Kinetic Analysis Based on Stolwijk's Model: Linear Relationship Between MTF and Feed Re Concentration Indicates Free Ions Transport in the SLM

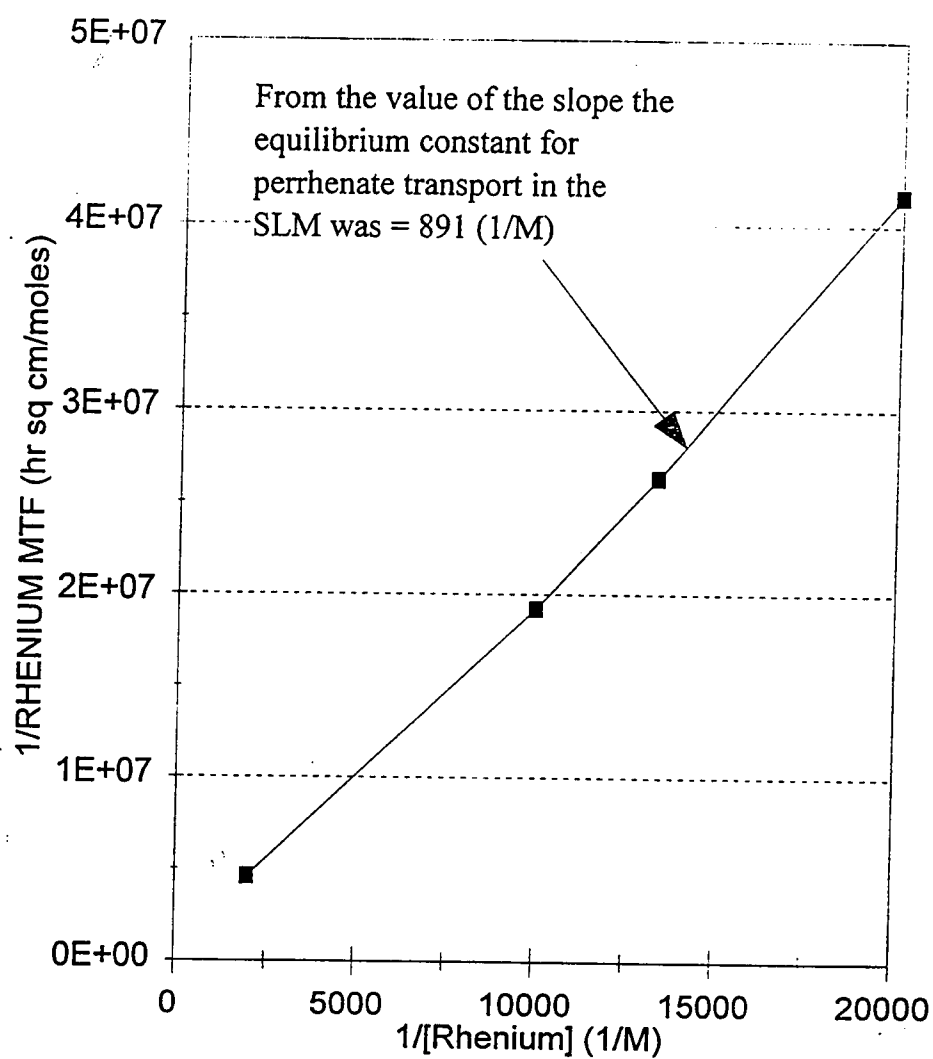


Figure 6.22: Kinetic Analysis Based on Cussler's Model:

equilibrium constant for perrhenate transport was  $891 \text{ M}^{-1}$  which is found by dividing the intercept with the slope. The corresponding effective diffusion coefficient was  $1.0 \text{ E-08 cm}^2/\text{sec}$  which is found by substituting the values of  $c$  and membrane thickness in the intercept formula of Equation 6.10. The experimentally determined  $D_{\text{eff}}$  of  $1.8 \text{ E-08 cm}^2/\text{sec}$  compares very well with the  $D_{\text{eff}}$  value of  $1.0 \text{ E-08 cm}^2/\text{sec}$  determined by the Cussler's model.

Equation 6.11 shows another relationship between MTF and initial ion concentration in the feed (Cussler, 1984).

$$J = k_m [2\sqrt{k_1 k_2}] C_0 + k_1 k_2 K_{\text{eq}} C_0 \quad (6.11)$$

where:

$k_1, k_2$  = Cation and anion distribution coefficients respectively.

Figure 6.23 shows a plot of  $\log J$  vs  $\log C$  for perrhenate transport. A slope of 1 would indicate free ion transport while a slope of 2 would indicate ion pair transport. Regression gives a slope of 0.94 indicating free ions as the predominant means of transport (Cussler, 1984). The corresponding  $R^2$  and standard error were 0.996 and 4% respectively.

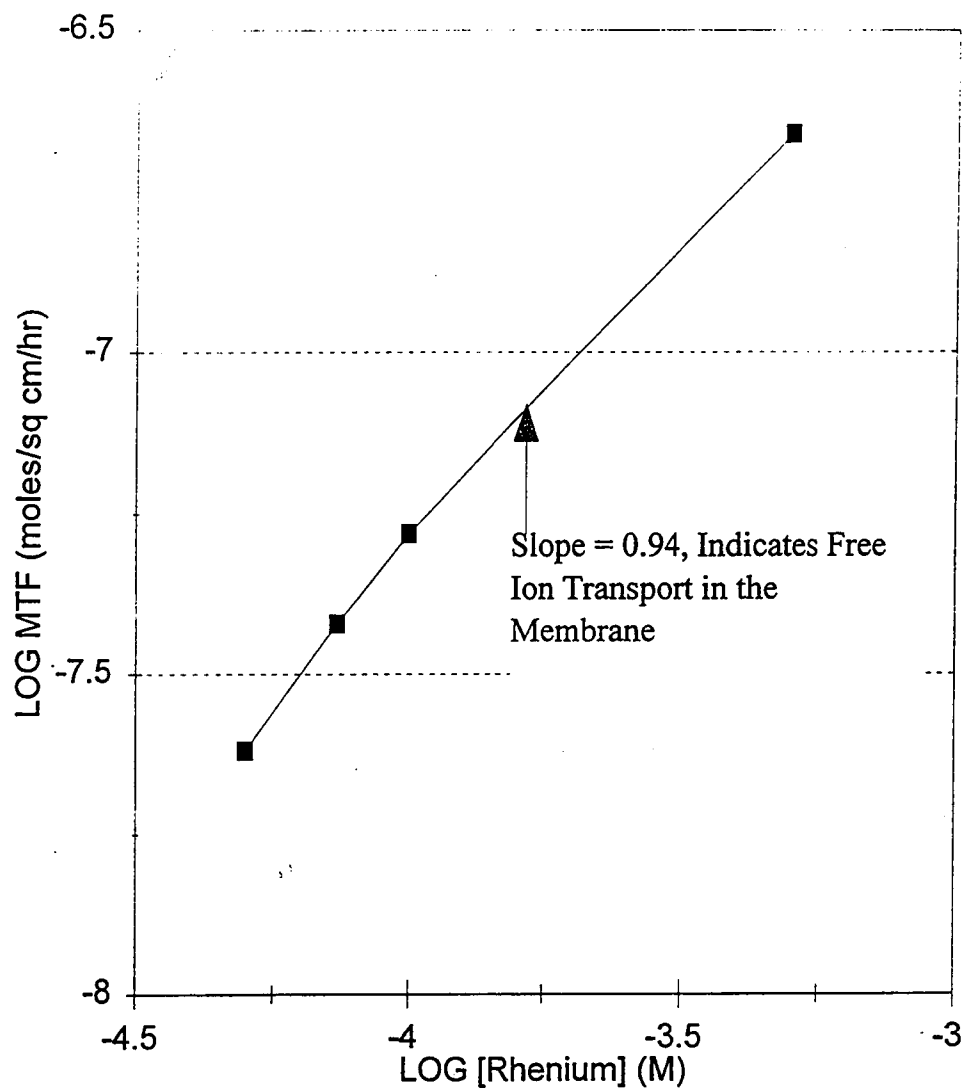


Figure 6.23: Kinetic Analysis based on Cussler's Model: A Plot of the Log. of Re MTF vs-Log. Feed Re Conc.

In summary, the actual membrane MTC was  $7.3 \text{ E-06 cm/s}$ , while the corresponding values and % difference from the actual values predicted by the Stoke-Einstein equation, Stolwijk's model and Cussler's model were  $14.3 \text{ E-06 cm/s}$  (96%);  $1.41 \text{ E-06 cm/s}$  (400%); and  $4 \text{ E-06 cm/s}$ , (45%) respectively. The author's model and the Cussler's model gave the closest predictions.

#### **6.1.4 Equilibrium/QSS Analysis (tasks 12,13 and 14)**

This section attempts to determine the feasibility of transporting sodium perrhenate against its own concentration gradient, propose and verify a hypothesis which accurately describes the mechanism of multi-ion co-transport in an SLM, and also discuss a typical equilibrium/QSS condition in an SLM experimental run.

##### **6.1.4.1 Up-Hill Transport and Back Transport Experiments**

###### **6.1.4.1.1 Hypothesis**

According to the author, the following hypothesis is the correct mechanism for coupled multi-ion transport in an SLM.

1. Contrary to the existing belief, the driving force for coupled co-transport of a cation or anion across an SLM is not provided by the concentration gradient of the

counter ion, but instead is provided by the difference in the product of the activities of the anion and cation between the feed and the strip solutions. Thus uphill transport of an ion against its own concentration gradient is possible in the right situation.

2. Such a co-transport will occur until the system reaches a "Quasi Steady State (QSS)". QSS is defined as the state where there is no net coupled transport across the SLM. It is important to note that a finite, unique and a separate QSS condition exists for each of the coupled ions being transported across the SLM. Also, in the present system it is possible that sodium perrhenate transport could be at QSS while sodium nitrate transport is not at QSS.
3. If the strip solution is spiked with sodium perrhenate beyond QSS concentration, then back transport of sodium perrhenate would occur from the strip to the feed solution even while sodium nitrate is being forward transported from the feed to the strip solution and vice versa. This back transport of perrhenate would occur even though sodium, the counter ion, is more concentrated in the feed solution by over 4 orders of magnitude.

Figures 6.24 and 6.25 show the time course of the concentration of perrhenate ions in the feed and the strip solution for 20 and 50 mg/L strip perrhenate concentrations. The feed perrhenate concentration was 20 mg/L throughout this study. Figure 6.24 shows

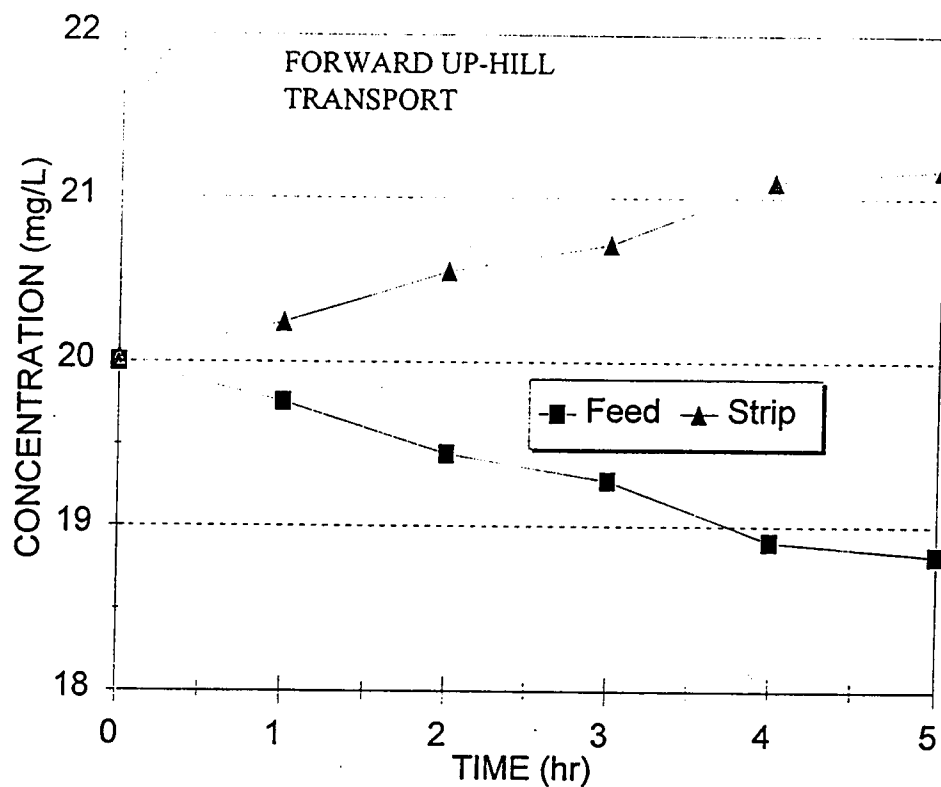


Figure 6.24: Time Course of Perrhenate Ion in Feed and Strip Solution at 20 ppm Strip Perrhenate Concentration. Feed Re Concentration = 20 ppm.

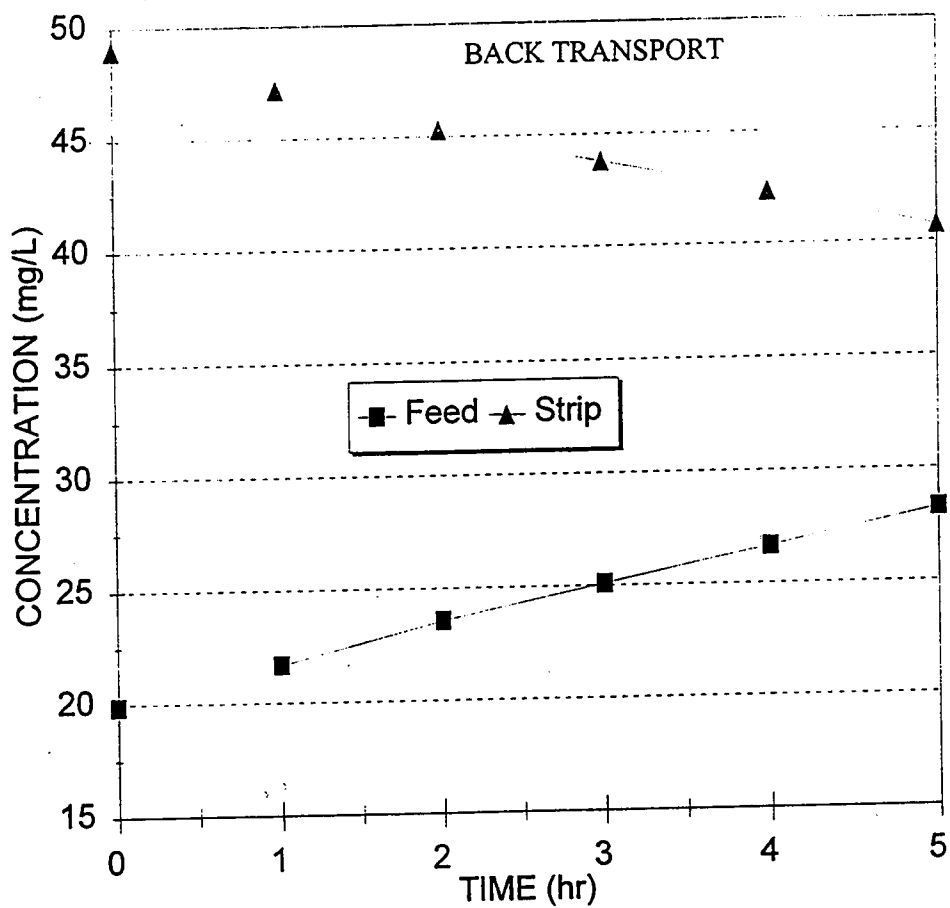


Figure 6.25: Time Course of Perrhenate Ion Concentration in Feed and Strip Solution at 50 ppm Strip Perrhenate Concentration. Feed Re conc. = 20 ppm

forward uphill transport as the strip concentration is increasing beyond 20 mg/L while the feed perrhenate concentration is decreasing to values less than 20 mg/L. This is a case of uphill transport because except at time  $t = 0$  the concentration of perrhenate in the strip is always  $>$  than the feed perrhenate concentration and the strip perrhenate concentration is increasing with time  $t$ . Figure 6.25 shows the opposite case when the strip perrhenate concentration is decreasing and the feed concentration is increasing with time  $t$  showing backward transport.

One of the major objectives of this research was to determine the conditions wherein rhenium could be transported against its concentration gradient ( $C_F/C_S < 1$ ). Equation 6.12 is derived from Equation 5.12 describes such a condition.

$$J_{Re} > 0 \rightarrow KC_F(1 - \frac{K_{d2} C_S}{K_{d1} C_F}) > 0 \rightarrow \frac{C_F}{C_S} > \frac{K_{d2}}{K_{d1}} \quad (6.12)$$

For uphill transport to occur the following conditions need to be satisfied: 1) strip perrhenate concentration should be greater than the feed perrhenate concentration and 2) perrhenate must be transported from the feed to the strip solution. As per convention the MTF,  $J$ , is considered positive if the transport is from feed to strip solution (forward transport, Figure 6.24). This is possible from Equation 6.12 if the ratio  $K_{d2}/K_{d1}$  is smaller than  $C_F/C_S$ . Hence the objective of any SLM design should be make the feed over strip

distribution coefficients ratio as small as possible to get maximum  $C_S/C_F$  ratio.

In a new set of experiments the strip solution was spiked with varying concentrations of sodium perrhenate ranging from 10 to 50 mg/L rhenium. MVWS waste spiked with sodium perrhenate to augment the rhenium concentration to 0.1 mM Re, was used as the feed solution. All experiments were conducted in a closed loop mode. Figure 6.26 shows a plot of Rhenium MTF as a function of strip Re concentration. There was a positive Re MTF, ie: rhenium transport from the feed to strip, when the strip rhenium concentration was between 10 and 30 mg/L for a feed concentration of around 20 mg/L Re. This indicates that indeed there was an up-hill Re transport for the case when the strip solution contained 30 mg/L strip Re concentration. However at 50 and 90 mg/L Re concentration in the strip, there was back transport of rhenium from the strip to the feed solutions indicating a potential quasi-steady state condition between 30 and 50 mg/L strip Re concentration. This result agrees with hypothesis 3.

Batch tests conducted at ORNL on MVWS waste and with NPOE as the diluent indicated that the  $K_{d1}$  was around 10 and the  $K_{d2}$  ranged around 4.2 to 8.33. This results in  $K_{d1}/K_{d2}$  ratio of 1.2 to 2.4. This ratio if applied to Equation 6.12 predicts an  $C_S/C_F = 1.20 - 2.4$ , which closely corresponds to the experimental results, because at 30 and 50 mg/L strip Re concentrations, the  $C_S/C_F$  ratio is 1.5 and 2.5 respectively. Therefore as per Figure 6.26 quasi steady-state for these conditions occurs between  $C_S/C_F$  ratio of 1.5 and 2.5. The dividing point between forward and reverse perrhenate transport is between 30

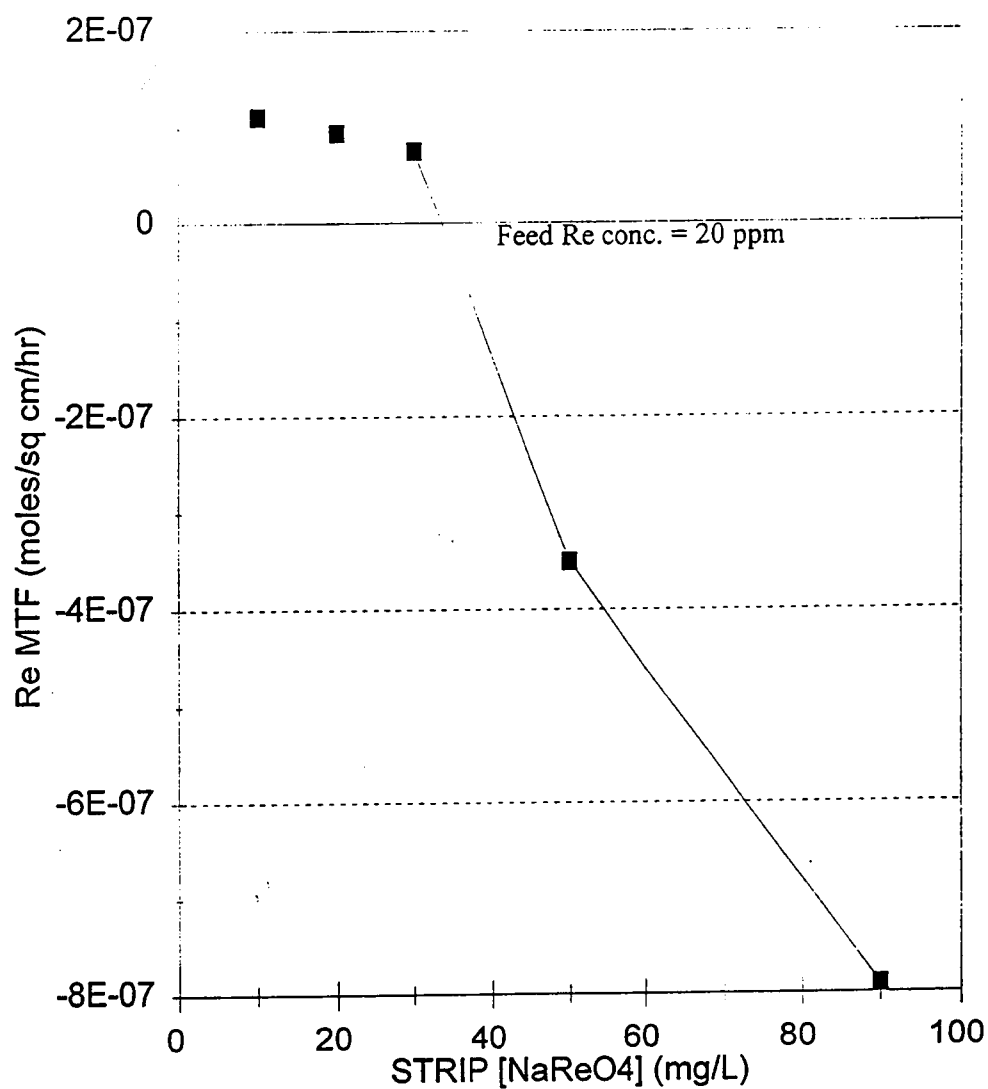


Figure 6.26: Dependence of Re MTF on the Sodium Perhenate Concentration in the Strip Solution

and 50 mg/L strip perrhenate concentration. At QSS the following condition will hold:

$$\frac{C_F}{C_S} = \frac{K_{d2}}{K_{d1}} \quad (6.13)$$

Hence from Equation 6.13 and the SLM experiments,  $K_{d1}/K_{d2}$  is between 1.5 and 2.5 which compares favorably with the batch experiments results. Thus it is possible to transport rhenium against its gradient. A concentration of 1.5 times has been achieved under these conditions and hence a volume reduction of at least 33% is possible.

Figure 6.27 shows the dependence of nitrate flux on perrhenate concentration in the strip solution. It is evident from the plot that increase in strip perrhenate concentration had no effect on the nitrate mass transfer flux. This agrees with the hypothesis proposed by the authors that nitrate and perrhenate transport depend only on their respective QSS condition which is unique and different (hypothesis 2).

#### 6.1.4.2 Strip Composition Experiments

The strip solution was spiked with varying concentrations of sodium nitrate in order to study the effect of a sodium nitrate build up on MTF in an actual closed loop SLM. Sodium nitrate addition ranged from  $10^{-4}$  to 1 M. Figure 6.28 shows the results of the strip composition experiments. Rhenium MTF remained stable throughout between  $7.2$  and  $8.0 \times 10^{-8}$  moles/cm<sup>2</sup>/hr. Sodium MTF remained stable until 0.01 M strip

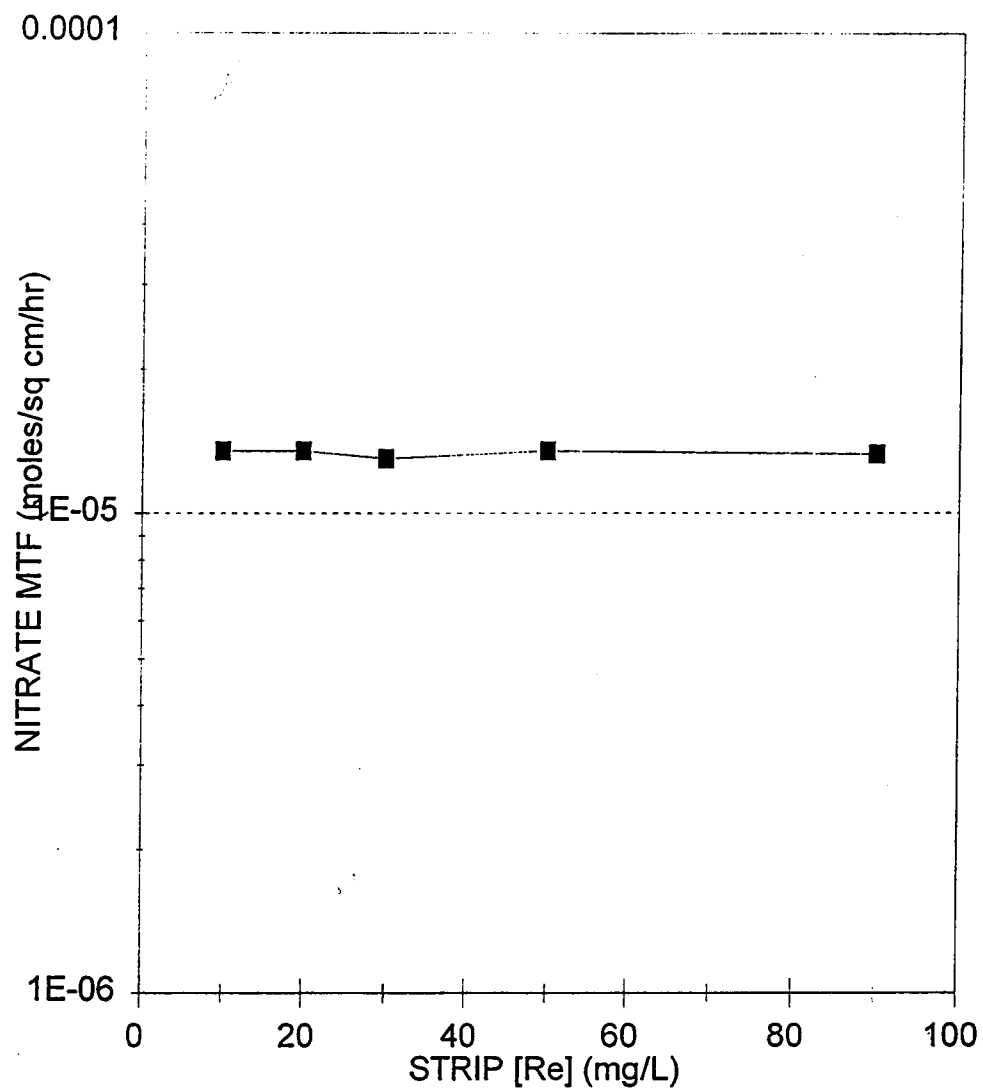


Figure 6.27: Effect of Strip Perrhenate Concentration on Nitrate MTF

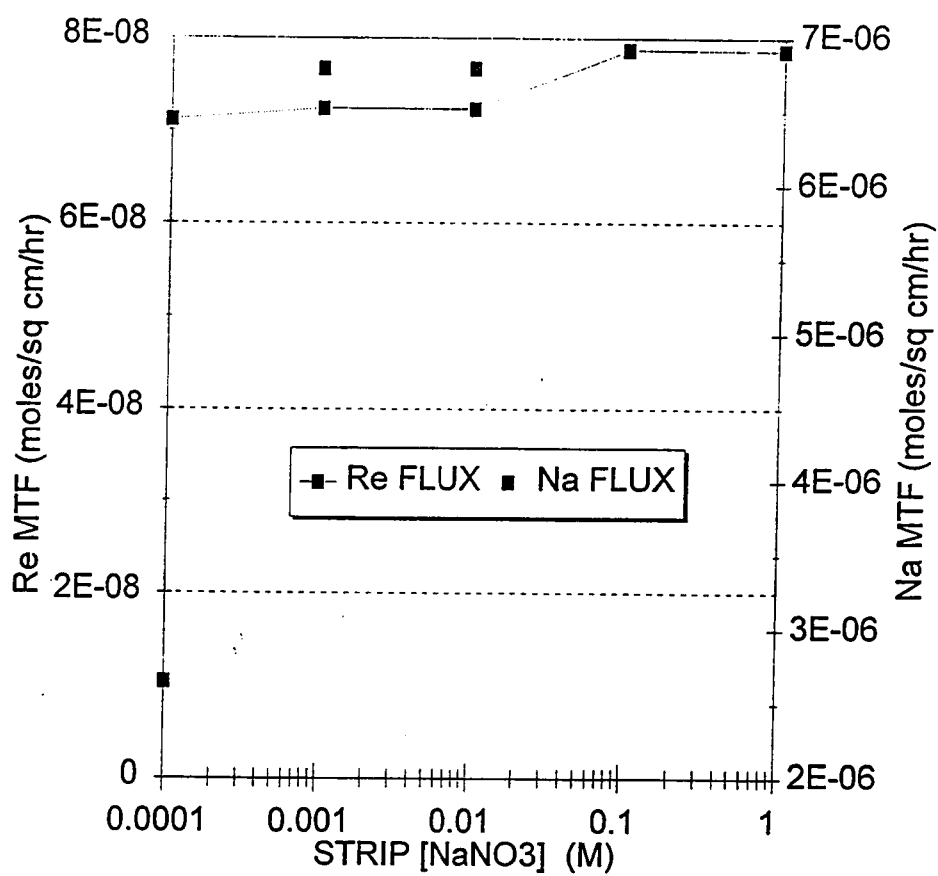


Figure 6.28: Effect of Strip Nitrate Concentration on Nitrate and Perrhenate MTF

sodium nitrate concentration. No sodium data were recorded at 0.1 and 1 M strip sodium nitrate concentrations. The results of the data indicate that a build-up in sodium nitrate concentration up to 1 M level would have no effect on the mass transport of an MVWS system because the concentration gradient is greater than 0.5 M (as postulated in section 6.1.1.5). The MVWS system has over 5 M sodium nitrate and thus the concentration gradient is over 4 M. This suggests that the strip solution can be operated in a closed loop for an extended period of time.

#### 6.1.4.3 "QSS" Experiments

At QSS the following mass balance would hold true for the case when the strip solution was initially deionized water (DI) (Teramoto, 1994):

$$V_F [Re]^0 = V_F [Re]_F + V_S [Re]_S + V_M [Re]_M$$

$$K_{d1,eq} = \frac{[Re]_{M,eq,Feed}}{[Re]_{F,eq}} \quad (6.15)$$

$$K_{d2,eq} = \frac{[Re]_{M,eq,Strip}}{[Re]_{S,eq}} \quad (6.16)$$

where:

$V_M$  = membrane volume

$V_F$  = Feed Volume

$V_S$  = Strip volume

Considering  $V_M$  as much less than  $V_F$  or  $V_S$ ,  $V_S = V_F$ , and  $K_{d1} = 20$  and  $K_{d2} = 6$  (in the present study) the following QSS conditions are obtained:

$$\frac{[Re]_F}{[Re]_F^0} = \frac{1}{1 + \frac{K_{d1}}{K_{d2}}} = \frac{1}{1 + \frac{20}{6}} = \frac{3}{13} \quad (6.17)$$

$$\frac{[Re]_{S,eq}}{[Re]_F^0} = \frac{1}{1 + \frac{K_{d2}}{K_{d1}}} = \frac{1}{1 + \frac{6}{20}} = \frac{10}{13} \quad (6.18)$$

This means that at QSS, the strip can potentially become 3.33 times more concentrated in rhenium than the feed solution. This is possible because of the different values of the feed and strip distribution coefficients. Also, the greater the  $K_{d1}/K_{d2}$  ratio, the greater is the ratio of strip QSS concentration over feed QSS concentration. A similar mass balance also exists for the case when the strip solution is spiked with sodium perrhenate.

The objective of this set of experiments was to determine the feed and strip perrhenate concentrations at "QSS" and compare the with the "QSS" values predicted by the model (section 5.5 in Chapter 5). For the case where the strip was initially DI water and the feed contained 20.32 mg/L of perrhenate, the "QSS" predicted feed and strip values were 4.69 and 15.63 mg/L while the corresponding experimental values were 5.27 and 15.05 mg/L respectively. This excellent correlation shows the applicability of the mass transport model. Figure 6.29 shows a plot of the experimental and predicted "QSS" feed and strip perrhenate concentrations respectively. "QSS" condition was achieved for perrhenate transport after 225 hours of continuous operation.

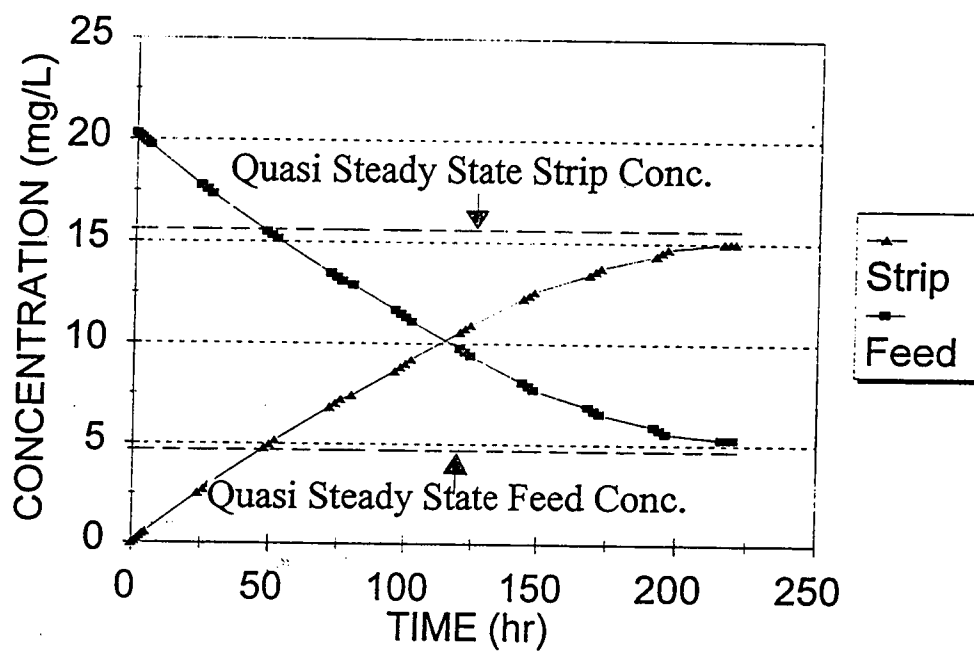


Figure 6.29: Time-course of Perrhenate Ion in Feed and Strip Solution. Strip: DI Water, Feed: MVWS.

# **CHAPTER 7**

## **STATISTICAL ANALYSIS**

### **7.1 Objective**

The objective of this chapter is to develop a statistical model which could predict the MTF as a function of several predictor variables and their interactions. This model could be used to predict at a 95% confidence limit MTF without the need for any experiments.

### **7.2 Methodology**

The methodology used in this study was a linear regression using the Statistical Analysis System Inc's SAS program which would include all the predictor variables and their interactions which effect MTF. These variables were chosen based on the results of the flux experiments. Two different regression models were run and incorporated all the experimental data collected during the course of this research. The first regression model studied the effect of crown ether concentration on MTF, and the second studied the combined effect of all the variables and all important interactions on MTF.

### 7.3 Results and Discussion

#### 7.3.1 Effect of Crown Ether on MTF

As is evident from the regression results that, a simple linear regression of MTF on initial crown ether concentration gave a fairly good fit with a  $R^2$  of 0.96. The probability based on the F value that this result was because of chance was 0.0006 ie: there is a 99.9% probability that this result was not because of chance. The regression has an intercept of  $3.89\text{E-}08$  and the coefficient on the crown ether concentration was  $4.95\text{E-}07$ . Note: All concentration terms in this chapter have units of moles/liter. Equation 7.1 illustrates the model, developed as a result of the regression analysis, which relates MTF to initial crown ether concentration. Figure 7.1 also shows a plot of the predicted line from Equation 7.1 and the experimental data. It is evident from the plot the predicted line did considerable justice to the experimental data except for the intercept which was not significant at the 90% confidence level (CL).

$$\text{MTF (moles/cm}^2\text{/hr)} = 3.89 \text{ E-}08 + 4.95 \text{ E-}07 [\text{CE}] \quad (7.1)$$

A quadratic regression of MTF on initial crown ether concentration using the General Linear Model (GLM) approach also gave a good fit with an improved  $R^2$  value of 0.976. The probability based on the F value that this result was because of sampling error was 0.0038. Type I analysis shows that by itself, the square of the crown ether concentration was unable to explain MTF variation within a 95% confidence level. Type

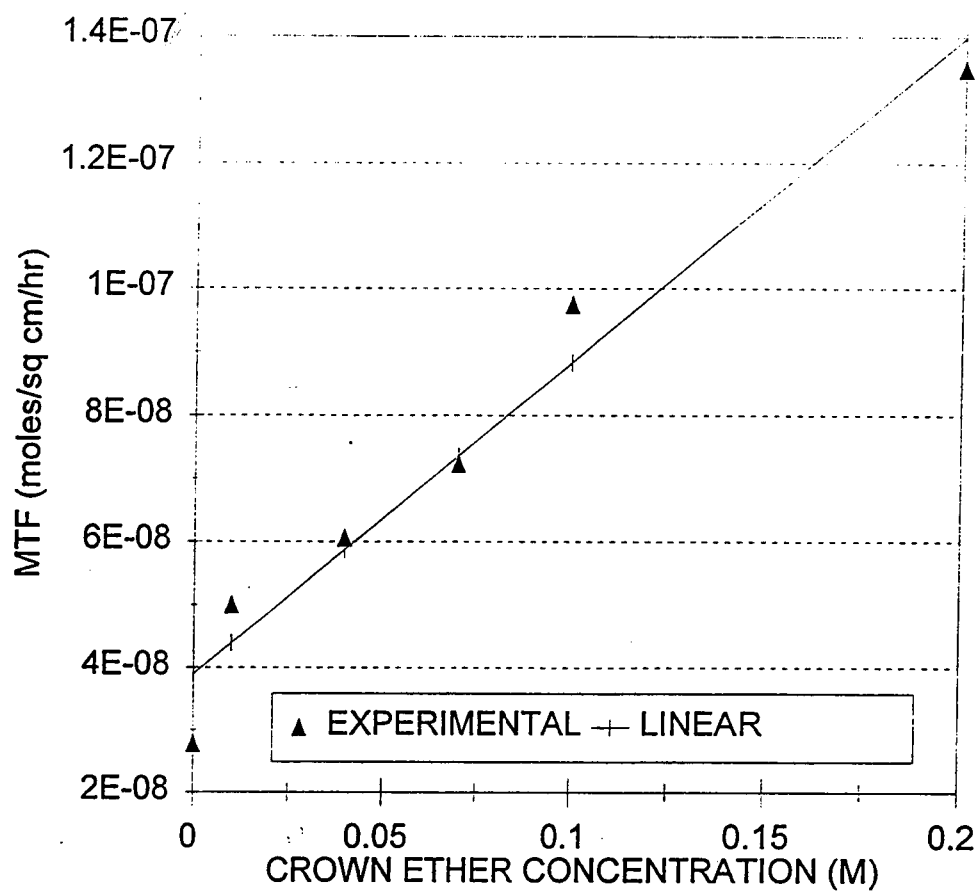


Figure 7.1: Experimental and Predicted MTF versus Initial Crown Ether Concentration. Predicted Data were Obtained from Equation 7.1.

III analysis shows that in addition to the linear term, the quadratic term was good at explaining the model at only about 75% confidence level while on the contrary the linear term in addition to the quadratic term explained the model at over 97% confidence limit. Figure 7.2 shows a plot of the predicted quadratic curve and the experimental data. It is also evident from the plot that the quadratic curve gave a better fit than the straight line (Figure 7.1).

From this program we can conclude that it is absolutely imperative to a linear dependence term in the model. However, we cannot completely disregard the quadratic term and conclude that MTF is linearly dependent on the initial CE concentration.

### **7.3.2 Effect of all Variables on MTF**

A new and comprehensive multiple regression of MTF on all the possible predictor variables and their interactions was computed using the regression model available in the SAS program. The variables used included all the variables in the preceding program plus aqueous feed and strip velocity, strip composition, nature of the diluent and membrane thickness.

The result of this multiple regression is a statistical model relating MTF to all predictor variables at a 90% confidence interval (Equation 7.2). The model eliminated all

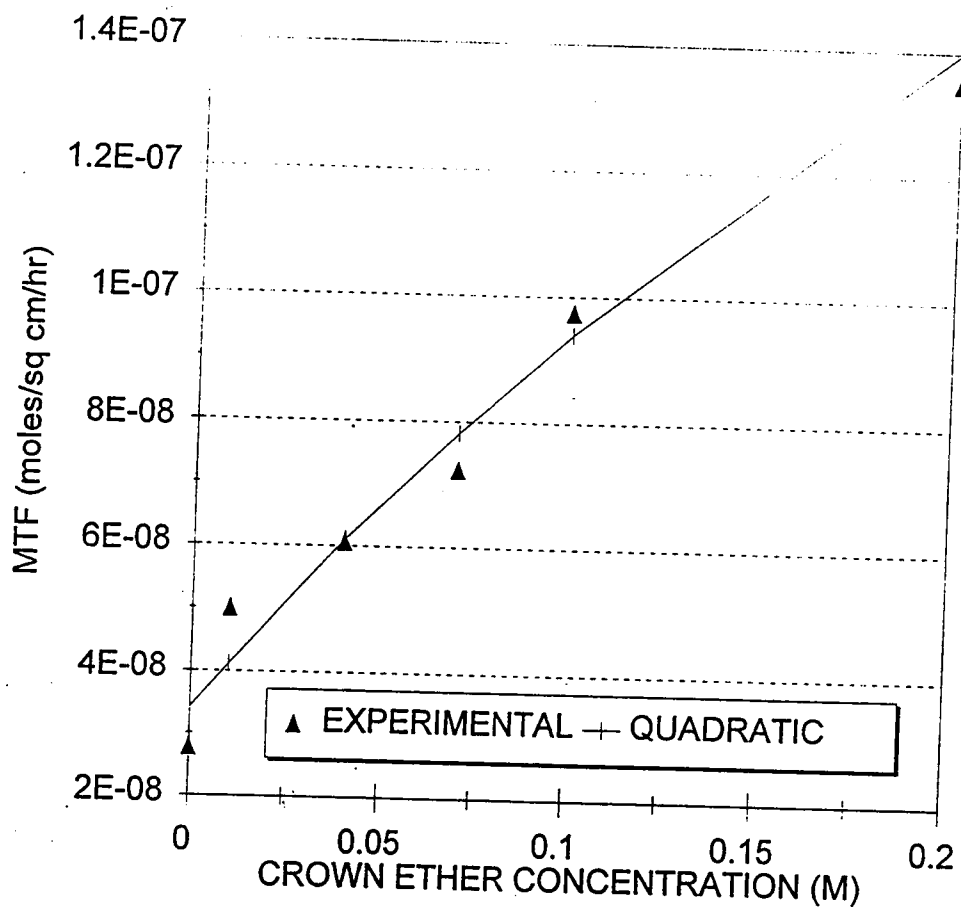


Figure 7.2: Experimental and Predicted MTF vs Initial Crown Ether Concentration. Predicted Data was Obtained from the Model.

the variables which were multi-collinear such as the product of the square of feed rhenium and sodium concentrations with initial crown ether concentrations (CEREF<sup>2</sup>, CENAF<sup>2</sup>), product of the square of the crown ether concentration and the diluent (CE<sup>2</sup>DIL), feed sodium and rhenium concentrations (NAF, REF) etc. The REG procedure chooses a non zero solution for all variables that are linearly independent of previous variables and a zero solution for all multi-collinear variables (SAS Users's Guide, 1994).

A multi-collinearity diagnostics test was also conducted on the data by building up the model two variables at a time. The following criteria were used to determine whether the system was multi-collinear. The variable/s was/were considered multi-collinear if:

1. The condition index (CI) of any of the variables was greater than 30.
2. Variance inflation factor (VIF) were much different from 1.
3. Tolerance (TOL) was very much less than 0.5.
4. Parameter coefficients varied significantly with each iteration.

The first model involved only 3 variables namely, [CE], [ReF2], [NaF2], the second model had two additional variables namely VF, and VS, the third model had in addition to these five, Diluent and Membrane thickness as the additional variables while the 4th model had strip sodium concentration in addition to the variables in the third model.

Regression analysis of all these 4 models with the collinearity diagnostics option produced an output with  $CI < 30$ ,  $VIF \approx 1$ , and  $TOL \approx 0.5$  showing no multi-collinearity.

However, when the interaction variables between crown ether concentration and initial feed rhenium and sodium concentration, [CEReF], [CENaF], were added to the 4th model, the regression produced an output which had a CI of 60, VIF > 70, TOL < 0.01. Also, all the parameter coefficients varied significantly from their previous values, suggesting multi-collinearity. Hence the interaction variables and [NaF<sub>2</sub>], [NaS] and the intercept which were insignificant at a 90% CL were removed from the model. Equation 7.2 shows the relationship between the MTF and all the significant non multi-collinear variables. The intercept was included in the model for completeness even though it was not statistically significant at a 90% CL. It may be noted that other models with higher R<sup>2</sup>, and lower Coefficient of Variation were not selected because of multi-collinearity.

$$\text{MTF} = 1.86\text{E-}08 + 5.22\text{E-}07 [\text{CE}] + 0.69 [\text{Re}]^2 + 9.01\text{E-}10 V_F + 9.69\text{E-}10 V_S - 2.68\text{E-}08 \text{Dil} - 7.13\text{E-}10 \text{Thk} \quad (7.2)$$

where:

MTF = Mass transfer Flux, moles/cm<sup>2</sup>/hr

[CE] = Crown ether concentration, M

[Re]<sup>2</sup> = Rhenium concentration square, M<sup>2</sup>

V<sub>F</sub>, V<sub>S</sub> = Velocity of feed and strip respectively, cm/s

Dil = Diluent

Thk = Membrane thickness (microns)

Diluent takes the value of 1 for NPPE and 0 for NPOE. Figure 7.3 shows the predicted

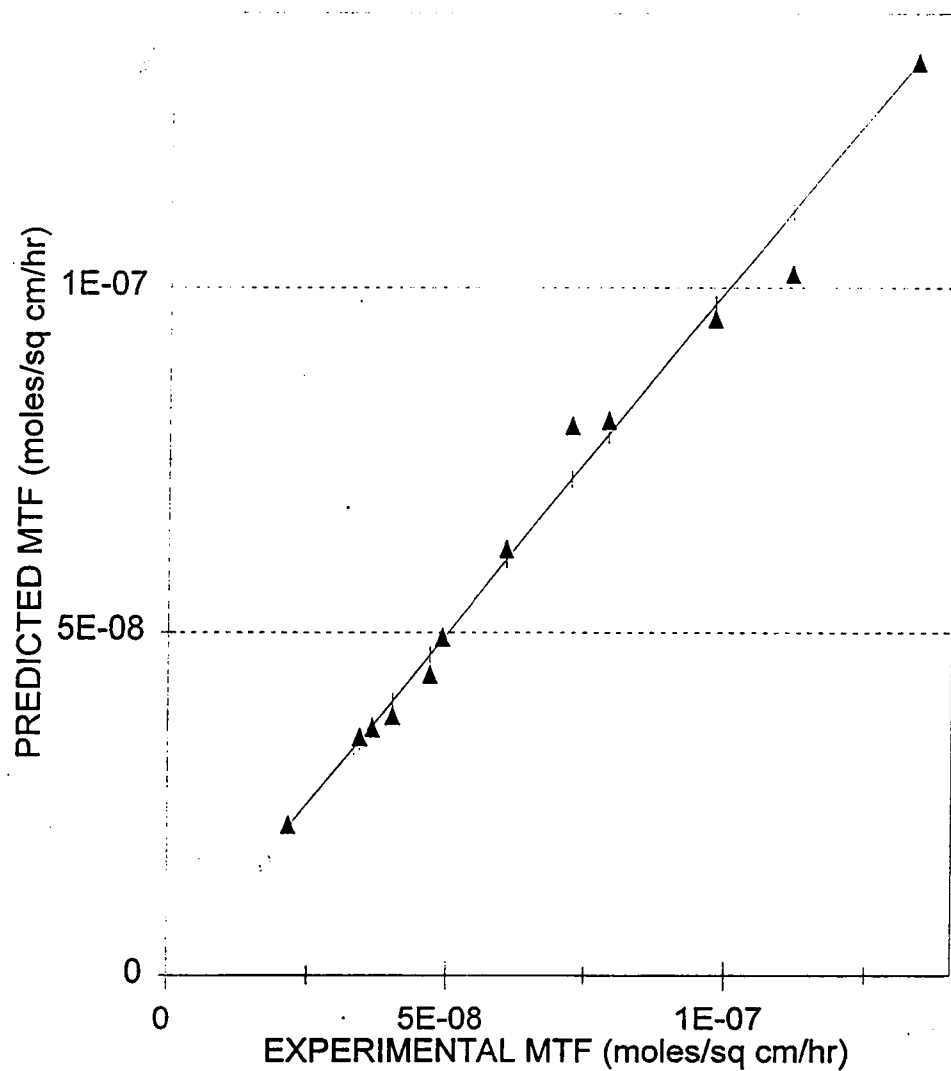


Figure 7.3: Predicted vs Experimental MTF. Predicted Data was Obtained from Equation 7.2.

MTF from equation 7.2 and the experimental MTF. Again, the predicted MTF agreed well with experimental data justifying the use of Equation 7.2 at a 90% CL

Finally, a test was conducted to see whether the selection procedures in SAS could predict the important predictor variables. SAS uses forward, backward and step-wise elimination procedures to eliminate unimportant variables at a 95% confidence level. As expected, the forward elimination procedure selected all the variables as important, the backward elimination procedure selected  $[CE]$ ,  $[CE] \times [Re]$ , Thickness,  $[Re]_{feed}$ , Diluent, Feed and Strip velocities and  $[Na]_{feed}$  as important variables and the step wise elimination procedure selected  $[CE] \times [Re]$ , Thickness,  $[Re]_{feed}$ , Diluent, Feed and Strip velocities and  $[Na]_{strip}$  as the important variables.

# **CHAPTER 8**

## **CONCLUSIONS & RECOMMENDATIONS**

### **8.1 Conclusions**

Some of the important conclusions based on the results of the experiments and the mass transport model include:

1. The feasibility of facilitated coupled transport of sodium perrhenate from an aqueous waste solution and a simple waste solution to an aqueous DI water strip solution has been demonstrated using an SLM containing crown ether as the extractant.
2. NPOE and NPPE were determined as the best diluents while dtbCH18C6 was determined as the best extractant (extractant), among those tested, for sodium perrhenate transport in an SLM.
3. The optimum extractant concentration is 0.04 M and the optimum feed and strip

flow velocity is 27 cm/sec.

4. The membrane was stable (there was no loss of crown ether from the membrane due to aqueous solubility) even after 10 days of continuous operation.
5. Membrane diffusion was the rate limiting step in mass transport and limited the overall mass transfer flux and coefficient.
6. Use of NPPE over NPOE as the diluent led to over 2.7 times increase in mass transfer flux.
7. Experimental aqueous feed and strip mass transfer coefficients, membrane mass transfer coefficients and the overall MTC compared favorably with predicted values.
8. Computer simulations on the mass transfer model predicted exit steady state pertechnetate concentrations to within 99% of the experimental values.
9. The ratio of the feed to strip side distribution coefficient was the most influential parameter affecting mass transport across an SLM.
10. The QSS/Equilibrium model was successful in accurately predicting QSS feed

and strip perrhenate concentrations.

11. Build-up of sodium nitrate, hence sodium concentration, in the strip solution did not limit MTF of sodium perrhenate.
12. There was no appreciable increase in MTF due to the presence of a sodium concentration gradient between the feed and the strip solutions beyond 0.5 M.
13. The ratio of the predicted and the experimental MTC for aqueous Reynolds number exceeding 200 was 1.45. This estimate has a precision error of 16.8%.
14. Free ions rather than ion pairs was the predominant means of membrane transport when NPOE and NPPE were used as diluents.
15. Average extractant (crown ether) loading in the SLM was 48.5%.
16. Facilitated uphill coupled transport of sodium perrhenate from an aqueous MVWS waste solution, an actual complex DOE waste, to an aqueous DI water strip solution has also been demonstrated using an SLM containing crown ether as the extractant.
17. QSS for the perrhenate transport occurred, as predicted by the batch experiments

and the model, between a  $C_F/C_S$  ratio of 1.5 and 2.5 showing the validity of the mass transport model developed by the author.

18. Also, as predicted beyond this ratio sodium perrhenate was back transported while sodium nitrate was forward transported showing that both these transport though competitive in chemistry behaved essentially as mutually exclusive events.
19. Statistical analysis showed that the square of the feed nitrate and perrhenate concentrations, their respective products with initial crown ether concentration were important parameters in predicting perrhenate MTF.
20. Finally, the model was successful in showing that transport in an SLM depends only on the product of the activities of the concerned cation and anion and that the QSS (no net transport for that species) for each transport is different and unique.

## **8.2 Recommendations for Future Work**

The author recommends that the following studies may be conducted as a follow-up to the present research study.

1. Transport of sodium perrhenate in hollow fiber membrane SLM contactors. It will be especially useful to develop a correlation between the MTF and MTCs obtained in flat sheet and hollow fiber SLMs.

2. Determination of the concentration threshold of the crown ether in the SLM. At this concentration the "Bucket Brigade" mechanism would play the dominant role in mass transport and would considerably increase the MTF.
3. Use of partially immobilized SLMs and polysiloxane bound crown ethers for enhanced SLM stability.
4. Use of "HLMs" or composite SLMs for enhanced selectivity.
5. Use of different crown ethers and diluents. This would broaden the scope of the research and would be useful if a patent application is filed.

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