

# **ELECTROCHEMICAL SPLITTING OF SODIUM SULFATE**

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# ELECTROCHEMICAL SPLITTING OF SODIUM SULFATE

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For Dad.

## **ACKNOWLEDGEMENTS**

Friends and family made this possible. I am eternally grateful for their love and support.

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## LIST OF SYMBOLS

A	Surface Area ( $\text{cm}^2$ )
C	Concentration ( $\text{moles cm}^{-3}$ )
D	Diffusion Coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
F	Faraday Constant ( $\text{C mole}^{-1}$ )
i	Current ( $\text{C s}^{-1}$ )
J	Flux ( $\text{moles cm}^{-2} \text{s}^{-1}$ )
j	Current Density ( $\text{C s}^{-1} \text{cm}^{-2}$ )
R	Gas Constant ( $\text{J mole}^{-1} \text{K}^{-1}$ )
T	Temperature (K)
t	Time (s)
V	Volume ( $\text{cm}^3$ )
x	Distance (cm)
z	Charge (unitless)
$\delta$	Membrane Thickness (cm)
$\phi$	Potential (volts)

## LIST OF ABBREVIATIONS

AEM	Anion Exchange Membrane
CEM	Cation Exchange Membrane
Cl <sup>-</sup>	Chloride
Cl <sub>2</sub>	Chlorine
COO <sup>-</sup>	Carboxylate
H <sub>2</sub>	Hydrogen
H <sup>+</sup>	Proton
H <sub>2</sub> O	Water
H <sub>2</sub> SO <sub>4</sub>	Sulfuric Acid
Na <sub>2</sub> SO <sub>4</sub>	Sodium Sulfate
Na <sup>+</sup>	Sodium
O <sub>2</sub>	Oxygen
OH <sup>-</sup>	Hydroxide
PTFE	Polytetrafluoroethylene
SO <sub>4</sub> <sup>2-</sup>	Sulfate
SO <sub>3</sub> <sup>-</sup>	Sulfonate

## SUMMARY

This work details an electrochemical cell designed for the salt-splitting of sodium sulfate cake from a pulp mill into sodium hydroxide and sulfuric acid. Such a cell would allow a pulp mill to reduce or eliminate the need to purchase sodium hydroxide as well as stop the sewerage of sodium sulfate into rivers.

This work focuses on the ion exchange membranes and the membranes' current efficiencies under different electrolysis conditions. Five cation exchange membranes and four anion exchange membranes were tested. It was found that of the membranes tested, DuPont Nafion 324 cation exchange membrane and Sybron Ionac MA-7500 anion exchange membrane were the most efficient because their ability to prevent product loss through migration and diffusion.

These two membranes were then tested with increasing sodium hydroxide catholyte concentrations to further an understanding of the roles of migration and diffusion in a salt-splitting cell. It is discovered that the cation exchange membrane current efficiency decreases as the sodium hydroxide catholyte concentration increases from 1 to 5 M. This decrease in current efficiency is attributed to an increase of back diffusion of hydroxide ions from the cathode compartment to the center compartment. Fickian diffusion of hydroxide ions increased due the larger concentration gradient across the CEM. The larger hydroxide concentration gradient not only provides a larger driving force for Fickian diffusion but also increases the coefficient of diffusion. The membrane coefficient of diffusion changes with the composition of the solutions in contact with the two surfaces of the membrane. The diffusion coefficient is larger at a 5 M hydroxide

concentration gradient than at a 1 M gradient. A larger diffusion coefficient leads to a faster rate of diffusion.

The three-compartment cell studied here is able to produce a 5 M (~17% wt/wt) sodium hydroxide solution at 27 % cathodic current efficiency using a single layer of DuPont Nafion 324. The cell also produce a 5 M sodium hydroxide solution at 48% current efficiency using two layers of DuPont Nafion 324, simulating a membrane that is twice as thick. There are also possibilities that a sodium hydroxide solution of up to 32% wt/wt (~10.5 M) could be produced with engineering modifications, such as additional compartments or electrodes, to the salt-splitting cell.

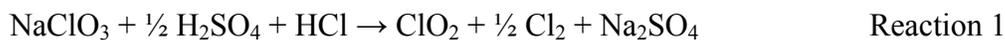
# CHAPTER 1

## PROJECT MOTIVATION AND INTRODUCTION TO SALT-SPLITTING

### 1.1 Sodium Sulfate Sources

Black liquor, a byproduct of pulp mills, is combusted in the power boiler for the energy contained in its organic components. However, black liquor also contains inorganic components such as sodium sulfate ( $\text{Na}_2\text{SO}_4$ ), which are recovered from the boiler flue gas by an electrostatic precipitator [6]. Some electrostatic precipitators produce nearly 50 dry tons per day of  $\text{Na}_2\text{SO}_4$ .

In addition to black liquor combustion, preparation of bleaching chemicals, such as chlorine dioxide ( $\text{ClO}_2$ ), also produce  $\text{Na}_2\text{SO}_4$  as a byproduct. Chlorine dioxide generation produces nearly 20 dry tons of  $\text{Na}_2\text{SO}_4$  per day. The R3 Single Vessel Process is based on the following reaction:



Other methods of  $\text{ClO}_2$  production have been created to reduce the amount of  $\text{Na}_2\text{SO}_4$  produced. Still, significant quantities of  $\text{Na}_2\text{SO}_4$ , referred to as saltcake, are produced and discharged to a sewer line. Environmental concerns of sewerage the saltcake has led to banning this practice in some interior British Columbian and Southern U.S. rivers [5]. This work is a study of an alternative to sewerage the effluent saltcake.

## 1.2 Electrochemical Methods of Ion Transport

Ions dissolved in an aqueous solution are transported by one or a combination of three possible methods: diffusion, migration, and convection. Diffusion is described by Fick's first and second laws, Equations 1 and 2 respectively. Diffusion is the result of a gradient in concentration of a species that builds across a porous control volume (in this study the control volume is an ion exchange membrane). When this concentration gradient builds, the species will diffuse to reach equilibrium. Fick's first law states that the diffusional flux of a species across a membrane,  $J^{\text{Diffusion}}_i$ , is proportional to the concentration differential across that plane,  $dC_i/dx$ . The proportionality factor is the diffusion coefficient,  $D_i$ . Fick's second law states that the rate of change of a species concentration,  $dC_i/dt$ , is proportional to the change in concentration gradient of the species. Note that the diffusion coefficient of a species is not constant, but dependent on species concentration and/or location within the control volume.

$$J^{\text{Diffusion}}_i = -D_i \frac{\partial C_i}{\partial x}$$

Equation 1: Fick's first law of diffusion.

$$\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( D_i \frac{\partial C_i}{\partial x} \right)$$

Equation 2: Fick's second law of diffusion.

Migration is the result of the potential difference across the control volume,  $d\phi/dx$ . When an electric field is applied across an electrolyte solution, all anions will be pulled to the positive electrode and all cations will be drawn to the negative electrode. The migrational flux of ions is given by Equation 3.

$$J^{Migration}_i = -D_i C_i \cdot \frac{z_i F}{RT} \cdot \frac{\partial \phi}{\partial x}$$

Equation 3: Migrational flux.

Ions also move with the bulk solution flow. The convective flux is given by equation 4.

$$J^{Convection}_i = C_i v$$

Equation 4: Convective flux.

The Nernst-Planck equation, Equation 5, describes the transport of ionic species in solution under the influence of an electric field. It states that the total ionic flux across the control volume,  $J_i$ , (in this work the control volume is an ion exchange membrane) is a combined result of the diffusional, migrational, and convective flux.

$$J_i = -D_i \frac{\partial C_i}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi}{\partial x} + C_i v$$

Equation 5: Nerst-Plank equation

The convection term of the Nernst-Planck equation may be excluded here because the electrolyte solutions are not stirred but remain stagnant.

$$J_i = -D_i \frac{\partial C_i}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi}{\partial x}$$

Equation 6: Nerst-Plank equation without convection.

### 1.3 Ion Exchange Membranes

Ion exchange membranes are designed to pass only ions of a specific charge. A Cation Exchange Membrane (CEM) will pass cations while an Anion Exchange Membrane (AEM) will pass anions. Ion exchange membranes are organic polymers that include a significant concentration of covalently bonded fixed ionic groups. The polymer is usually styrene divinylbenzene or a substituted perfluorinated alkene. CEMs contain fixed ionic groups of negative charge; usually sulfonate ( $\text{SO}_3^-$ ) or carboxylate ( $\text{COO}^-$ ) anions. Figure 1.3.1 and Figure 1.3.2 show the chemical structures of styrene divinylbenzene and DuPont Nafion CEMs.

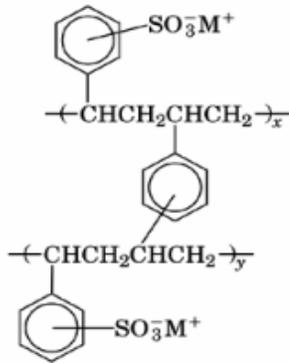


Figure 1.3.1: Chemical structure of a styrene divinylbenzene CEM.

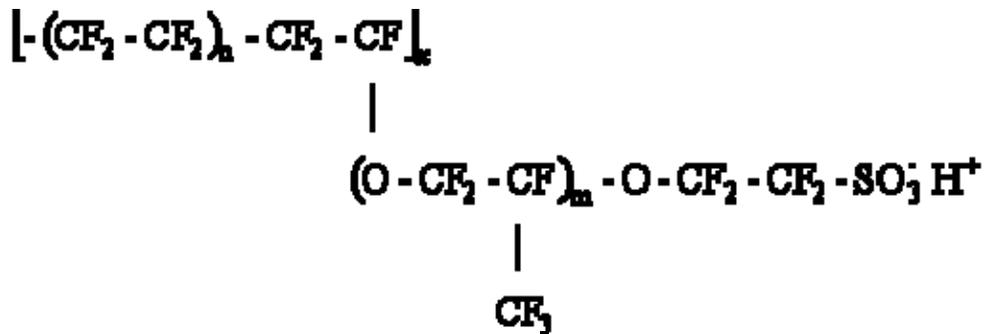


Figure 1.3.2: Chemical structure of a DuPont Nafion membrane.

Instead of negatively charged  $\text{SO}_3^-$  or  $\text{COO}^-$  fixed sites, an AEM relies on quaternary ammonium ( $(\text{CH}_3)_3\text{CH}_2\text{N}^+$ ) fixed positive sites to facilitate anion transport and cation rejection. Figure 1.3.3 shows the chemical structure of a styrene divinylbenzene AEM.

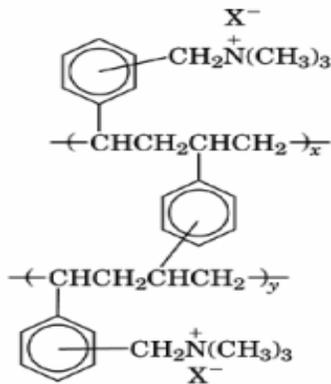


Figure 1.3.3: Chemical structure of a styrene divinylbenzene AEM.

Ions of opposite charge as the fixed ions within a membrane are known as counter-ions. Ions of like charge as the fixed ions within a membrane are known as co-

ions. Since a CEM contains fixed groups of negative charge, cations that pass through the membrane are referred to as the counter-ions. Anions, which are ideally repelled by the fixed negative charges, are referred to as the co-ions. Conversely, anions which are intended to pass through an AEM are counter-ions and the cations which are to be rejected are the co-ions.

Counter-ion to co-ion selectivity is the most important property of an ion exchange membrane. It is critical that a CEM pass cations while repelling anions. Likewise an AEM should pass anions and repel cations. A 100 % counter-ion to co-ion selective membrane would not allow any co-ions to permeate. Membrane counter-ion to co-ion selectivity is different when the membrane is used in different electrolytic conditions.

Water content is an important property of ion exchange membranes. It is the absorption of water by the polymer matrix. Water content is not to be confused with water permeability. Water content is the percentage of membrane volume that is occupied by water due to absorption. Water permeability refers to the volume of water that will penetrate an area of membrane over a period of time. However, the two both relate to the hydrophilicity of a membrane. If a membrane is more hydrophilic, it will accommodate more water in its pores and its water content increases. If a membrane is more hydrophilic, it will also transport water more readily; its water permeability increases. The more water a membrane will absorb the more readily the water will permeate the membrane.

This absorption of water leads to swelling of the membrane. As the membrane swells, zones of aqueous electrolyte are created. As more aqueous electrolyte is accommodated within the membrane more dissolved ions, including unwanted co-ions, are accommodated.

T. Davis et al [2] find that initially increased water content appears to be advantageous, as an increase in electrical conductivity accompanies the water absorption.

However, this will eventually come at the expense of a sizeable loss in counter-ion to co-ion selectivity. The aqueous zones within the polymer enlarge to an ample volume such that co-ions, which should be excluded, are now included within the membrane. Furthermore, the electrostatic repulsion between the fixed ionic groups and the oppositely charged co-ions becomes insufficient to prevent migration of the co-ions through the membranes when a potential field is applied.

The character of styrene divinylbenzene is such that the entire membrane is hydrophilic and will therefore readily absorb water. On the other hand, perfluorinated polymer membranes are known to have discrete hydrophobic and hydrophilic zones. The polymer backbones,  $[-(\text{CF}_2-\text{CF}_2)_n -\text{CF}_2-\text{CF}]_x$ , form the hydrophobic zones, which impart physical stability to the membrane. The molecular interactions between the polymer chains within the hydrophobic regions act to limit the extent of swelling of the polymer. It is the presence of the hydrophobic zones that makes perfluorinated CEMs, like DuPont Nafion, more advantageous than styrene divinylbenzene CEMs in a chlor-alkali cell and a salt-splitting cell such as the one detailed in this work. Styrene divinylbenzene membranes are designed for use in electrodialysis cells where the dilution of a stream is the goal. Whey processing for the manufacture of baby formula is an example of an industrial use of styrene divinylbenzene based ion exchange membranes.

The ion exchange capacity is the measure of the number of fixed ionic groups per unit weight of dry membrane polymer. Exchange capacity is important to membrane performance; however, it will be shown that it is not the only figure of merit in determining the counter-ion to co-ion selectivity of a membrane.

Since co-ions are ideally excluded by electrical repulsion from the fixed ionic charges within the membrane; it follows that a higher concentration of (closer proximity between) fixed ionic charges within the membrane leads to a more selective and efficient membrane. Counter-ion to co-ion selectivity is related to the concentration of fixed ionic sites per unit volume. A denser packing of fixed ionic sites within a wetted membrane

would yield a more counter-ion to co-ion selective membrane. However, the exchange capacity does not correspond to the concentration of fixed ionic charges per unit volume. Remember, the exchange capacity is defined as the number of fixed ionic groups per unit weight of *dry* polymer. When a styrene divinylbenzene membrane is soaked in the aqueous electrolyte solution it absorbs the solution and expands. As a result, the number of fixed ionic sites remains the same even though the volume of polymer has increased. In effect the concentration of fixed sites decreases when the polymer swells. Swelling diminishes the concentration of fixed ionic sites because the number of fixed sites remains constant but the volume of membrane increases.

Figure 1.3.4 is an illustration that demonstrates the decline of fixed ionic site concentration that accompanies the swelling of a styrene divinylbenzene membrane. The top figure is a dry styrene divinylbenzene CEM and the bottom figure is the same membrane after immersion in aqueous electrolyte. It is true that both have three fixed ionic groups. However, in the wet membrane (bottom figure) the fixed ionic groups are more spread out and the volume of the wet membrane is greater than the dry membrane, therefore the concentration of fixed sites per unit volume is less after immersion in the electrolyte. The concept of exchange capacity is based on weight of dry polymer. The concept of concentration is based on volume (wet or dry). The degree of membrane swelling depends on the composition of the electrolyte solutions in contact with each surface.

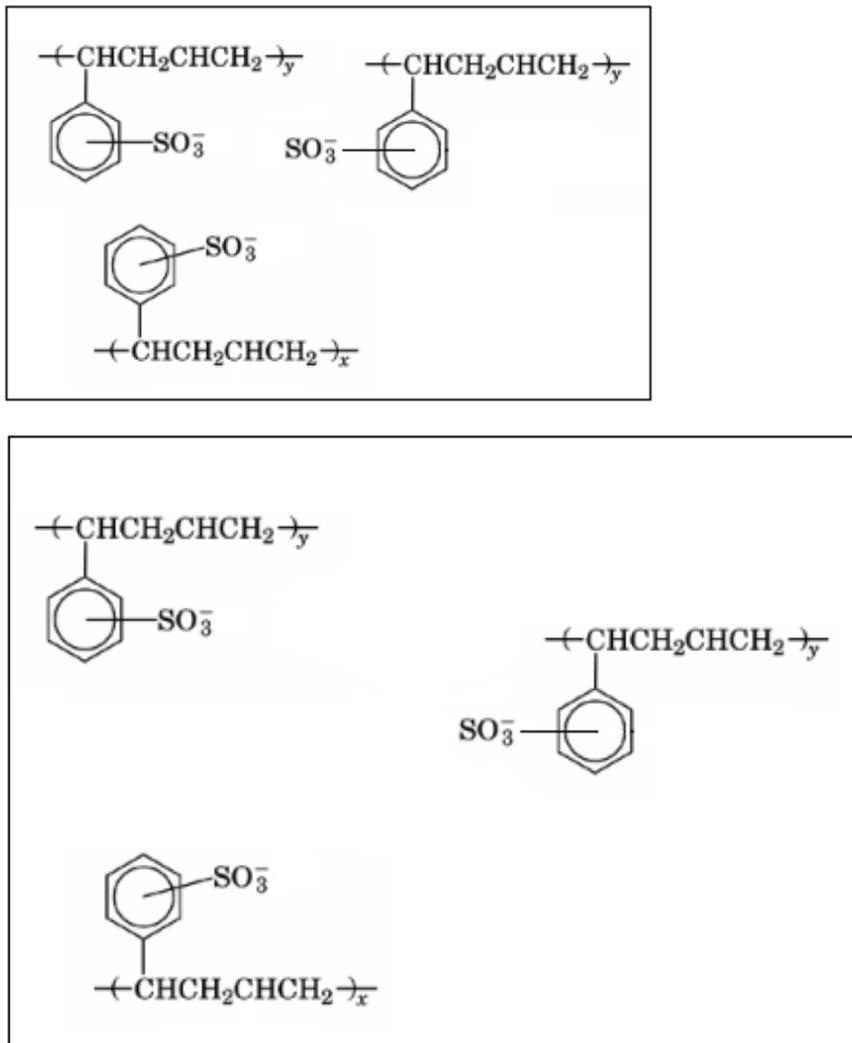


Figure 1.3.4: Absorption of aqueous electrolyte causes the concentration of fixed ionic sites to decrease. The top illustration is the dry polymer. The bottom illustration is the wet polymer.

Most membrane properties depend on the nature of the two solutions in contact with the surfaces of the membrane. When comparing the advertised properties of ion exchange membranes from different manufacturers one must bear in mind that the conditions at which the membrane properties were measured may not be the same. Therefore, a direct comparison of the manufacturers' literature values may not be

accurate. The properties of ion permeable membranes cannot be discussed without reference to the two solutions in contact with the two surfaces of the membrane.

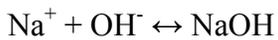
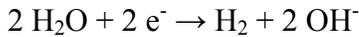
#### 1.4 The Chlor-Alkali Process

CEMs are important to the chlor-alkali process, an electrochemical process for the production of caustic soda (sodium hydroxide) and chlorine gas. Figure 1.4.1 is a schematic of the chlor-alkali membrane process. A chlor-alkali reactor is a two compartment electrochemical cell separated by a CEM. DuPont Nafion 900 series CEMs are the leading membranes for the chlor-alkali industry. The anode compartment is fed an approximately 25% (wt/wt) sodium chloride (NaCl) solution. Dilute sodium hydroxide (NaOH) is fed to the cathode compartment. The electrochemical reduction of water takes place at the cathode to form hydroxide anions ( $\text{OH}^-$ ) and hydrogen gas ( $\text{H}_2$ ). A catalytic coated nickel cathode is used to lower the overpotential for  $\text{H}_2$  evolution. The electric field drives the sodium cations ( $\text{Na}^+$ ) to the cathode compartment where NaOH is formed and charge neutrality is maintained.

Simultaneously, an oxidation reaction takes place at the anode. The anode reaction is the production of chlorine gas ( $\text{Cl}_2$ ) from  $\text{Cl}^-$  anion. A competing anodic reaction is the oxidation of water to form protons ( $\text{H}^+$ ) and oxygen gas ( $\text{O}_2$ ). In fact the oxidation of water is thermodynamically favored. However, due to the high concentration of  $\text{Cl}^-$ ,  $\text{Cl}_2$  evolution is kinetically favored and becomes the dominant reaction. In addition, ruthenium-oxide coated titanium anodes help to promote  $\text{Cl}_2$  evolution. Different metal-oxides may promote different reactions. For example, use of an iridium-oxide coated titanium anode would elevate  $\text{O}_2$  evolution. The CEM prevents chloride ions ( $\text{Cl}^-$ ) from entering the cathode compartment. It also prevents the  $\text{OH}^-$  produced at the cathode from entering the anode compartment. The cathode and anode reactions are given in Reaction 2 and Reaction 3.

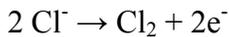
Chlor-Alkali Cathode Reactions

Reaction 2



Chlor-Alkali Anode Reaction

Reaction 3



Unfortunately, the CEM does not prevent all  $\text{OH}^-$  ions from crossing into the anode compartment at high NaOH product concentrations. Both  $\text{Na}^+$  and  $\text{OH}^-$  ions are subject to diffusion and migration as described in the Nernst-Planck equation. However, a CEM is designed so that the diffusion coefficient for sodium cations,  $D_{\text{Na}^+}$ , is much larger than the diffusion coefficient for hydroxide anions,  $D_{\text{OH}^-}$ . It is the fixed negative charges in the CEM that lower  $D_{\text{OH}^-}$  and help prevent diffusion and migration of  $\text{OH}^-$  into the anode compartment. At low NaOH product concentrations the driving force for diffusion of hydroxide ions,  $\Delta C_{\text{OH}^-}/\delta_{\text{CEM}}$ , is small and therefore the CEM is quite effective in preventing  $\text{OH}^-$  from moving into the anode compartment. However, at high NaOH product concentrations,  $\Delta C_{\text{OH}^-}/\delta_{\text{CEM}}$  is large and the CEM is not as effective in keeping  $\text{OH}^-$  ions in the cathode compartment. Additionally, the diffusion coefficient of a species is proportional to that species concentration. The more concentrated the species, the higher the diffusion coefficient and the easier it will permeate the membrane. Thus there is a NaOH concentration limit to the process.

When using a CEM the chlor-alkali produces a 32% wt/wt NaOH product which is evaporated to 50% wt/wt before shipping. The cell voltage is typically around three volts and the membrane current efficiency is greater than 90%.

Chlor-alkali cells may also be constructed with a perforated polymer diaphragm instead of a CEM. Diffusion of all species in solution occurs through the electrolyte filled pores in the diaphragm. The result of this diffusion is the NaOH product contains a substantial amount of impurities (such as  $\text{Cl}^-$ ) that are undesirable to many industries. A pulp mill's tolerance of  $\text{Cl}^-$  impurity is such that the membrane cell is preferred over the diaphragm cell.

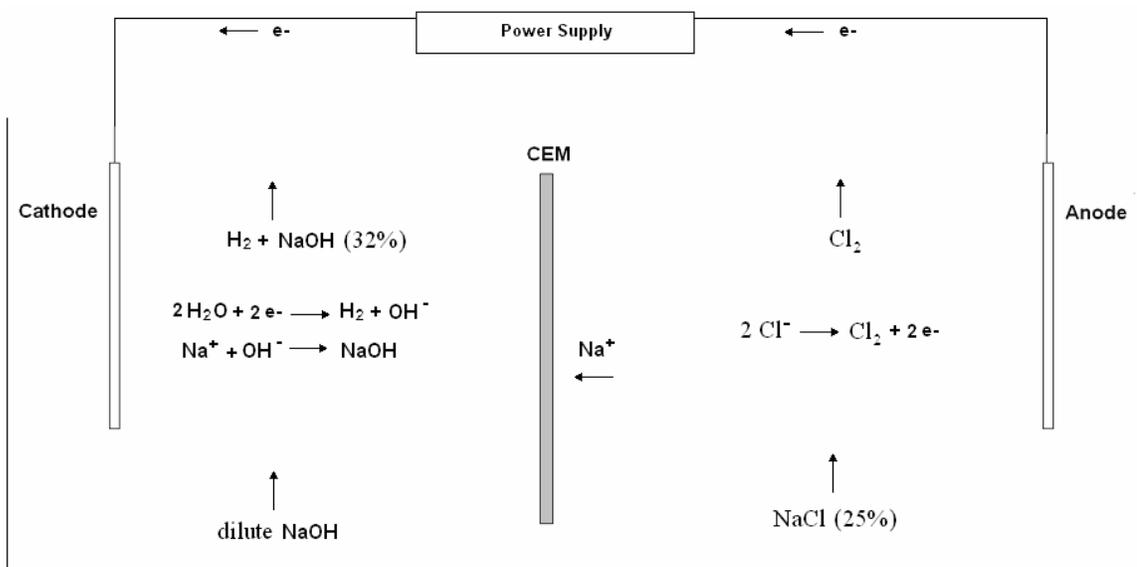


Figure 1.4.1: Schematic of a chlor-alkali membrane cell.

### 1.5 Electrochemical Cell for Saltcake Recycling

Based on the principles described in the Nerst-Plank equation and the counter-ion to co-ion selective property of ion exchange membranes, an electrochemical cell may be used to separate the dissolved ions which make up the saltcake,  $\text{Na}^+$  and  $\text{SO}_4^{2-}$ , and produce a useful acid and base. This process is known as salt-splitting. The salt-splitting of  $\text{Na}_2\text{SO}_4$  in a three compartment cell is quite similar to the chlor-alkali process that also

utilizes an electric field and ion exchange polymers to produce a NaOH solution. A schematic of this cell is shown in figure 1.5.1.

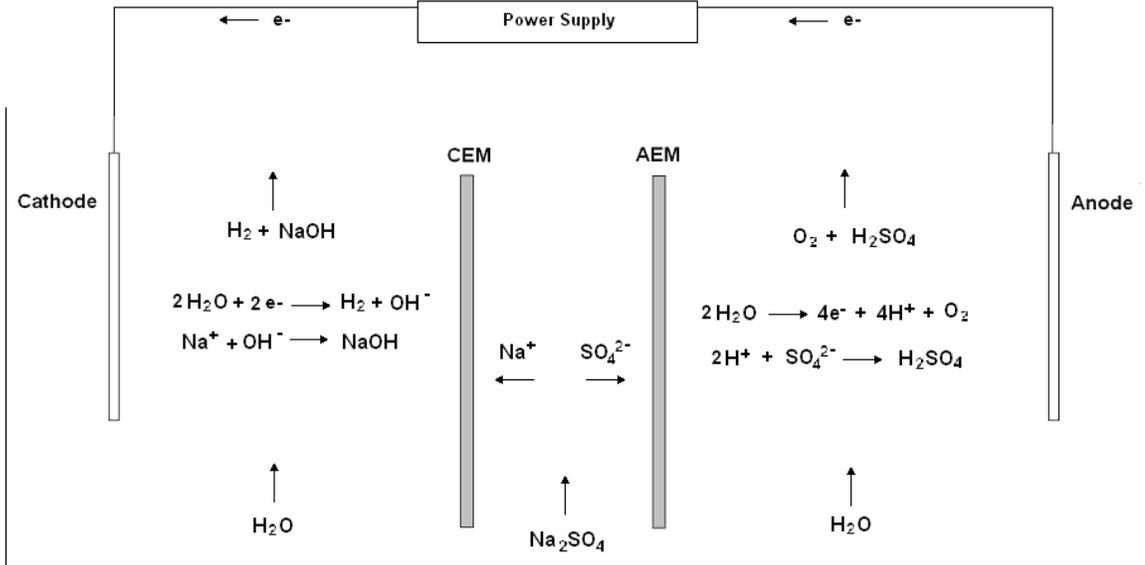


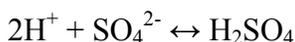
Figure 1.5.1: Three compartment electrochemical cell for the separation of Na<sub>2</sub>SO<sub>4</sub> into NaOH and H<sub>2</sub>SO<sub>4</sub>.

Under the influence of an electric field, the cations (H<sup>+</sup>, Na<sup>+</sup>) will migrate towards the cathode (the negative electrode) and the anions (OH<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) will migrate towards the anode (the positive electrode). Water is electrolyzed in both the cathode and anode chambers. In the cathode chamber water is reduced; OH<sup>-</sup> and H<sub>2</sub> are produced. As Na<sup>+</sup> migrates across the CEM into the cathode chamber to neutralize the charge, NaOH is formed. These are the same cathodic reactions as the chlor-alkali process. A CEM will prevent the migrating OH<sup>-</sup> from crossing to the anode and SO<sub>4</sub><sup>2-</sup> from entering the cathode. In the anode chamber water is oxidized; H<sup>+</sup> and O<sub>2</sub> are formed as shown in reaction 3. An AEM will prevent H<sup>+</sup> from crossing to the cathode and neutralizing the OH<sup>-</sup> product. It will also prevent Na<sup>+</sup> from entering the anode compartment. As SO<sub>4</sub><sup>2-</sup>

enters the anode chamber, sulfuric acid is formed. The thermodynamic energy required for electrochemical production of  $\text{OH}^-$ ,  $\text{H}^+$ ,  $\text{H}_2$ , and  $\text{O}_2$  is about two volts. The anode reactions of salt-splitting are given in Reaction 4.

Salt-Splitting Anode Reactions

Reaction 4



Salt-splitting is not to be confused with electrodialysis. Salt-splitting is the conversion of a salt into its corresponding acid and alkali. Electrodialysis is a method of dilution and concentration of salt solutions using an electric field. Salt-splitting differs from electrodialysis in that it requires electrolysis to form the acid and base. Electrodialysis, by contrast, uses ion exchange membranes to facilitate a separation.

The Salt-splitting process is subject to the same inefficiencies as the chlor-alkali process, co-ion transport. The keystone of salt-splitting is the counter-ion to co-ion selectivity of the ion exchange membranes. Movement of a co-ion across an ion exchange membrane has a negative effect on the product concentration because product is either lost to the center compartment or neutralized by acid-base reaction. There are two undesired processes in this three-compartment salt-splitting cell. The first is the transport of  $\text{OH}^-$  across the CEM. The second is the transport of  $\text{H}^+$  across the AEM. Each of the two inefficiencies has two driving forces. The first is Fickian diffusion; the second is migration. Diffusion and migration are the most important issues of salt-splitting electrolysis. The back diffusion and migration of co-ions across the ion exchange membranes are the only undesired processes. The forward migration of counter-ions is what makes salt-splitting electrolysis and electrodialysis possible.

The transport of co-ions through ion exchange membranes must be mitigated to create a more efficient salt-splitting cell. Only the porous polymer and fixed ionic sites within an ion exchange membrane act as a barrier to prevent co-ions from diffusing or migrating into the center compartment.

Current efficiency is the percentage of the electric current that is effectively used to obtain the desired product. Current efficiency is functionally defined as the ratio of the net product made ( $\text{OH}^-$  or  $\text{H}^+$ ) over the theoretical production. Because there is no competing reaction at either electrode in this cell, the only the explanation for the current efficiency falling below 100 % is that one of the membranes is less than 100 % counter-ion to co-ion selective; which is why the most important attribute of ion exchange membranes in salt-splitting is counter-ion to co-ion selectivity. In some processes there may be a competing electrochemical reaction at either electrode. For example, the oxidation of the anode metal to a metal-oxide or the plating of the cathode by the reduction of metal cations. Such a reaction would cause the current efficiency to be lower than 100 %. In this application there is no competing reaction that occurs at either electrode. If a membrane current efficiency is less than 100 % in this cell, it is because co-ions have permeated one of the membranes. Counter-ion to co-ion selectivity is enhanced by increasing the concentration of fixed ionic charges per unit volume. Because there is no competing electrochemical reaction, the current efficiency and counter-ion to co-ion selectivity of the membranes will be identical.

The need for high purity NaOH is another reason that the salt-splitting cell diagramed in figure 1.5.1 would be beneficial to a pulp mill. Chloride ions can be harmful to some equipment in pulp mills. Any  $\text{Cl}^-$  impurities present in the  $\text{Na}_2\text{SO}_4$  feed would migrate into the anode compartment and be oxidized to  $\text{Cl}_2$ . In fact,  $\text{Cl}^-$  is a more mobile anion than  $\text{SO}_4^{2-}$  and would more readily transport from the center to the anode compartment. The NaOH product from this type of salt-splitting cell would be virtually  $\text{Cl}^-$  free.

Instead of sewerage  $\text{Na}_2\text{SO}_4$ , it can be used to generate NaOH which is useful to a pulp mill. The costs are capital and electricity. About two volts is required to make the products, there is approximately a 0.5 volt overpotential, and approximately 3.5 volt  $iR$  drop due to membrane and solution resistances. The overall cell potential for this three-compartment, two-membrane cell varies between 5.5 and 6 volts. This voltage is rather high compared to the chlor-alkali process. However, the cell used in this study has a very high length to area ratio. The cell voltage could be lowered by building a cell of thinner geometry.

## CHAPTER 2

### REVIEW OF RELATED LITERATURE AND PATENTS

A similar device was built and operated by J. P. Millington in England during the 1980's with less success than the device reported in this work [12]. The salt-splitting cell is a three-compartment flow cell operated at 60 °C. The cell detailed in this thesis is a three-compartment batch cell operated at room temperature (approximately 22 °C). Millington's cell produces a dilute NaOH stream of approximately 100 g/L (about 2.5 M) and a dilute stream of H<sub>2</sub>SO<sub>4</sub> of approximately 200 g/L (about 2.0 M) at less than 50% current efficiency. Millington writes that the shortcomings of a three-compartment electrolysis cell are attributed to the acidic side of the cell. Due to the high rate of sulfuric acid back-diffusion across the AEM, achieving a high concentration of sulfuric acid is not possible. Additionally, the center compartment becomes acidic. The higher proton concentration is detrimental to current efficiency because much of the current carried across the CEM is by H<sup>+</sup>. The transport of H<sup>+</sup> instead of Na<sup>+</sup> results in poor current efficiency of NaOH production because the H<sup>+</sup> neutralizes the OH<sup>-</sup> product.

This thesis will argue that a significant fraction of the current is carried across the CEM by OH<sup>-</sup> and not H<sup>+</sup>. Since a high concentration H<sub>2</sub>SO<sub>4</sub> product is not important (NaOH is the more valuable product), the acidity of the anode and central compartments are controlled (to an extent) to limit the charge carriers across the CEM to Na<sup>+</sup> and OH<sup>-</sup>. The results of this study support Millington's statement that an H<sub>2</sub>SO<sub>4</sub> concentration of value to a pulp mill cannot be produced in this type of three compartment salt-splitting cell by direct electrolysis. Therefore the majority of this study focuses on the cathode side of the cell and the production of more concentrated NaOH.

In 1999, A.D. Martin studied a three-compartment, two-membrane, batch-operation, salt-splitting cell with recirculating electrolyte [10] and patented a more complex salt-splitting cell based on two compartments separated by a DuPont Nafion 324 CEM [11]. The two-compartment cell utilizes pH control and temperatures near 80 °C in the anode compartment to achieve a higher concentration of Na<sub>2</sub>SO<sub>4</sub> anolyte; resulting in a NaOH product near 20% wt/wt at 70% current efficiency.

Martin states the AEM of a three-compartment cell is extremely sensitive to basic pH conditions. The cell voltage is much higher due to the use of two membranes and three electrolytes. The AEM did not exhibit selectivity sufficient to producing a sulfuric acid stream concentrated enough to be of value. The AEM normally operates at different current efficiencies than the CEM. Therefore, pH control of the central compartment is necessary to avoid damage to either or both membranes. Because of these issues, Martin favors a two-compartment cell to a three-compartment cell.

N Tzanetakis et al [14] also studied two and three-compartment salt-splitting cells and found the two-compartment cell more to their liking, because of the lower cell voltage that is associated with the removal of the AEM and the high current efficiency of NaOH production remains. The cells utilized a closed-flow system; essentially a batch operation system with circulating electrolyte solutions. However, the authors suggest that the flowrate did not have a crucial influence on the current efficiency. The three-compartment cell uses a Pall R1010 CEM and Pall R1030 AEM. These membranes appear to have a much higher maximum current density limit than the membranes studied in this work, with the exception of the DuPont Nafion membranes. However, the authors note that while production rate increases at higher current densities, the membrane current efficiencies are higher at lower current densities.

The authors report 98% current efficiency for the production of NaOH in the two-compartment cell compared to 91% current efficiency of NaOH production in the three-

compartment cell. However, the NaOH product concentration in these experiments is less than 0.6 M.

While it is true that a two-compartment cell has the advantage of requiring a lesser cell voltage than a three-compartment cell, this comes at the expense of the purity of one of the streams (acid or alkaline dependent on the use of an AEM or CEM as the separator). If an AEM is used to separate a two-compartment cell, there will be significant  $\text{Na}^+$  contamination in the acid product stream.

Still, Tzanetakis et al consider only low acid and alkaline concentrations, (maximum concentrations of 0.88 M  $\text{H}_2\text{SO}_4$  and 1.72 M NaOH). This work focuses more on NaOH product concentrations that would be of interest to a pulp mill. A 15 to 25% wt/wt (4.5 to 8 M) NaOH concentration produced electrochemically would considerably reduce the cost of evaporation to 50% wt/wt.

M Paleologou et al [13] study the buffering effect of the divalent  $\text{SO}_4^{2-}$  anion in improving current efficiency in a two-compartment salt-splitting cell separated with a Nafion 417 CEM. The authors utilize a unique simultaneous steady-state flow and batch operation cell. Basically, one of the two compartments operates in steady-state flow mode while the other compartment operates in batch mode.

The cell operates in two fashions. The first operation mode utilizes steady-state production of a 1.04 M NaOH solution at the cathode half of the cell. Meanwhile the anode half of the cell utilizes batch operation. The anolyte is initially a 1.5 M sodium sesquisulphate  $\text{Na}_3\text{H}(\text{SO}_4)_2$  solution. The anolyte composition shifts throughout electrolysis from 1.5 M  $\text{Na}_3\text{H}(\text{SO}_4)_2$  to 1.5 M  $\text{NaHSO}_4$  to a 1.5 M  $\text{NaHSO}_4 + \text{H}_2\text{SO}_4$  solution. During this time the current efficiency of NaOH production falls from 78% to 10%. The current efficiency of NaOH production is steady, near 78%, while the  $\text{H}^+$  concentration in the anode compartment is less than 0.7 M. However, when the  $\text{H}^+$  concentration exceeds 1.0 M the current efficiency begins to decline rapidly.

This suggests that as long as the  $\text{OH}^-$  concentration in the cathode compartment is significantly higher than the  $\text{H}^+$  concentration in the anode compartment, the acidity of the anode compartment does not significantly impact the cathodic current efficiency. This idea is supported by Jorissen and Simmrock [9].

The second operation mode, one more likely to be used industrially, is a steady-state flow operation of both anode and cathode compartments. Constant concentrations of  $\text{NaOH}$  (1.09 M) and  $\text{Na}_3\text{H}(\text{SO}_4)_2$  (0.71M  $\text{Na}_2\text{SO}_4$  + 0.74 M  $\text{NaHSO}_4$ ) were continuously produced by feeding water into the cathode side and a  $\text{Na}_2\text{SO}_4$  solution into the anode side respectively. The current efficiency for both product streams is 78%; however the authors report that there is a 2 mole percent  $\text{SO}_4^{2-}$  contamination of the cathode product stream. However, like Tzanetakis et al, Paleologou et al study relatively low  $\text{NaOH}$  concentrations. This work is focused on producing the strongest  $\text{NaOH}$  concentration possible by electrochemical means.

## CHAPTER 3

### EXPERIMENTAL SETUP

The electrolysis is done in a modified QuickCell QC200, dual cell setup from Astris Energi Inc. A center compartment constructed of translucent polycarbonate was added between the two factory compartments. The bulk of the factory compartments are sealed so that smaller volumes of electrolyte may be used. The cell is shown in Figures 3.1 and 3.2. The electrodes are 5 cm<sup>2</sup> platinized titanium disks. Platinized titanium electrodes were used for water electrolysis. An industrial electrolysis cell would more than likely take advantage of a less expensive cathode material such as catalyzed-nickel.

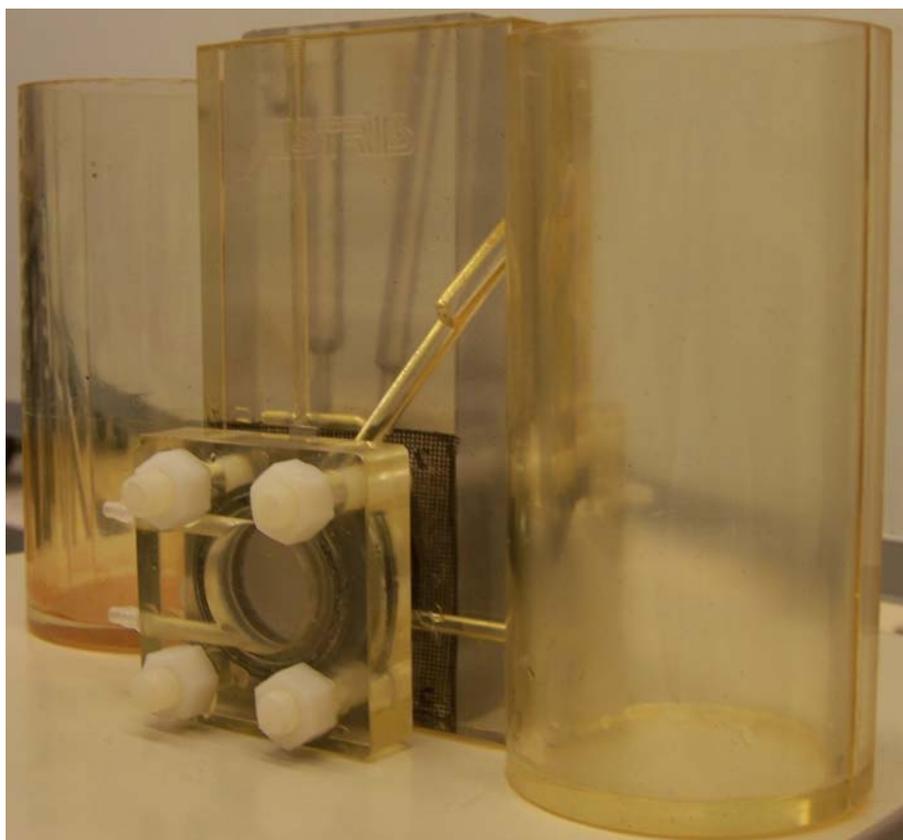


Figure 3.1: Three-compartment electrochemical cell.

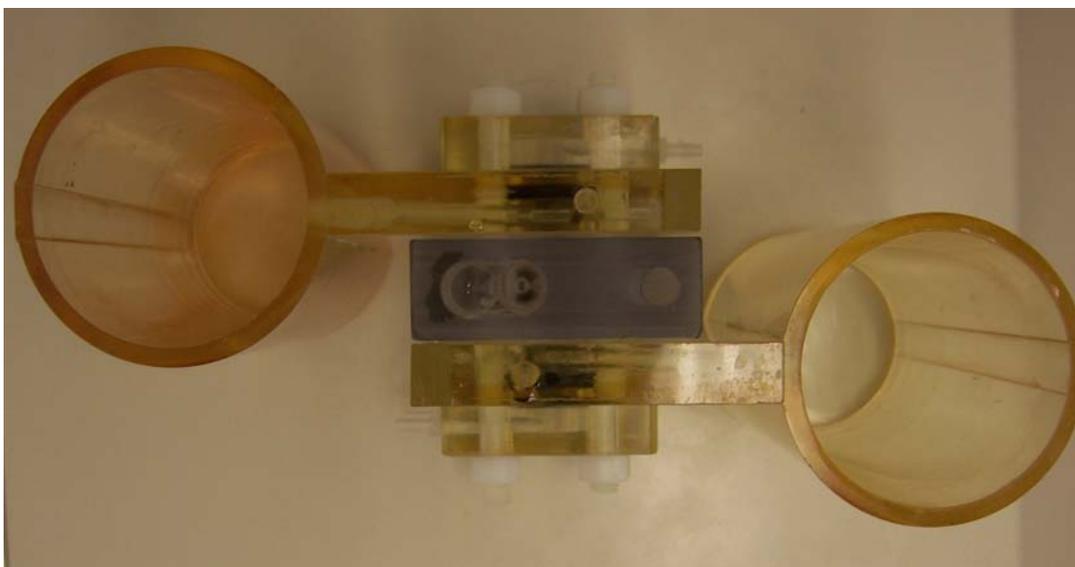


Figure 3.2: Three-compartment electrochemical cell (bird's eye view).

Before the membranes can be placed in the cell for electrolysis, they must be preconditioned according to manufacturers' specifications. Each manufacturer has its own specifications for membrane preconditioning. Most only require that the membrane be soaked in the solution of interest for several hours so that they may expand. The DuPont Nafion membranes require soaking in a NaOH solution of pH 11-12 for at least four to twelve hours. The Electropure Excellion membranes require expansion in 80 °C de-ionized water for 48 hours. After preconditioning the membranes are ready to be used in an electrolysis cell.

The electrolyte solutions are injected into the proper compartments and left overnight so that membranes absorb the equilibrium amount of electrolyte solution. After a twenty to thirty minute pre-electrolysis (approximately 10 – 20% electrolysis of the center electrolyte), the contents of the cell are removed and each compartment of the cell is rinsed with the proper electrolyte. The percent electrolysis refers to the number of  $\text{Na}^+$  cations in the center compartment that will ideally be transported to the cathode compartment by the application of an electric field. For example, if the center compartment contains about 15 mL of 1 M  $\text{Na}_2\text{SO}_4$  electrolyte, approximately 0.03 moles

of  $\text{Na}^+$ . The time of electrolysis is set such that 0.003 moles  $\text{Na}^+$  (10% of the total  $\text{Na}^+$  moles) move to the cathode compartment. Approximately 294 coulombs of charge must be passed to achieve this; therefore electrolysis occurs for nearly 20 minutes operating at a near maximum current density of  $50 \text{ mA cm}^{-2}$ . After the rinse, each compartment of the cell is again filled with the proper electrolyte; this time the mass of the electrolyte of each compartment is recorded using an electronic balance. The anode and cathode compartments contain about 7.7 mL of electrolyte.

The cell is connected to a Hewlett Packard 6629A System DC Power Supply. The constant current is set to 245 mA. Electrolysis occurs for twenty minutes (approximately 10% electrolysis of the center electrolyte).

After electrolysis the electrolyte solutions are removed from the cell with a syringe. Electrolyte samples before and after electrolysis are analyzed by acid-base titration. A one-milliliter aliquot is diluted in about 70 mL of de-ionized water. The samples are titrated using phenolphthalein indicator and an Orion model 410A pH meter in tandem to determine the endpoint. The alkaline samples are titrated using potassium hydrogen phthalate. The one-milliliter alkaline aliquot is diluted with de-ionized water and a drop of phenolphthalein indicator is added to the beaker. Potassium hydrogen phthalate is added to the beaker until the solution turns from dark pink to colorless. When the solution is colorless the endpoint has been reached, about  $\text{pH} = 8.6$ . The Orion model 410A pH meter is used to help determine the rate of potassium hydrogen phthalate addition.

The acid samples are prepared like the alkaline samples. A one-milliliter aliquot is diluted with de-ionized water and a drop of phenolphthalein indicator is added to the beaker. The solution is titrated using NaOH until the solution turns from colorless to dark pink. After the sample has turned dark pink, it is then back-titrated with potassium hydrogen phthalate to determine the sample concentration. When the solution is

colorless the endpoint has been reached, again around  $\text{pH} = 8.6$ . The Orion model 410A pH meter is used to help determine the rate of potassium hydrogen phthalate addition.

To appraise membrane performance, the current efficiency of each experiment was measured. Current efficiency is the percentage of the electric current that is effectively used to obtain the desired product. Current efficiency is functionally defined as the ratio of the net product made ( $\text{OH}^-$  or  $\text{H}^+$ ) over the theoretical production. Since  $\text{Na}^+$  and  $\text{SO}_4^{2-}$  ions were not directly measured in this work, the  $\text{OH}^-$  and  $\text{H}^+$  ion concentrations were determined by titration. The principle of charge neutrality links each  $\text{OH}^-$  anion in the cathode compartment to a  $\text{Na}^+$  cation, likewise for  $\text{H}^+$  and  $\text{SO}_4^{2-}$  ions in the anode compartment. Since approximately 294 coulombs of charge are passed in each electrolysis experiment, approximately 0.00304 moles of  $\text{Na}^+$  and/or  $\text{OH}^-$  are the maximum available to cross the CEM. Ideally, 0.00304 moles of  $\text{Na}^+$  would cross from the center to the cathode and no  $\text{OH}^-$  anions would cross the CEM into the center compartment. Additionally, 0.00304 moles of  $\text{OH}^-$  are generated at the cathode. If it is determined by titration that there is a less than 0.00304 mole increase of  $\text{OH}^-$  ions in the cathode compartment after passing 294 coulombs of charge, then the current efficiency is less than 100%. Note that the CEM and the AEM of a three-compartment cell will likely have different current efficiencies. Here the current efficiency for producing NaOH, which is affected by the properties of the CEM, is referred to as the cathodic current efficiency. The current efficiency for producing  $\text{H}_2\text{SO}_4$  is the anodic current efficiency.

Water transport is not considered in this work when determining the current efficiency. Water molecules accompany dissolved ions as a hydration shell even as the ions pass through ion exchange membranes. Xie and Okada [15] document the transport of water across a CEM as water of hydration and by osmosis. These phenomena would alter the volume of electrolyte in each compartment across the cell. However, they are outside the scope of this work and are not measured. Likewise, the change in electrolyte volume due to the release of  $\text{H}_2$  and  $\text{O}_2$  gas by water electrolysis is also not considered.

Also the volume change of electrolyte from these phenomena is considered insignificant. If three molecules of water accompany each  $\text{Na}^+$  cation transported to the cathode compartment, a 10% electrolysis experiment of 100% cathodic current efficiency would result in the transport of 0.009 moles or 0.16 mL of  $\text{H}_2\text{O}$  from the center compartment to the cathode compartment. Simultaneously if one mole of  $\text{H}_2\text{O}$  is lost from the cathode compartment (as  $\text{H}_2$  gas and  $\text{OH}^-$  anion) for every mole of  $\text{Na}^+$  transported to the cathode compartment, only 0.0537 mL of  $\text{H}_2\text{O}$  are lost. Combining the water lost by electrolysis with the water gained as the  $\text{Na}^+$  hydration shell, there is a less than 1.5% change in the catholyte volume. Therefore it is not imperative to include the effects of water transport in this study.

## CHAPTER 4

### RESULTS

#### 4.1 CEM Comparison

Table 4.1.1 shows the CEMs tested in this study and some of their properties as listed by the manufacturer. The CEMs were selected to test a variety of properties such as the polymer backbone of the membrane, the ion exchange capacity (sometimes referred to as the acid capacity), and electrical resistance (the reciprocal of electrical conductivity).

Table 4.1.1: CEMs studied and their properties as listed by the manufacturer.

Membrane	Electropure Excellion I-100	GE Ionics CR67-HMR	Sybron Ionac MC-3470	Dupont Nafion 324	Dupont Nafion 982
Polymer Matrix	Sytrene Divinylbenzene	Sytrene Divinylbenzene	Sytrene Divinylbenzene	PTFE	PTFE
Exchange Capacity (meq gm <sup>-1</sup> )	1.8 - 2.0	2.1	1.4	0.91 - 1.0	0.91 - 1.0
Water Permeability (ml hr <sup>-1</sup> ft <sup>2</sup> )	< 1	80	25	X	X
Electrical Resistance (Ohm cm <sup>2</sup> )	12.5 - 7.5 0.5 M NaCl	10 0.01 M NaCl	25 - 10 0.1 - 1.0 M NaCl	4.5 0.6 M KCl	2.6 24% NaCl 1%NaOH
Thickness (cm)	0.033	0.06	0.0381	0.030	0.023

The performances of several CEMs were compared in a three-compartment, two-membrane cell under identical electrolyte conditions to determine which CEM is best for this application. Two sets of electrolytic conditions were used. The first set was conducted with a 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte in all three compartments. The results of the first set are shown in Figure 4.1.1. The second set was conducted with a 1 M NaOH

catholyte, a 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, and a 1 M H<sub>2</sub>SO<sub>4</sub> anolyte solution. The results of the second set are shown in Figure 4.1.2. Both sets of experiments used the Electropure Excellion I-200 AEM. It is shown in later sections of this work that membrane properties and cell performance change with the composition of the electrolyte. Since this is a batch-operation cell, the electrolyte concentration in each compartment changes from the beginning to the end of the experiment. Ten percent electrolysis is chosen so that the electrolyte compositions do not change significantly during a single experiment. Also the center electrolyte is being depleted of Na<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> ions during electrolysis. The current and the flux of ions through the membranes are dependent on both the concentration of ions in solution and the voltage drop across the membranes. The experiments are run in constant current mode (constant flux of ions). If the concentration of center electrolyte is significantly depleted, the cell voltage necessary to maintain constant current will increase substantially.

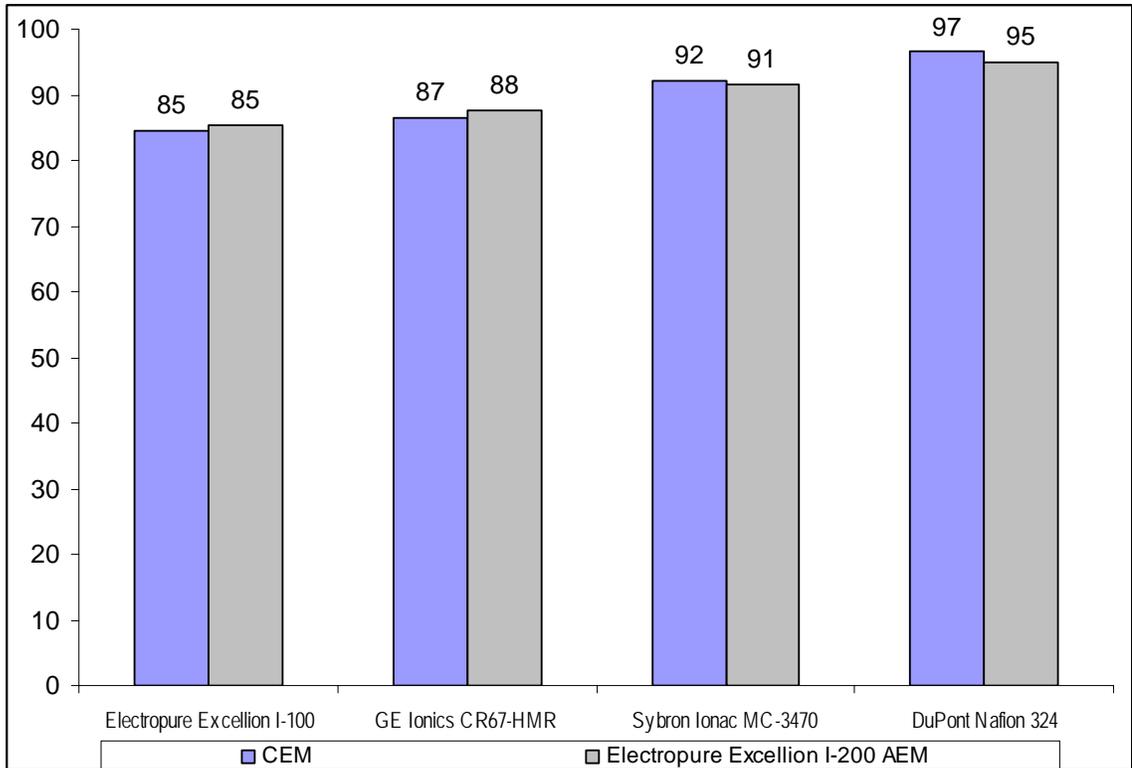


Figure 4.1.1: CEMs and Electropure Excellion AEM Current efficiency after 10% electrolysis using 1 M Na<sub>2</sub>SO<sub>4</sub> electrolyte in all three compartments.

As seen from Figure 4.1.1, when using an electrolyte of neutral pH (1 M Na<sub>2</sub>SO<sub>4</sub>) in each of the three compartments of the cell, the CEMs perform about the same. The fluorinated DuPont Nafion 324 shows slightly better current efficiency. After switching to electrolyte conditions of polarized pH (acidic anolyte, neutral center electrolyte, basic catholyte), a difference in CEM performance is noticed. This is shown in figure 4.1.2. Table 4.1.2 shows the center compartment pH after electrolysis in the polarized pH conditions. In this set, the polytetrafluoroethylene based CEMs show much better current efficiency than the styrene divinylbenzene based CEMs. Also the CEM efficiency is far greater than the AEM efficiency when using polarized pH electrolytic conditions.

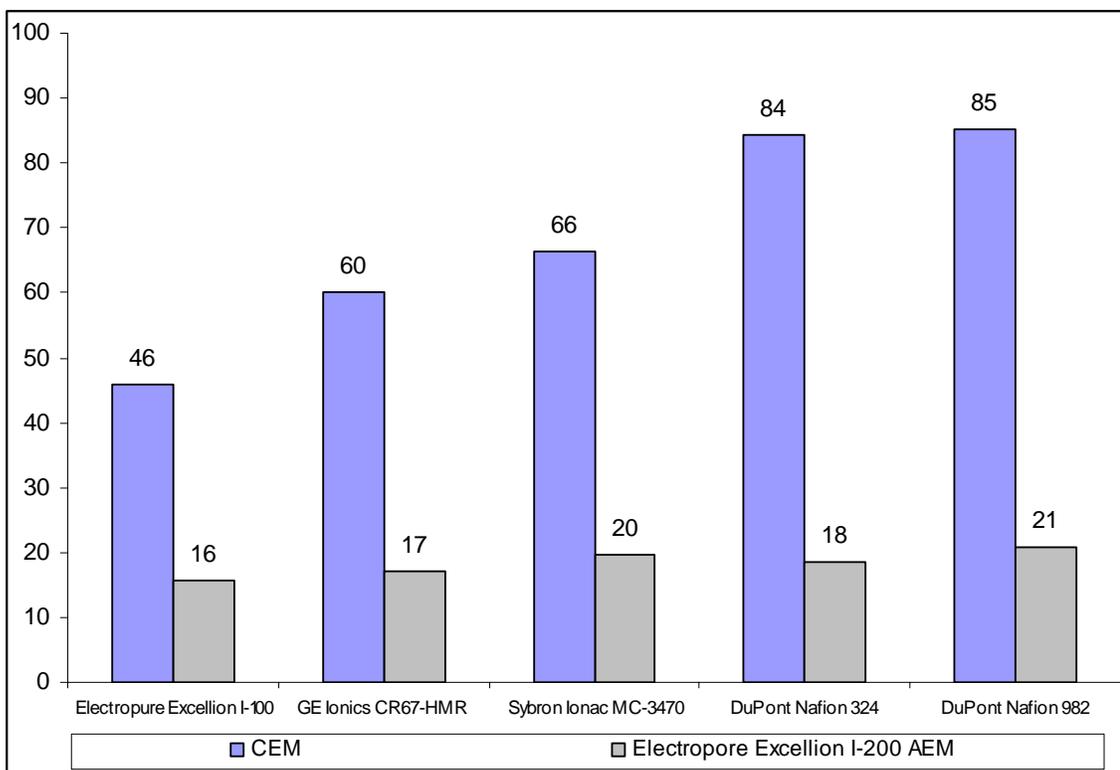


Figure 4.1.2: CEMs and Electropore Excellion I-200 AEM Current efficiency after 10% electrolysis using 1 M NaOH catholyte, 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, and 1 M H<sub>2</sub>SO<sub>4</sub> anolyte.

Table 4.1.2: Center compartment pH after electrolysis in polarized pH electrolyte conditions using various CEMs.

Cation Exchange Membrane	CEM Current Efficiency (%)	AEM Current Efficiency (%)	Center Compartment pH
GE Ionics CR67-HMR	60	17	2.02
Sybron Ionac MA-3470	66	20	1.94
DuPont Nafion 324	84	18	1.85
DuPont Nafion 982	85	21	1.83

## 4.2 AEM Comparison

It was determined that the DuPont Nafion 324 is the best choice of CEMs for this application; reasons for this are discussed in the next chapter. Another set of experiments were conducted to determine the best choice of AEM. Table 4.2.1 shows the AEMs tested and some of their properties as listed by the manufacturer. This set was conducted with a 1 M NaOH catholyte, a 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, and a 1 M H<sub>2</sub>SO<sub>4</sub> anolyte solution, just as the second set of CEM testing experiments. Again 10% electrolysis of the center electrolyte occurs to assure that the composition of each compartment does not change significantly. Figure 4.2.1 shows the anodic current efficiencies of the AEMs tested. Each AEM was paired with DuPont Nafion 324 CEM which yields between 83 and 85% cathodic current efficiency. Table 4.2.2 shows the center compartment pH after electrolysis using each of the four AEMs. The Sybron Ionac MA-7500 is chosen as the best AEM for the remainder of this work. The reason for this choice is discussed in the next chapter.

Table 4.2.1: AEMs studied and their properties as listed by the manufacturer.

Membrane	<b>Electropure Excellion I-200</b>	<b>Sybron Ionac MA-3475</b>	<b>Sybron Ionac MA-7500</b>	<b>GE Ionics AR204-SZRA</b>
Polymer Matrix	Sytrene Divinylbenzene	Sytrene Divinylbenzene	Sytrene Divinylbenzene	Sytrene Divinylbenzene
Exchange Capacity (meq gm <sup>-1</sup> )	0.08 - 0.09	0.9	1.1	2.4
Water Permeability (ml hr <sup>-1</sup> ft <sup>2</sup> )	< 1	25	50	60
Electrical Resistance (Ohm cm <sup>2</sup> )	5 - 10 0.5 N NaCl	50 - 25 0.1 N - 1.0 NaCl	30 - 10 0.1 N - 1.0 NaCl	7 0.01 N NaCl
Thickness (cm)	0.033	0.041	0.046	0.05

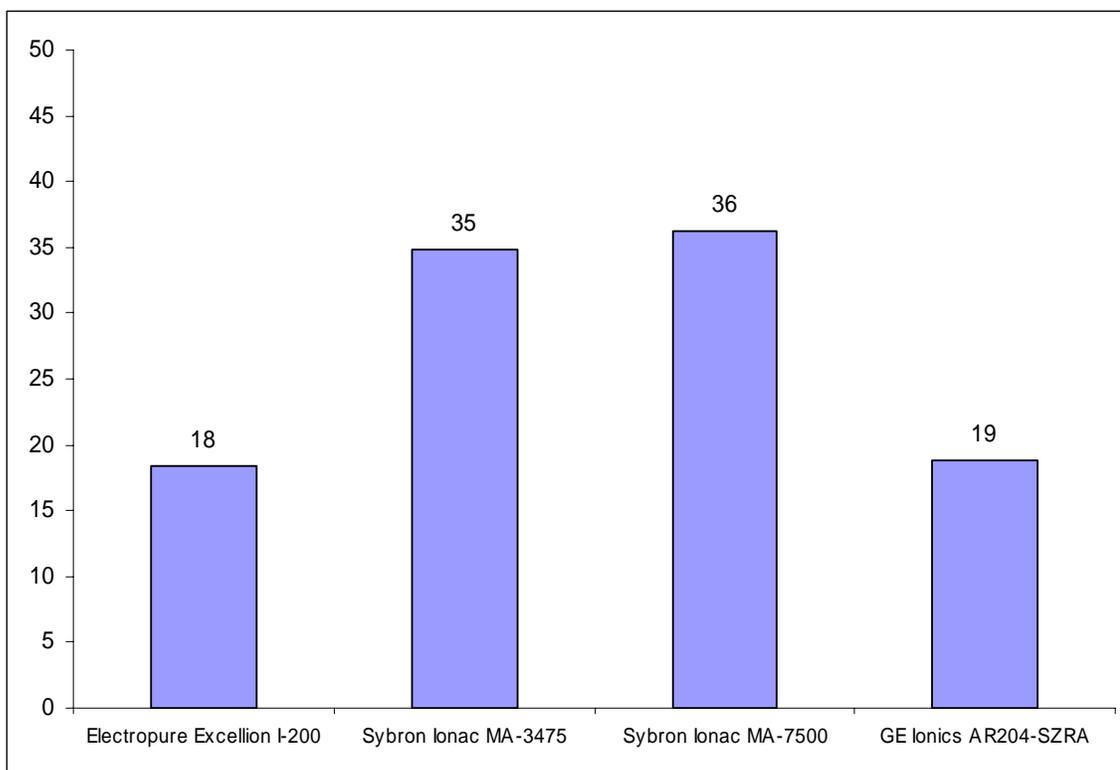


Figure 4.2.1: AEMs current efficiency after a 10% electrolysis using 1 M NaOH catholyte solution, 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte solution, and 1 M H<sub>2</sub>SO<sub>4</sub> anolyte solution. The DuPont Nafion 324 CEM separates the cathode and center compartments and has 83% to 85% current efficiency in all cases.

Table 4.2.2: Center compartment pH after electrolysis in polarized pH electrolyte conditions using various AEMs.

Anion Exchange Membrane	CEM Current Efficiency (%)	AEM Current Efficiency (%)	Center Compartment pH
Electropure Excellion I-200	84	18	1.85
GE Ionics AR204-SZRA	84	19	1.85
Sybron Ionac MA-3475	85	35	1.93
Sybron Ionac MA-7500	83	36	1.94

### 4.3 CEM and AEM Efficiency vs. NaOH Product Concentration

Once the best CEM and AEM were selected (DuPont Nafion 324 and Sybron Ionac MA-7500), the next step was to determine the strength of NaOH that could be produced in this three-compartment setup. The anodic current efficiency is much lower than the cathodic current efficiency in the above experiments. It was thought that with a 1 M H<sub>2</sub>SO<sub>4</sub> anolyte concentration, the concentration of free H<sup>+</sup> is high enough that excessive back diffusion and migration of H<sup>+</sup> across the AEM occurs. The H<sup>+</sup> ion is the smallest and most mobile cation, and therefore the co-ion that would most readily pass through an AEM. To test the theory the anolyte was changed to limit the concentration of free H<sup>+</sup>. The anolyte was changed to a ½ M NaHSO<sub>4</sub> + ½ M Na<sub>2</sub>SO<sub>4</sub> solution that buffers near pH 2. The new anolyte solution ionizes to 1.5 M Na<sup>+</sup>, 0.5 M SO<sub>4</sub><sup>2-</sup>, and 0.5 M HSO<sub>4</sub><sup>-</sup>. This solution will have much less free H<sup>+</sup> because HSO<sub>4</sub><sup>-</sup> is a weak acid, while H<sub>2</sub>SO<sub>4</sub> is a strong acid. This is also done in an attempt to fix the anodic current efficiency so that the cathode side of the cell may be isolated and studied independently. This set was conducted with a varying NaOH catholyte solution, a 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, and a ½ M NaHSO<sub>4</sub> + ½ M Na<sub>2</sub>SO<sub>4</sub> buffered anolyte solution. The starting concentration of NaOH catholyte was varied from 1 to 5 M.

Figure 4.3.1 shows the CEM and AEM current efficiencies as a function of NaOH catholyte concentration. Table 4.3.1 shows the effect of increasing catholyte concentration and declining CEM efficiency on the pH of the center compartment. Table 4.3.2 shows the approximate voltage portioning across the three-compartment cell.

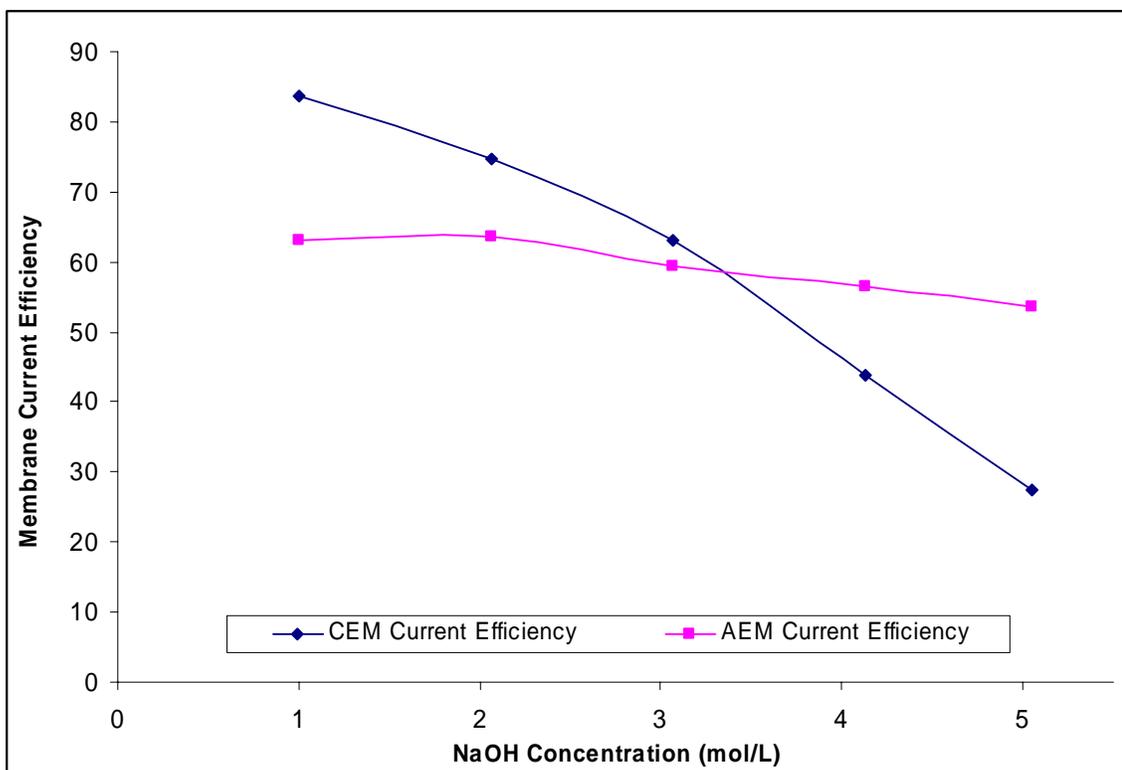


Figure 4.3.1: Current efficiency vs. NaOH concentration after a 10% electrolysis using a DuPont Nafion 324 CEM and a Sybron Ionac MA-7500 AEM. The analyte is a  $\frac{1}{2}$  M  $\text{NaHSO}_4 + \frac{1}{2}$  M  $\text{Na}_2\text{SO}_4$  buffered solution and the center electrolyte is a 1 M  $\text{Na}_2\text{SO}_4$  solution.

Table 4.3.1: CEM current efficiency and center compartment pH after a 10% electrolysis using DuPont Nafion 324 CEM and Sybron Ionac MA-7500 AEM. The analyte is a  $\frac{1}{2}$  M  $\text{NaHSO}_4 + \frac{1}{2}$  M  $\text{Na}_2\text{SO}_4$  buffered solution and the center electrolyte is a 1 M  $\text{Na}_2\text{SO}_4$  solution.

NaOH Concentration ( M )	CEM Efficiency (%)	Center Compartment pH after electrolysis
1.01	84	3.25
2.07	75	3.25
3.07	63	3.38
4.13	44	3.62
5.05	27	8.37

Table 4.3.2: Calculated voltage portioning across the three-compartment cell.

DuPont Nafion 324 CEM	
Calculated Voltage Drop from Membrane Resistance Specifications $\Delta E_{\text{CEM}}$ ( V )	0.221
Sybron Ionac MA-7500 AEM	
Calculated Voltage Drop from Membrane Resistance Specifications $\Delta E_{\text{AEM}}$ ( V )	0.98
Calculated Solution iR ( V )	2.65
Thermodynamic Voltage Requirement for Product Generation [H <sup>+</sup> , OH <sup>-</sup> , O <sub>2</sub> , H <sub>2</sub> ] ( V )	2.06
Calculated Cell Potential ( V )	5.908
Measured Cell Potential ( V )	5.5 - 6.0
Current ( A )	0.245

#### 4.4 Additional Experiments to Determine the Sources of Inefficiency.

Before trying to determine the major sources of CEM inefficiency and why cathodic current efficiency decreases with increasing NaOH product concentration the possibilities are reviewed.

Three Possible Sources of Cathodic Current Inefficiency:

1. Destruction of OH<sup>-</sup> by migration of H<sup>+</sup> across the cell.

Protons are generated at the anode. Because they are positively charged, they will migrate toward the cathode. Ideally the AEM will prevent this from happening. However, due to the small size of the proton, it is possible that it passes through the AEM into the center compartment and then to the cathode compartment where an unwanted neutralization reaction occurs.

If case 1 is the cause of CEM inefficiency, the pH of the center compartment would remain the same even (slightly acidic) as the NaOH catholyte concentration is increased. Also elimination of  $H^+$  by using an alkaline electrolyte in all three compartments will result in an increase of CEM current efficiency to near 100%.

2. Diffusion of  $OH^-$  from the cathode to the center compartment.

As a concentration gradient of  $OH^-$  builds across the CEM, Fickian diffusion occurs. The rate of diffusion is dependent on the size of the concentration gradient.

3. Migration of  $OH^-$  from the cathode toward the anode.

The opposite of the first possibility;  $OH^-$  is generated at the cathode and migrates toward the anode because of its negative charge. The stronger the electric field is, the greater the effects of migration will be.

If case 2 or 3 is the cause of CEM inefficiency, the pH of the center compartment will increase with NaOH catholyte concentration. If case 2 is the dominant cause of efficiency loss then using an alkaline electrolyte in all three compartments will result in higher CEM efficiency because the driving force for diffusion of  $OH^-$  across the CEM, the concentration gradient of  $OH^-$  across the CEM, is decreased from about  $\Delta C_{OH^-} = 1 \text{ M}$  to  $\Delta C_{OH^-} < 1 \text{ M}$ .

To test these possibilities, an additional experiment was conducted using 1 M NaOH electrolyte in all three compartments separated with the DuPont Nafion 324 CEM and Sybron Ionac MA-7500 AEM. The result is compared to the other two experiments using the DuPont Nafion 324 CEM and Sybron Ionac MA-7500 AEM (1 M  $Na_2SO_4$  anolyte solution and  $\frac{1}{2}$  M  $NaHSO_4$  +  $\frac{1}{2}$  M  $Na_2SO_4$  buffered anolyte solution). This comparison is shown in Figure 4.4.1.

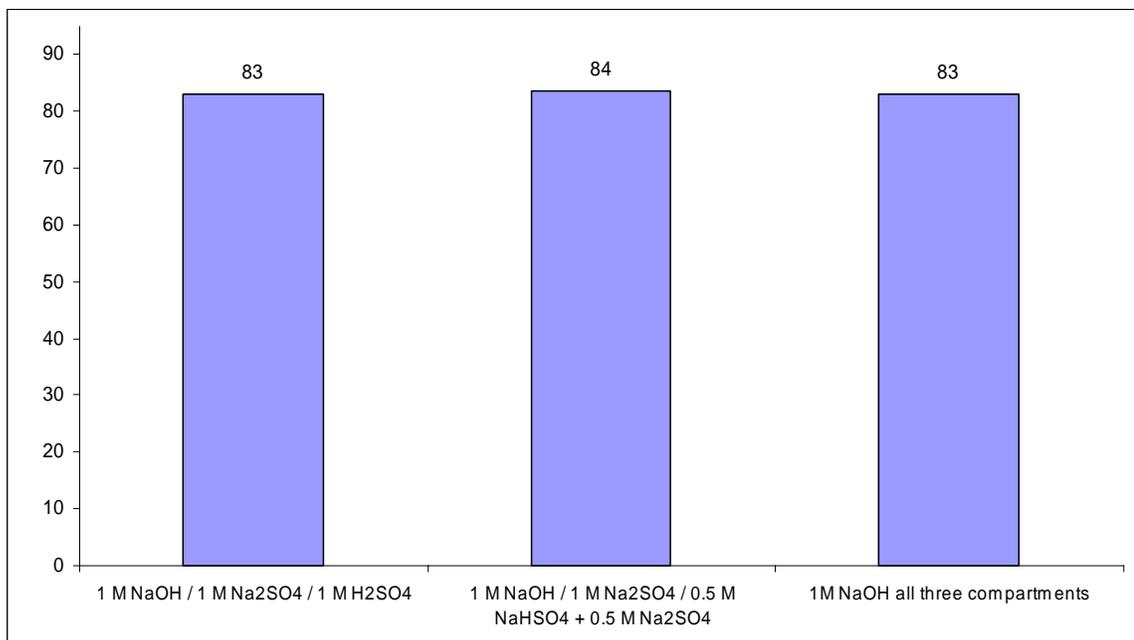


Figure 4.4.1: Cathodic current efficiencies of a 10% electrolysis using a Nafion 324 CEM and Sybron Ionac MA-7500 AEM under various electrolyte compositions.

To further understand the changes in the CEM efficiency from 1 M NaOH catholyte to 5 M NaOH catholyte three additional experiments were conducted. The results are shown in Figure 4.4.2. First, two layers of DuPont Nafion 324 CEM pressed together to simulate a thicker CEM used with a single layer of Sybron Ionac MA-7500 as the AEM. The catholyte, center electrolyte, and anolyte solutions were 5 M NaOH, 1 M Na<sub>2</sub>SO<sub>4</sub>, and ½ M NaHSO<sub>4</sub> + ½ M Na<sub>2</sub>SO<sub>4</sub> respectively.

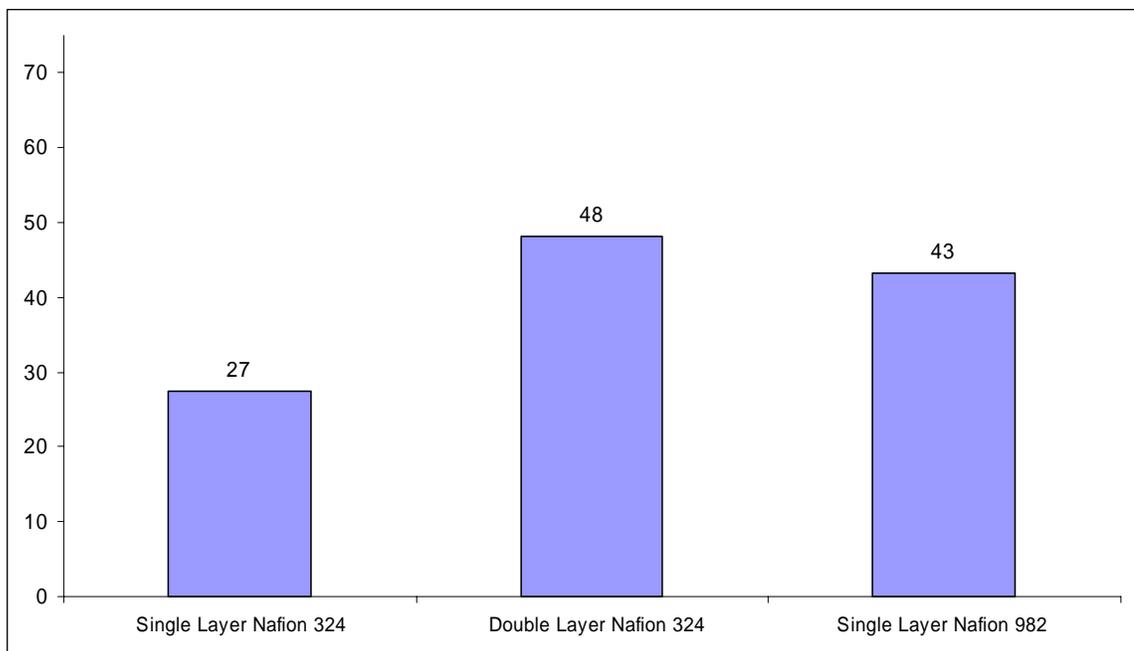


Figure 4.4.2: Cathodic current efficiencies of a 10% electrolysis using 5 M NaOH catholyte and various CEM options.

#### 4.5 Diffusion Only Experiments.

To isolate diffusional effects from migrational effects, the cell was set up as if for an electrolysis experiment (single layer of CEM). However, no current was applied. After 20 minutes (the same time as a 10% electrolysis at 245 mA), the electrolyte from each compartment was analyzed. The first diffusion only test used DuPont Nafion 324 CEM, Electropure Excellion AEM, 1 M NaOH catholyte, 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, and 1 M H<sub>2</sub>SO<sub>4</sub> anolyte. The second diffusion only experiment used DuPont Nafion 324 CEM, Sybron Ionac MA-7500 AEM, 5 M NaOH catholyte, 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, and 0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M NaHSO<sub>4</sub> anolyte. The electrolyte concentration of each compartment at the beginning and end of the experiments is shown in Table 4.5.1.

Table: 4.5.1 Compartment concentrations of diffusion only experiments.

Membranes	Catholyte Compartment		Center Compartment		Anode Compartment	
	t = 0 minutes	t =20 minutes	t = 0 minutes	t =20 minutes	t = 0 minutes	t =20 minutes
DuPont Nafion 324 CEM / Electropure Excellion I-200 AEM	0.988 M	0.988 M	pH = 7.07	pH = 2.18	1.937 M	1.920 M
DuPont Nafion 324 CEM / Sybron Ionac MA-7500 AEM	5.060 M	5.006 M	pH = 6.92	pH = 2.55	pH = 1.94	pH = 1.97

## CHAPTER 5

### DISCUSSION

#### 5.1 AEM and CEM Efficiency at Neutral pH Electrolyte Conditions.

Figure 4.1.1 shows the polytetrafluoroethylene based CEMs (DuPont Nafion 324 and Nafion982) display only slightly better current efficiency than the styrene divinylbenzene based CEMs when electrolyte of neutral pH is used in all three compartments. However, Figure 4.1.2 shows the polytetrafluoroethylene based CEMs display much better current efficiency than the styrene divinylbenzene based CEMs at polarized electrolyte conditions (acidic anolyte, neutral pH center, basic catholyte). A change in membrane current efficiency has accompanied the change in anolyte and catholyte composition. In fact nearly all membrane properties that affect the current efficiency are influenced by the two solutions in contact with the two surfaces.

When electrolyte of neutral pH is used in all compartments the product concentrations after 10% electrolysis are relatively low. The final  $\text{OH}^-$  product concentration ranged from 0.321 M (Electropure Excellion I-100 CEM) to 0.384 M (DuPont Nafion 324 CEM). The titratable  $\text{H}^+$  product ranged from 0.324 M to 0.378 M (Electropure Excellion I-200 AEM). An ion's rate of transport through a membrane by diffusion is proportional to the concentration differential of the ion across the membrane (Fick's first law). The flux of ions through a membrane due to migration is also dependant on the concentration of the ion (Equation 3). Both the diffusional and migrational ionic flux is also related to the diffusion coefficient, which Dammak et al [1] show to be proportional to the ion concentration as well. At the cathode side of the cell the  $\text{OH}^-$  concentration is small so that the rate of transport through the CEM by both migration and diffusion is slow and the product loss is minimal. At the anode side of the

cell, the  $H^+$  created by the oxidation of water combines with the  $SO_4^{2-}$  anion to form  $HSO_4^-$  anion. The free  $H^+$  concentration in the anolyte is less than the  $OH^-$  concentration in the catholyte. Again, the product loss is minimal at this neutral pH electrolytic condition. All of the membranes perform similarly because ion exchange membranes are made to resist co-ion transport by migration and diffusion, phenomena which are minimized by the electrolyte composition. Each membrane has a product concentration limit. At these conditions, the product concentration is so far from the limit of each membrane, that they display similar current efficiency.

Jorissen et al [8] suggest that multivalent ions complicate AEM analysis in a salt-splitting cell because they interact with the ions in solution. The divalent  $SO_4^{2-}$  anion interacts with free  $H^+$  cations in the anolyte or center electrolyte to form the monovalent bisulfate ( $HSO_4^-$ ) anion. Jorissen et al observe that at near neutral conditions in the anode and center compartments, the AEM current efficiency is quite high. This is shown in Figure 4.1.1. Jorissen et al attribute this high anodic current efficiency to the formation of the  $HSO_4^-$  anion. As  $H^+$  is produced in the anode compartment it combines with the  $SO_4^{2-}$  anion to form the  $HSO_4^-$  anion ( $K_{a2} = 1.2 \times 10^{-2}$ ). Now the  $H^+$  cation is not driven toward the cathode compartment by migration because it is part of the  $HSO_4^-$  anion and driven towards the anode. Hasdou et al [7] utilized radiotracer ions and Raman spectroscopy to determine that it is mostly  $HSO_4^-$  anions as opposed to  $SO_4^{2-}$  anions that transfer across the AEM during  $Na_2SO_4$  electrolysis, which supports the claim of Jorissen et al that formation of the monovalent  $HSO_4^-$  anion, from the divalent  $SO_4^{2-}$  anion and  $H^+$  cation, mitigates  $H^+$  losses across the AEM by migration due to the electric field.

## **5.2 AEM and CEM Efficiency at Polarized Electrolyte Conditions.**

However, when the polarized pH electrolytic conditions are used the concentrations of the products are greater so that the effects of migration and diffusion

are greater. Here the product concentration is closer to the limit of each membrane than the previous experiments. The differences in performance capabilities surface at these conditions. The styrene divinylbenzene membranes exhibit lower cathodic current efficiency because  $\text{OH}^-$  anions are crossing the CEMs into the center compartment by diffusion and migration at a faster rate than through the perfluorinated CEMs.

Styrene divinylbenzene based CEMs are more hydrophilic and have higher water content than polytetrafluoroethylene based CEMs. Polytetrafluoroethylene based CEMs have hydrophilic and hydrophobic zones, so their water content is lower. Greater hydrophilicity and water content in a CEM lead to greater accommodation of co-ions, like  $\text{OH}^-$ . The increased presence of  $\text{OH}^-$  within the CEM in turn leads to more extensive back diffusion and migration of  $\text{OH}^-$  anions.

Table 4.1.2 shows the center compartment pH is more acidic when the perfluorinated Nafion CEMs are used (1.83-1.85) as opposed to the styrene divinylbenzene based CEMs (1.94-2.02). The center electrolyte is acidic because  $\text{H}^+$  ions cross the AEM at a faster rate than  $\text{OH}^-$  ions cross the CEM. Because the styrene divinylbenzene CEMs allow faster  $\text{OH}^-$  transport across the CEM into the center compartment than the perfluorinated CEMs, the pH of the center compartment is less acidic. The DuPont Nafion CEMs are better at preventing back diffusion and migration of  $\text{OH}^-$  from the cathode to the center compartment. The result is a lower pH of the center compartment. If a 100% efficient CEM were used in a three-compartment cell, the pH of the center compartment would solely depend on the efficiency of the AEM.

### **5.3 Styrene Divinylbenzene CEM Exchange Capacity vs. Current Efficiency.**

Figure 5.3.1 shows the exchange capacity of a styrene divinylbenzene based membrane does not appear to influence the CEM current efficiency. Little correlation between exchange capacity and current efficiency can be drawn from this data. This is surprising because one would think that the current efficiency would be proportional to the exchange capacity. Since the exchange capacity is a measure of fixed ionic sites and it is the fixed ionic sites that promote counter-ion transport and co-ion rejection; it could be hypothesized that a higher exchange capacity would lead to a more counter-ion to co-ion selective membrane, which would in turn lead to a higher current efficiency. However, styrene divinylbenzene based CEM current efficiency does not improve with exchange capacity.

Still surprising is the membrane with the lowest exchange capacity exhibits the highest current efficiency; which is counterintuitive to what one would expect. Co-ion rejection, and therefore current efficiency, is increased with the concentration of fixed sites per unit volume within the membrane. Therefore one would predict that a membrane with higher exchange capacity will also have a higher concentration of fixed sites per unit volume and exhibit higher current efficiency. However, as stated before, the exchange capacity and concentration of fixed sites per unit volume are not the same. Concentration is based on the number of fixed sites per unit volume of wetted membrane, not weight of dry polymer.

However, exchange capacity is not the single figure of merit when determining the concentration of fixed sites and current efficiency. Other factors, such as water content, also contribute to the concentration of fixed sites and current efficiency. Dammak et al [1] show that the concentration of co-ion within a membrane (therefore indirectly membrane efficiency) depends not only on the concentration of fixed ionic

sites, but also the volume of absorbed electrolyte. Other work states that the volume of a membrane expands when it absorbs aqueous electrolyte and that the degree of expansion depends on the type of polymer, exchange capacity, and composition of the electrolyte [2]. If a membrane expands, the number of fixed sites per unit volume decreases. The authors state that styrene divinylbenzene membranes maintain counter-ion to co-ion selectivity by extensive cross-linking designed to limit water content and membrane swelling. Water content, membrane expansion and concentration of fixed sites are not measured in this work.

The perfluorinated CEMs are not included in this comparison because the nature of the polytetrafluoroethylene polymer is so different from styrene divinylbenzene polymer that a comparison of exchange capacities does not yield useful information concerning a relationship between exchange capacity and current efficiency. In the case of styrene divinylbenzene polymers, the exchange capacity is influenced by the extent of cross-linking and how the fixed ions are introduced to the benzene ring. In the case of perfluorinated membranes, the ion exchange capacity depends on the ratio of substituted (subscript  $m$  in Figure 1.3.2) to un-substituted chains (subscript  $x$ ). Additionally, the DuPont Nafion membranes are non-homogeneous in exchange capacity. They are composite membranes with two layers differing in exchange capacity. The layer containing the lower exchange capacity and greater electrical resistance faces the cathode. This layer provides co-ion rejection. The side with the higher exchange capacity provides the conductivity for the membrane and faces the anode side of the cell.

It is not possible to choose a membrane for salt-splitting based on ion exchange capacity alone. As noted, many other properties such as polymer backbone, water content, and membrane expansion also factor in to membrane performance. Increasing exchange capacity does increase the electrical conductivity of the membrane (lowers the electrical resistance). It is shown in section 5.7 that current efficiency increases with membrane resistance.

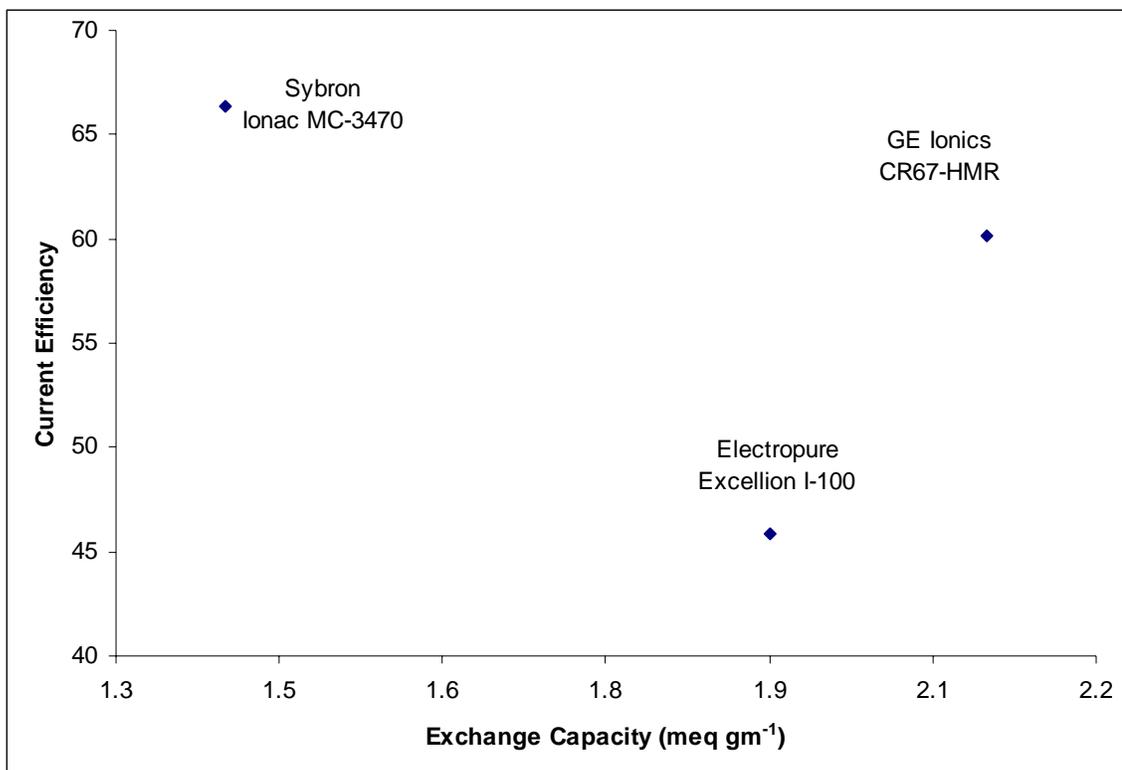


Figure 5.3.1: Styrene divinylbenzene based CEM current efficiency vs. the membrane exchange capacity after a 10% electrolysis using 1 M NaOH catholyte, 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, 1 M H<sub>2</sub>SO<sub>4</sub> anolyte, and Electropure Excellion I-200 AEM.

#### 5.4 DuPont Nafion 324 vs. Nafion 982

DuPont Nafion 324 is chosen over Nafion 982 based on the information given in the DuPont Nafion user's guide and information bulletins [3, 4]. Nafion 300 series membranes are reinforced composites of two sulfonate films that differ in equivalent weight (exchange capacity). The 300 series membranes are used for producing a 12-20% NaOH solution. Nafion 900 series membranes are designed to give optimum performance in the production of Cl<sub>2</sub> and NaOH. They are reinforced composite

membranes, having sulfonate ( $\text{SO}_3^-$ ) and carboxylate ( $\text{COO}^-$ ) polymer layers. The  $\text{SO}_3^-$  and  $\text{COO}^-$  layers refer to the type of fixed anion used to facilitate counter-ion transport and co-ion rejection. The Nafion 982 membrane is used to produce a 32% NaOH solution. The  $\text{COO}^-$  layer has a greater capacity to reject co-ions and deter  $\text{OH}^-$  diffusion across the CEM. However, it is stated that the  $\text{COO}^-$  layer is intolerant to  $\text{SO}_4^{2-}$ . Any ion in solution will be present in the membrane because the hydrophilic zones absorb water and anything dissolved in it.

The DuPont Nafion user's guide and information bulletins [3, 4] define brine impurities as anything in the brine except  $\text{Na}^+$ ,  $\text{Cl}^-$  ions, and water. If the impurities are soluble in the anolyte they will likely pass into the membrane, assisted by the electric field or water flow. These impurities may then precipitate in the membrane at some point as the pH changes from the mildly acidic anolyte (pH 4-5) to the strongly caustic catholyte. If the impurity is only moderately soluble, it can precipitate in the membrane in crystals large enough to disrupt the polymer. This causes a decline in current efficiency. Calcium and sulfate impurities are examples of moderately soluble impurities that crystallize within the membrane. The damage caused by physical disruption of the polymer is irreversible. The user's guide lists that  $\text{SO}_4^{2-}$  concentration in excess of 10 g L<sup>-1</sup> will lead to crystallization and cause a large current efficiency decline. Thus Nafion 324, which has only  $\text{SO}_3^-$  layers, is the CEM of choice for a three compartment  $\text{Na}_2\text{SO}_4$  salt-splitting cell, given this serious limitation to Nafion 982.

### **5.5 Comparing AEMs at Polarized Electrolyte Conditions.**

Since a perfluorinated polymer based AEM does not exist, only styrene divinylbenzene based AEMs could be studied. Figure 4.2.1 shows the current efficiency of the four AEMs tested under polarized pH electrolyte conditions. As discussed earlier the counter-ion to co-ion selectivity of an ion exchange membrane depends on the

concentration of fixed sites per unit volume within the membrane. The Electropure Excellion I-200 AEM has a much lower exchange capacity than the other AEMs. Also, according to the Electropure specifications, the Excellion membranes will expand 15% to 20 % in all directions after preconditioning. Again, the exchange capacity and concentration of fixed sites are not the same. The exchange capacity is based on the number of fixed sites per unit weight of *dry* membrane. Its value is determined by the synthesis procedure and will not change with electrolyte composition. The concentration is based on the number of fixed sites per unit *volume* of membrane. This value changes depending on how much the membrane expands after electrolyte absorption. The degree of membrane expansion will vary with electrolytes of different composition. The Electropure Excellion I-200 AEM has a relatively low number of fixed sites at dry conditions. After swelling 15% to 20% in all dimensions after preconditioning, the concentration of fixed sites decreases. The GE Ionics AR204-SZRA AEM is nearly twice as thick as and has nearly 25 times the exchange capacity as the Electropure Excellion I-200 AEM, yet exhibits the same current efficiency. There are several possible explanations for this. The GE Ionics AR204-SZRA is the most water permeable AEM tested. If water is moving from the anolyte to the center electrolyte then any dissolved ions, including co-ions, will move with it. It is possible that the pore-size of the GE Ionics AR204-SZRA AEM is significantly larger than the other AEMs, facilitating easier  $H^+$  transport to the center. Additionally, the GE Ionics ion exchange membranes are designed for whey processing and not strong acid-strong alkaline production.

The Sybron Ionac AEMs display better current efficiency, even though the exchange capacity of these membranes falls between the other two AEMs. Styrene divinylbenzene membrane swelling has been linked to exchange capacity in the past [2]. Higher exchange capacity lead to greater swelling. Swelling lowers the concentration of fixed sites per unit volume. It is possible that the Sybron Ionac AEMs have an optimal

exchange capacity that limits membrane swelling and preserves a favorable concentration of fixed sites per unit volume.

Figure 5.5.1 shows the AEM current efficiency first increases with exchange capacity then after reaching a maximum, the current efficiency decreases. This seems to support the theory that the Sybron Ionac AEMs possess an optimal exchange capacity to ensure a desirable concentration of fixed sites. However, membrane swelling and concentration of fixed sites were not measured in this work. Again an AEM cannot be selected by exchange capacity alone. Other factors such as thickness, pore-size (which is not measured), and water permeability change from membrane to membrane. These factors also contribute to AEM current efficiency. Section 5.7 shows that the AEM current efficiency depends strongly on the electrical resistance of the membrane.

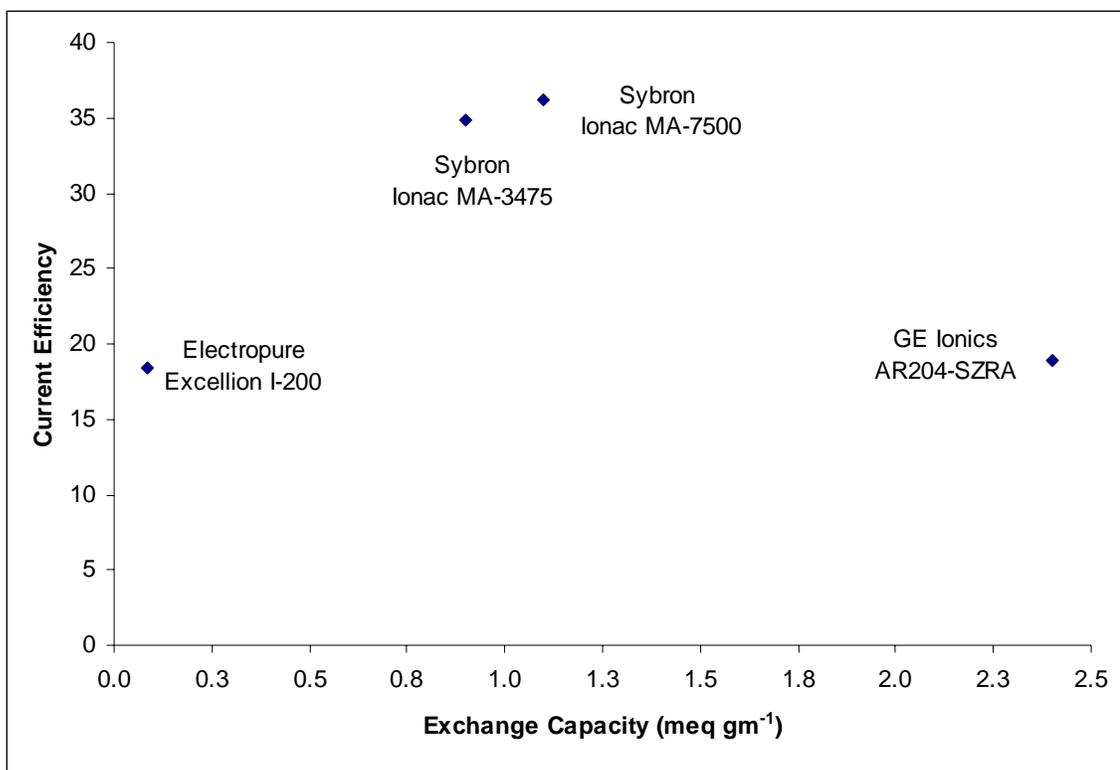


Figure 5.5.1: AEM current efficiency vs. exchange capacity after a 10% electrolysis using 1 M NaOH catholyte, 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, 1 M H<sub>2</sub>SO<sub>4</sub> anolyte, and DuPont Nafion 324 CEM.

The Sybron Ionac MA-7500 is manufactured to perform similarly to the Ionac MA-3475, but with lower electrical resistance (greater conductivity). The increased conductivity results in a lower voltage drop across the membrane, but the Ionac MA-7500 sells for a higher price than its Ionac MA-3475 counterpart. Since it is desirable to lower the cell potential, the Sybron Ionac MA-7500 is chosen as the best AEM for this application.

Table 4.2.2 is interesting in that it too shows that the center compartment pH is determined by the membrane of lowest current efficiency. In each case, the DuPont Nafion 324 CEM is about 85% efficient. In each case the AEM efficiency is much lower. Therefore the center compartment is acidic because H<sup>+</sup> is crossing the AEM at a faster

rate than  $\text{OH}^-$  crosses the CEM. The Electropure Excellion I-200 and GE Ionics AR204-SZRA AEMs exhibit the same current efficiency; as a result the center compartment pH after electrolysis in these experiments is the same. The Sybron Ionac MA-3475 and MA-7500 AEMs also exhibit the same current efficiency; the center compartment pH of these experiments is also the same. The Sybron Ionac AEMs are more efficient; as a result the center compartment is less acidic.

### **5.6 Multivalent Anions and Three-Compartment Salt-Splitting.**

Jorissen et al [8] consider various complications that arise when studying the transport of multivalent anions through AEMs in a three-compartment salt-splitting cell; proposing that multivalent ions may interact with singly charged fixed ionic sites; reducing the effective charge of the membrane. Jorissen et al suggested a divalent  $\text{SO}_4^{2-}$  anion may interact with only one quaternary ammonium fixed singly positive charged. This would reverse the polarity of the membrane at the location of the interaction. The AEM is partially a CEM where the multivalent anion interacts with only one monovalent fixed cation. Jorissen et al tested anions of different valency ( $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}_4^-$ ) and found that a more intense charge of the multivalent anion lead to a greater polarity reversal. The result is a decline in current efficiency. Because the AEM is partially converted to a CEM at the location of the multivalent anion/monovalent fixed cation interaction, co-ions, such as  $\text{H}^+$ , are free to migrate to the center compartment. This may explain why the AEM current efficiency is much lower than the CEM current efficiency at polarized electrolyte conditions.

### **5.7 Electrical Conductivity and Current Efficiency.**

Figure 5.7.1 and Figure 5.7.2 show CEM and AEM efficiency vs. electrical resistance. It appears that the more resistive (less conductive) membranes exhibit higher current efficiency. Higher current efficiency indicates better counter-ion to co-ion

selectivity. Dammak et al [1] indicate that both counter-ion and co-ion diffusion coefficients increase with conductivity (decrease with resistance). Also, that the co-ion diffusion coefficient has a greater dependency on conductivity than the counter-ion diffusion coefficient. Therefore if a membrane resistivity is increased, the co-ion diffusion coefficient decreases more than the counter-ion diffusion coefficient and the counter-ion to co-ion selectivity increases. This does not mean that an infinitely resistive membrane will result in 100% current efficiency. In such a case no current would flow and no ions would permeate the membrane; therefore electrolysis could not occur. It is likely that as the resistivity of the membrane increases, the counter-ion to co-ion selectivity increases and in turn the current efficiency increases until a point where the membrane becomes so resistive that it impedes the movement of all ions at this point the current efficiency will decrease.

The polytetrafluoroethylene based CEMs are not included in this comparison because they are non-homogeneous in electrical resistance as well as exchange capacity. The DuPont Nafion membranes are composed of two layers that differ in exchange capacity and electrical conductivity. Interestingly, the more resistive layer of DuPont Nafion 324 faces the cathode because it provides better co-ion rejection. This supports the idea that resistivity improves counter-ion to co-ion selectivity.

However, a membrane should not be selected for a salt-splitting cell based on electrical resistance alone. The Sybron Ionac MA-7500 performs similarly to its counterpart, Ionac MA-3475. Yet the Sybron Ionac MA-7500 has a much lower electrical resistance. Membranes are continuously being improved to offer high counter-ion to co-ion selectivity at low electrical resistance. Composite membranes such as DuPont Nafion 300 series utilize two layers differing in ion exchange capacity and electrical resistance to optimize co-ion rejection and potential drop across the membrane respectively. Factors other than ion exchange capacity and electrical resistance, such as chemical stability and should be considered as well.

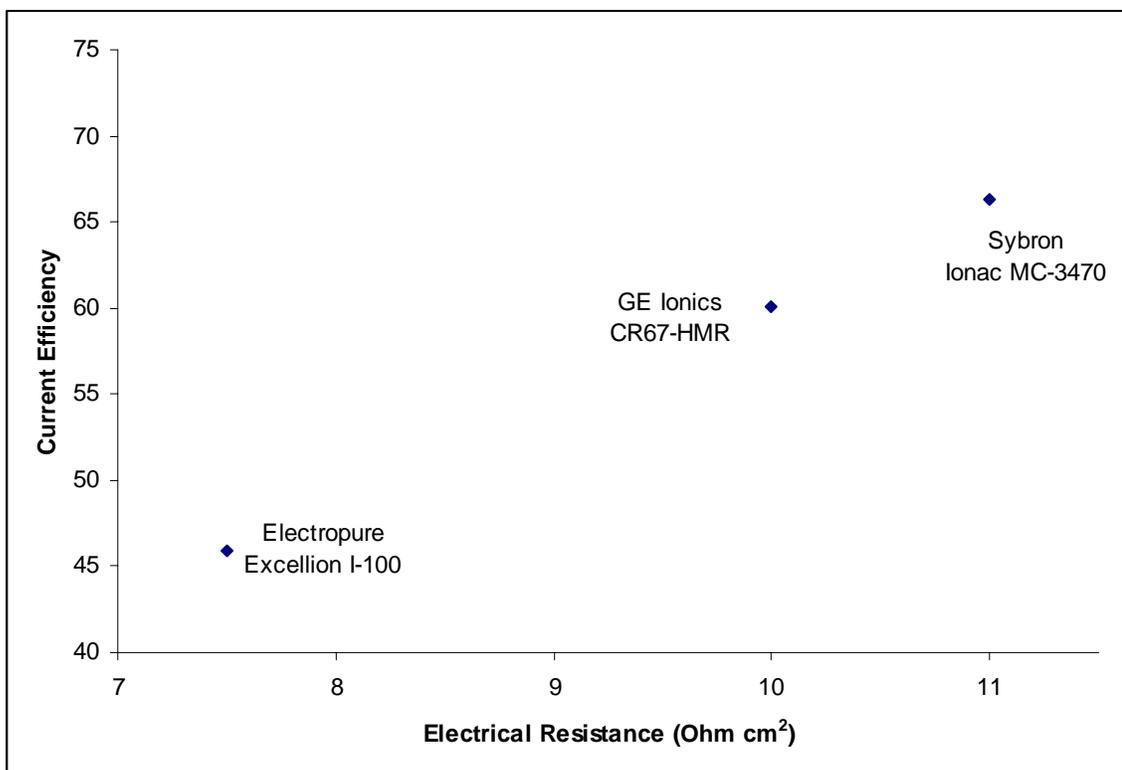


Figure 5.7.1: Styrene divinylbenzene based CEM current efficiency vs. membrane electrical resistance after a 10% electrolysis using 1 M NaOH catholyte, 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, 1 M H<sub>2</sub>SO<sub>4</sub> anolyte, and Electropure Excellion I-200 AEM.

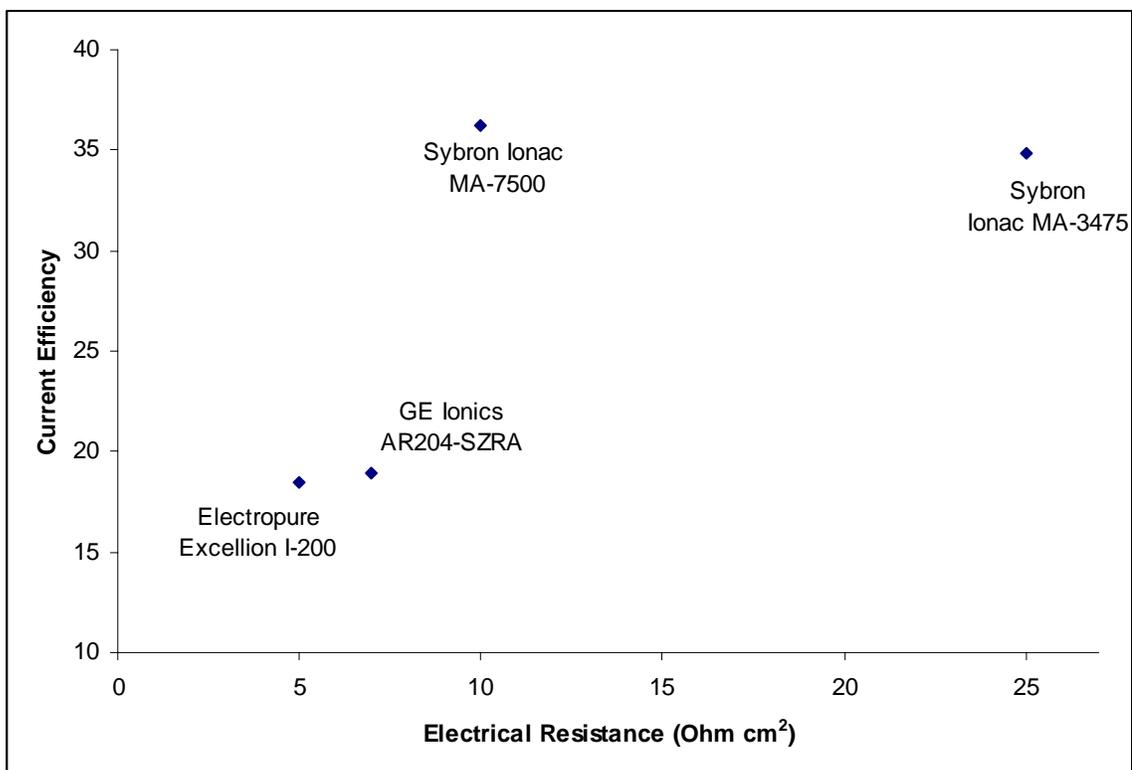


Figure 5.7.2: AEM efficiency vs. membrane electrical resistance after a 10% electrolysis using 1 M NaOH catholyte, 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte, 1 M H<sub>2</sub>SO<sub>4</sub> anolyte, and DuPont Nafion 324 CEM.

### 5.8 Alkaline Electrolyte in All Compartments

Section 4.4 describes the possible sources of CEM inefficiency. It also describes how changing the anolyte composition is used to determine which possibility is the most dominant. Figure 4.4.1 compares the effects of anolyte composition on cell performance. The first two experiments use a 1 M NaOH catholyte and 1 M Na<sub>2</sub>SO<sub>4</sub> center electrolyte. The first data point uses a strongly acidic anolyte (1 M H<sub>2</sub>SO<sub>4</sub>). The second uses a buffered anolyte (0.5 M Na<sub>2</sub>SO<sub>4</sub> + 0.5 M NaHSO<sub>4</sub>). The third experiment uses an alkaline electrolyte (1 M NaOH) in all three compartments. This comparison is made to determine the chief source of OH<sup>-</sup> product loss at cathode.

By changing the anolyte and center electrolyte compositions, the possibility of proton migration from the anode into the cathode compartment is ruled out. Because the electrolyte of each compartment is alkaline, protons are almost nonexistent. The diminution of protons from the center compartment does not result in an increase of CEM efficiency for a 1 M NaOH product; therefore destruction of OH<sup>-</sup> product by neutralization- reaction is ruled out.

For a 1 M NaOH product, diffusion of OH<sup>-</sup> from the cathode to the center does not seem to be the major source of inefficiency. When a 1 M NaOH electrolyte is used in all compartments, the OH<sup>-</sup> concentration gradient across the CEM (the driving force for diffusion) is greatly diminished. In this case the CEM efficiency does not increase. This rules out diffusion as the dominant source of OH<sup>-</sup> loss in the case of a 1 M NaOH product. Migration of OH<sup>-</sup> through the CEM, toward the anode is the only remaining possibility. The DuPont Nafion 324 is less than 100% selective when using both 1 M Na<sub>2</sub>SO<sub>4</sub> and 1 M NaOH catholyte solutions because the electric field causes OH<sup>-</sup> anions to back migrate across the CEM. In the case of 1 M NaOH catholyte, it appears that back diffusion of OH<sup>-</sup> anions is not a significant factor in the CEMs' current efficiency.

Another interesting result of using 1 M NaOH electrolyte in all three compartments is the destruction of the AEM. An inefficient CEM results in movement of OH<sup>-</sup> to the center compartment. The center compartment becomes alkaline. High pH causes problems for AEMs, which are less stable under alkaline conditions. Figure 5.8.1 shows the degradation of the AEM after this experiment. Initially, the membrane is cream-colored. The dark circle in the center of the membrane is the portion that was in contact with the 1 M NaOH solution. Before throwing this degraded membrane away, it was soaked in a 0.1 M NaOH solution. The entire membrane slowly changed to the dark color. This supports Martin's statement that pH control of the center compartment is necessary to protect the life of one or both membranes.

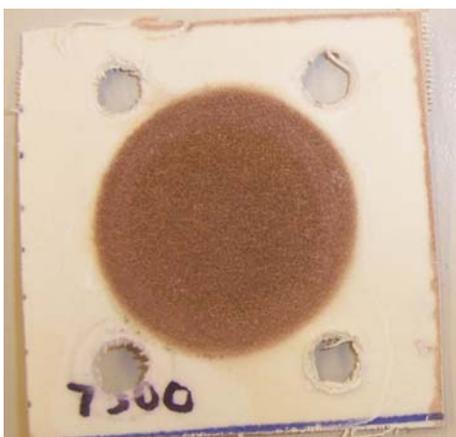


Figure 5.8.1: Sybron Ionac MA-7500 AEM after electrolysis using 1 M NaOH in all three compartments.

### **5.9 Cell Performance at High NaOH Product Concentration.**

The use of alkaline electrolyte in all three compartments proved that at 1 M NaOH product the current efficiency is limited by back migration of  $\text{OH}^-$  (the system is migration controlled). However, the fact that diffusional losses are insignificant at 1 M NaOH product concentration does not explain the increased product loss with increasing product concentration shown in Figure 4.3.1. The cell potential is always between 5.5 and 6 volts for all catholyte compositions between 1 M and 5 M NaOH. Since the cell voltage, and therefore the strength of the electric field, is similar in all the experiments; the  $\text{OH}^-$  losses due to migration are similar. Yet CEM selectivity decreases with NaOH concentration. This indicates that as the NaOH concentration increases, the role of diffusion increases as well.

To test whether the system is diffusion controlled or migration controlled at 5 M NaOH concentration, two layers of CEM are pressed together to simulate a membrane that is twice as thick. When two layers of CEM are used, diffusion is mitigated by the increased thickness of the barrier, therefore the current efficiency increases.

Because the same charge is passed in both the single layer and double layer experiments, the same amount of  $\text{OH}^-$  anions is created in the anode compartment by the electrochemical reduction of water. To maintain charge neutrality, one of two events must occur. Either an amount of  $\text{OH}^-$  equivalent to the single layer experiment must cross to the center compartment; which means the final NaOH product concentration, cathodic current efficiency, and CEM cation to anion selectivity remain the same. This situation would correspond to migrational control. Alternatively, an amount of  $\text{OH}^-$  less than that of the single layer experiment crosses to the center compartment. In this case a greater amount of  $\text{Na}^+$  than the single layer experiment must cross into cathode compartment; which means the final NaOH product concentration, cathodic current efficiency, and CEM cation to anion selectivity increases. This situation corresponds to diffusional control.

With diffusion controlled systems, the ratio of  $\text{Na}^+$  to  $\text{OH}^-$  ions that cross the CEM is increased with membrane thickness (given that the concentration differential remains the same in the two experiments). With migration controlled systems, the ratio of  $\text{Na}^+$  to  $\text{OH}^-$  ions that cross the CEM is increased only if the ratio of  $\Delta E_{\text{CEM}} / \delta_{\text{CEM}}$  is increased.

When using two membranes the cell potential increases from 6 volts to about 6.5 volts and the current efficiency increases from 27% to 48%. The ratio of  $\Delta E_{\text{CEM}} / \delta_{\text{CEM}}$  remains the same in the two experiments and the current efficiency increases. Therefore the system is not migration controlled. The  $\text{OH}^-$  concentration differential remains the same in the two experiments and the current efficiency increases with membrane thickness. This indicates that at 5 M NaOH product concentration the system is diffusion controlled.

### 5.10 Diffusion Only Experiments.

The above results suggest that the role of diffusion has increased significantly from 1 M to 5 M NaOH product concentration. The CEM current efficiency is migration limited in the case of 1 M NaOH product. The CEM current efficiency is diffusion limited in the case of 5 M NaOH product. It is reasonable to expect that diffusion and migration contribute equally at some intermediate product concentration.

Table 4.5.1 shows the electrolyte concentration of each compartment for two diffusion only experiments. When a 1 M OH<sup>-</sup> concentration differential is used no change in catholyte concentration is observed; the rate of diffusion is very slow. However, when a 5 M OH<sup>-</sup> concentration differential is examined, the OH<sup>-</sup> concentration in the catholyte dropped from 5.06 M to 5.01 M. This loss corresponds to about 20% of the total loss in the analogous electrolysis experiment. Although the losses are migration-dominant, the system is diffusion controlled.

As the OH<sup>-</sup> concentration differential is increased from 1 M to 5 M, the driving force for Fickian diffusion is increased and diffusion occurs more rapidly. In addition, the properties of the membrane, such as electrolyte absorption, change with the nature of the electrolyte in contact with the membrane. These properties are changing in a way that more readily facilitates diffusion of co-ions.

In all of the electrolysis experiments shown in Figure 4.3.1 the cell potential is between 5.5 and 6 volts. Therefore the driving force of migration,  $d\phi/dx$ , does not change significantly. However, the rate of loss due to migration still increases with product concentration. Equation 3 (section 1.2) shows that the migrational flux of an ion is dependent on that ion's concentration in the solution. Yet the double thickness and diffusion only experiments show that the rate of diffusional losses increases more with product concentration than migrational losses.

### 5.11 Comparing This Cell with Other Salt-Splitting Cells.

Millington [12] claims that a significant amount of acid crosses the AEM and the  $H^+$  migrates into the cathode neutralizing the  $OH^-$  product. Yet this work claims that it is the back diffusion and migration of  $OH^-$  from the cathode compartment into the center compartment that is the chief source of  $OH^-$  product loss. This discrepancy is explained by Jorissen and Simmrock [9], who use a two-compartment cell, similar to one used by Paleologou et al [13], to explain the current efficiency losses with respect to the nature of the electrolyte solutions in contact with the membrane surfaces. At high NaOH concentration in the catholyte and low  $H^+$  concentration in the anolyte losses in the CEM current efficiency are caused by migration of  $OH^-$  ions. Like the current efficiency of CEMs for chlor-alkali electrolysis, improvement can only be made by suppression of  $OH^-$  ion migration (this is done by increasing the counter-ion to co-ion selectivity of the CEM, which is dependent on the concentration of fixed ionic sites).

In such a case, the membrane is said to be in an alkaline state. Hydroxide ions are present through the entire thickness of the membrane and an alkaline boundary layer is developed on the anode surface of the membrane. The presence of the said anode side alkaline boundary layer is supported by their results using an insufficiently pure anolyte, acid soluble earth alkaline hydroxides precipitate on the membrane surface on the anode side.

CEMs in the alkaline state are not influenced by the acid concentration of the solution on the anode side of the membrane. The  $H^+$  ions are already neutralized by the alkaline boundary layer. Therefore any change of  $H^+$  ion concentration in the anolyte will not change the current efficiency of the CEM as long as the membrane remains in the alkaline form. Table 4.2.2 shows that the CEM current efficiency is not affected by the pH of the center compartment. When the less efficient AEMs are used the pH of the center compartment is lower, yet the DuPont Nafion 324 CEM current efficiency is

unaffected. Table 4.3.1 shows that the pH of the center compartment increases as the back diffusion and migration of  $\text{OH}^-$  across the CEM increases; therefore the CEM must be in the alkaline state to lower the acidity of the center compartment.

However if the conditions change such that the  $\text{H}^+$  concentration in the anode compartment is significantly higher than the  $\text{OH}^-$  concentration in the cathode the membrane will cease to be in the alkaline state. More  $\text{H}^+$  ions migrate from the anolyte to the boundary later of the membrane than  $\text{OH}^-$  ions arrive at the boundary layer through the membrane from the catholyte. Under these circumstances the alkaline boundary layer disappears. Now, the  $\text{H}^+$  ions migrate through the membrane to the catholyte and form an acid boundary layer at the cathode side of the CEM. The membrane is now in the acidic state. When the membrane is in this state, the  $\text{OH}^-$  concentration has no influence on the CEM current efficiency because the  $\text{OH}^-$  ions are neutralized in the acid boundary layer.

This theory explains the change in gradient of the current efficiency function with increasing  $\text{H}^+$  concentration noted by Paleologou et al [13]. It also explains Millington's theory that  $\text{H}^+$  and not  $\text{Na}^+$  carries the bulk of the current across the CEM. When state of the membrane changes from the alkaline to the acidic, the mechanism for inefficiency changes from co-ion back migration to neutralization by forward migration of  $\text{H}^+$ .

The presence of co-ions ( $\text{OH}^-$ ) transfers the CEM into the alkaline state. Transport of  $\text{OH}^-$  ions through the alkaline state CEM is influenced only by the  $\text{OH}^-$  concentration in cathode compartment. As long as the membrane state does not change, the composition of the solution on the opposite side of the CEM has no influence on the CEM current efficiency (Table 4.3.1).

However, if the CEM turns over into the acidic state, the ion transport which decreases the current efficiency is not caused by the  $\text{OH}^-$  co-ion. In the acidic state of the CEM, migration of  $\text{OH}^-$  is repressed by the fixed ionic sites of the membrane, but additional counter-ions (i.e.  $\text{H}^+$  ions) in the CEM are mobile with respect to the required

function of the membrane. That is to say, when the CEM has entered the acidic state the transport of  $H^+$  cannot be prevented by increasing the selectivity. A transition from the alkaline state into the acid state implies a fundamental change of the transport mechanism within the membrane.

This is the phenomena occurring in the experiment described by Paleologou et al [13] where the production of NaOH is held at a steady-state concentration of 1.04 M and the  $H^+$  concentration is allowed to build in the batch mode anode compartment. As the  $H^+$  concentration builds from 0.3 M to 0.7 M, the current efficiency for NaOH production does not change. Here the CEM is in the alkaline state. In the alkaline state the  $H^+$  concentration in the anode compartment does not influence the current efficiency. Only the  $OH^-$  concentration in the cathode compartment influences the current efficiency of a CEM in the alkaline state. Since the NaOH concentration in the cathode compartment is held constant at 1.04 M the current efficiency remains steady at 78%. As the  $H^+$  concentration increases from 0.7 M to 1.5 M, the CEM current efficiency falls from 78% to 10%. Here the CEM turns from the alkaline state to the acidic state. In the acidic state the  $OH^-$  concentration in the cathode compartment no longer influences the CEM current efficiency. The current efficiency of a CEM in the acidic state is determined by the  $H^+$  to  $Na^+$  ratio in the anode compartment. As the  $H^+$  to  $Na^+$  ratio increases, the current efficiency decreases.

Jorissen and Simmrock also note that increasing the selectivity of a CEM will not improve the performance of the cell if the CEM is in the acidic state. Because  $H^+$ , like  $Na^+$ , is a counter-ion it will readily transport across the CEM. This is important for determining optimal operating conditions of a salt-splitting cell. To optimize the NaOH product concentration, the solution on the anode side of the CEM must remain at a high enough pH to prevent the CEM from entering the acidic state and the formation of the acidic boundary layer at the cathode side of the CEM. As long as the CEM is in the alkaline state, there will be a trade off between current efficiency and product

concentration. In the alkaline state current efficiency losses are dependent on the co-ion ( $\text{OH}^-$ ) concentration in the cathode alone. Unless a membrane can be created that maintains a high selectivity at large  $\text{OH}^-$  concentration gradients this trade off will continue to exist.

However trade off between current efficiency and NaOH product concentration can be mitigated by increasing the thickness of the CEM as shown in Figure 4.4.2. Yet, this solution creates another trade off. When the thickness of the membrane is increased, so is the overall cell voltage. The new trade off becomes higher product concentration and current efficiency with high cell potential or lower product concentration and current efficiency with lower cell potential.

### **5.12 Comparing This Cell to the Chlor-Alkali Process.**

DuPont Nafion 982 CEM was tested in a 10% electrolysis experiment using 5 M NaOH catholyte, 1 M  $\text{Na}_2\text{SO}_4$  center electrolyte, and  $\frac{1}{2}$  M  $\text{NaHSO}_4$  +  $\frac{1}{2}$  M  $\text{Na}_2\text{SO}_4$  buffered anolyte solutions. The CEM current efficiency is 43%. DuPont Nafion 900 series CEMs are used in the chlor-alkali industry, where the current efficiency is near 90%

DuPont specifies that the  $\text{SO}_4^{2-}$  concentration should not exceed 4 g/L when using the Nafion 982 CEM [3, 4]. T. Davis et al [2] offer an additional explanation of the current efficiency decline. This bi-layer membrane was designed for use in a traditional chlor-alkali application. In a traditional chlor-alkali cell there are two compartments. The cathode compartment is a 32% (wt/wt) NaOH solution and the anode compartment a neutral to slightly acidic NaCl solution. The anode compartment does not contain  $\text{SO}_4^{2-}$  ions nor does it become strongly acidic.

T. Davis et al suggest that to maintain ionic conductivity in the membrane, the carboxylic acid fixed sites must not become protonated ( $\text{COO}^- + \text{H}^+ \rightarrow \text{COOH}$ ). Since these weak acid ion exchange groups have a  $\text{pK}_a$  of 2-3, the pH in the central

compartment cannot be such that a significant portion of charge is carried by  $H^+$  rather than  $Na^+$ . If the central compartment does become acidic, then only the sulfonic acid fixed sites are used. This limits the NaOH concentration that can be achieved at good current efficiency to 15-20% (wt/wt).

Jorissen and Simmrock [9] also state that DuPont Nafion 900 series CEMs cannot be used in  $Na_2SO_4$  electrolysis. Because DuPont Nafion 900 series membranes have a rather small permeability for  $OH^-$  ions, a low acid concentration at the anode side of the membrane is sufficient to shift the CEM into the acid state. Additionally the 900 series'  $COO^-$  fixed ionic sites are weak acids and dissociate only in the alkaline state of the membrane. In the acid state there are insufficient freely mobile counter-ions. That is in the acid state the  $COO^-$  fixed sites have become protonated to form  $COOH$ . Once this occurs, this layer of the membrane is no longer counter-ion conductive. As a result the voltage drop in the membrane increases. This is another reason to control the pH of the center compartment.

However, the explanation that  $H^+$  is carrying a significant portion of the charge and protonating the carboxylic acid sites is contradictory to the results of this work. The center compartment is only slightly acidic; the number of  $Na^+$  ions is far greater than the number of  $H^+$  ions. The bulk of charge is carried across the CEM by  $Na^+$  and  $OH^-$  ions. The pH of the center compartment is about the same in both the 1 M NaOH and 5 M NaOH experiments. The current efficiency decreases from the 1 M NaOH case to the 5 M NaOH case and  $H^+$  is not carrying a significant fraction of the total charge. Therefore it must be  $Na^+$  carrying less of the total charge across the CEM in the 5 M NaOH case and  $OH^-$  carrying more. It is highly unlikely that the  $COO^-$  sites have been protonated in this work.

Additionally, DuPont specifies [3, 4] that the Nafion CEMs should be operated at a current density between 150 and 600  $mA\ cm^{-2}$ . Above the maximum current density physical damage occurs and current efficiency is lost. Below the minimum current

density, the membrane will not be harmed but the current efficiency will decline. This cell was operated at approximately  $50 \text{ mA cm}^{-2}$ , which is the maximum current density of the AEMs tested. Above  $50 \text{ mA cm}^{-2}$ , the AEM will suffer irreversible physical damage. It is possible that a conical cell geometry that allows the AEM to operate at  $50 \text{ mA cm}^{-2}$  and the DuPont Nafion 982 to operate within current density specifications would result in higher CEM current efficiency and stronger NaOH product concentration without damaging the AEM.

Cell geometry is the reason that the chlor-alkali process operates at a lower cell potential (3 volts) than this salt-splitting device (6 volts). This cell has a 1.2 cm gap between a membrane and electrode and measures 5.08 cm from electrode to electrode. The chlor-alkali process uses at most a 3 mm gap. The result of a smaller gap is a lower iR drop and a more cost effective reactor.

Table 4.3.2 shows the calculated voltage portioning across the cell. The calculated cell potential is within the range of measured cell potentials. A significant portion of the calculated cell voltage is that of the solution resistance. Reducing the cell thickness would reduce the fraction of the cell voltage from solution resistance. However, it is likely that the voltage drops across the ion exchange membranes contribute more to the total than calculated. This is because the voltage drops across the membranes are calculated from the area resistances given by the manufacturers and the current passing through the cell. The area resistances given by the manufacturers are measured in NaCl solutions of various concentrations. Membrane conductivity, like other membrane properties, depends on the composition of the electrolyte solutions in contact with the two surfaces. Nonetheless, improvements to cell geometry would lower the overall cell potential.

### 5.13 The Cost of Making NaOH with the Three-Compartment Salt-Splitting Cell.

One dry ton of  $\text{Na}_2\text{SO}_4$  contains 12,774 moles of  $\text{Na}^+$ . To produce 12,774 moles (approximately 0.56 dry tons) of NaOH,  $1.23 \times 10^{+9}$  Coulombs of charge are required. If the cell operates at 6 volts and the CEM current efficiency is 100%, the energy required is 2,054 kWhr. At this time the cell produces a 5 M NaOH solution at 27% current efficiency with a single layer of CEM and 48% current efficiency with a double layer of CEM. At 50% CEM current efficiency the charge requirement doubles to  $2.46 \times 10^{+9}$  Coulombs.

If electricity is purchased at  $\$.05 \text{ kWhr}^{-1}$ , then it will cost approximately \$183 to produce one dry ton of NaOH at 100% CEM current efficiency or \$365 at 50% CEM current efficiency. The 5 M NaOH solution will be evaporated to approximately 8 M. This would increase the cost by  $\$67 \text{ dry-ton}^{-1}$ . The cost becomes \$250 per dry ton of NaOH at 100% CEM current efficiency and \$432 per dry ton of NaOH at 50% CEM current efficiency. These calculations do not include the cost of equipment and labor. In 2005 the cost of NaOH was about \$400 per dry ton. However, this figure likely includes the cost of equipment and labor.

Modification of cell geometry would improve the cell performance by lowering the cell potential and possibly improving the current efficiency as DuPont Nafion CEMs exhibit better current efficiency at higher current densities than tested in this work. Thinner cell geometry would reduce the  $iR$  drop and lower the cell potential. A conical design would possibly improve the current efficiency. If the AEM is larger than the CEM the current density of the AEM would be lower. DuPont Nafion CEM would operate at  $150 \text{ mA cm}^{-2}$  and the AEM would operate at  $50 \text{ mA cm}^{-2}$ . The AEM would be protected from operating above the maximum current density and the CEM would operate at a much more efficient current density. Such modifications would increase the economic value of the cell.

Yet even if the cost of producing NaOH with a Na<sub>2</sub>SO<sub>4</sub> salt-splitting cell is greater than the purchasing price of NaOH from a chlor-alkali plant, it is still to a pulp mill's advantage to use the salt-splitting process. Salt-splitting would eliminate the sewerage of Na<sub>2</sub>SO<sub>4</sub> into rivers reducing environmental pollution.

## CHAPTER 6

### MODELING OF SALT-SPLITTING CELLS

#### 6.1 Batch Operation Cell

An analytical model of salt-splitting cell would help predict which operating conditions yield desired concentrations of NaOH at acceptable current efficiencies, given specific membrane properties.

The first model is written for a laboratory scale, batch operation, salt-splitting cell. This is a transient model and focuses only on the cathode side of the cell. The model is a simplified material balance of OH<sup>-</sup> ions. The control volume is the CEM. The accumulation of OH<sup>-</sup> ions on the cathode side of the CEM is equal to the rate at which the ions are generated by the electrolysis reaction minus the rate at which the ions are lost to the center compartment by diffusion and migration. Figure 6.1.1 shows the control volume and the production and loss methods of OH<sup>-</sup>. The symbols used in this model are defined in the List of Symbols on page *x*.

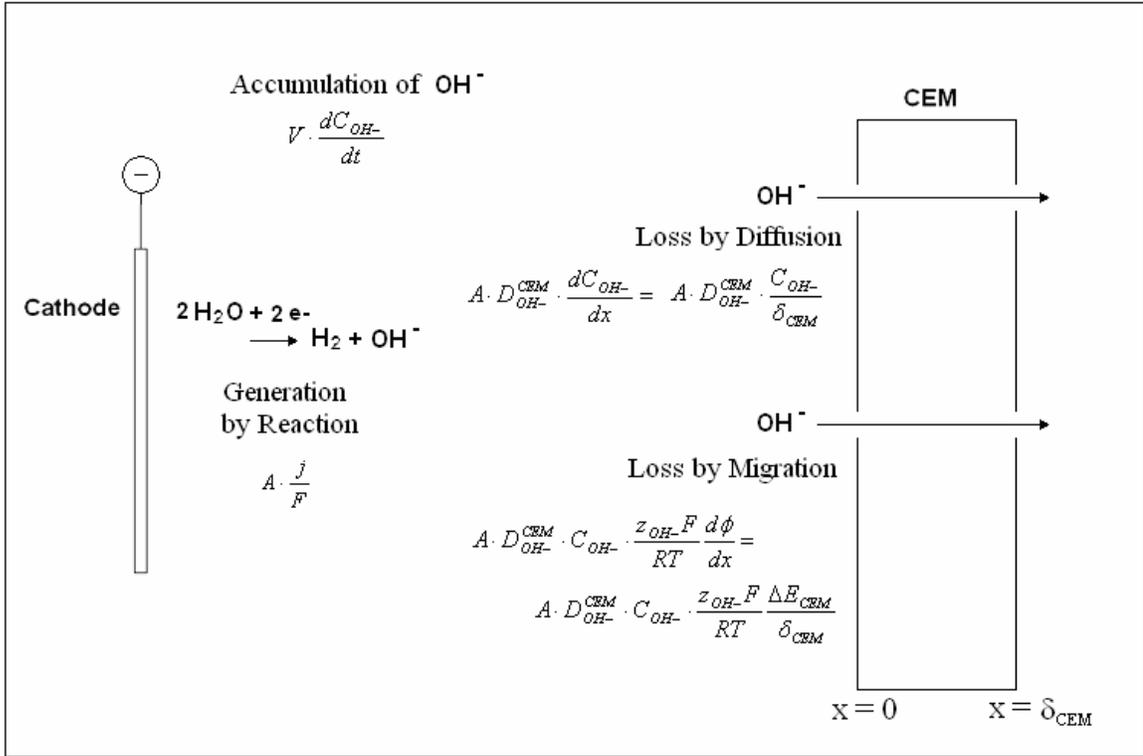


Figure 6.1.1: Transient material balance of  $\text{OH}^-$  ions in the cathode compartment.

The rate of accumulation of  $\text{OH}^-$  anions in the catholyte is given by Equation 7.

$$V \cdot \frac{dC_{\text{OH}^-}}{dt} = \text{Rate of OH}^- \text{ Accumulation}$$

Equation 7: Rate of accumulation of  $\text{OH}^-$  ions in the cathode compartment

The loss of  $\text{OH}^-$  by diffusion is given by Fick's first law, Equation 1 (section 1.2), and is simplified in Equation 8. The electrolyte solutions are assumed to be well mixed so that at  $x = 0$  the  $\text{OH}^-$  concentration is equal to that of the bulk concentration of the catholyte. At  $x = \delta$ , the concentration is equal to that of the bulk concentration of the center electrolyte. Since the center compartment is generally acidic, the concentration of  $\text{OH}^-$  in the center compartment,  $(C_{\text{OH}^-}^{\text{Center}})$  is conservatively taken to be zero for added simplicity.

$$J_{OH}^{Diffusion} = A \cdot D_{OH^-}^{CEM} \cdot \frac{dC_{OH^-}}{dx} = A \cdot D_{OH^-}^{CEM} \cdot \frac{C_{OH^-} - C_{OH^-}^{Center}}{\delta_{CEM}} = A \cdot D_{OH^-}^{CEM} \cdot \frac{C_{OH^-}}{\delta_{CEM}}$$

Equation 8: Loss of OH<sup>-</sup> ions from the cathode compartment by Fickian diffusion.

As the concentration differential across the membrane increases the rate of loss by diffusion increases as well. Additionally, increasing the thickness of the membrane will decrease the rate of diffusional losses. However, it does not express the fact that the potential needed to drive the same current increases when the membrane thickness is increased, which is described by migration.

The migrational flux or loss of OH<sup>-</sup> by migration due to the electric field is given by Equation 3 (section 1.2) and is simplified in Equation 9. The potential gradient across the control volume ( $d\phi/dx$ ) is simplified to the voltage drop across the CEM over the CEM thickness ( $\Delta E_{CEM}/\delta_{CEM}$ ). Increasing  $\Delta E_{CEM}$  increases the rate of migrational loss of OH<sup>-</sup> through the CEM. However, increasing  $\Delta E_{CEM}$  also increases the rate of migration of Na<sup>+</sup> cations into the cathode compartment, which is the desired ion migration. According to Ohm's law ( $V = i \times R$ ), increasing the cell potential,  $V$ , also increases the electric current,  $i$ , which in turn increases the rate of OH<sup>-</sup> generation by water reduction,  $i/F$ .

$$J_{OH}^{Migration} = A \cdot D_{OH^-}^{CEM} \cdot C_{OH^-} \cdot \frac{z_{OH^-} F}{RT} \frac{d\phi}{dx} = A \cdot D_{OH^-}^{CEM} \cdot C_{OH^-} \cdot \frac{z_{OH^-} F}{RT} \frac{\Delta E_{CEM}}{\delta_{CEM}}$$

Equation 9: Loss of OH<sup>-</sup> ions from the cathode compartment by migration

The rate of generation of the OH<sup>-</sup> ions by the electrochemical reduction of water is given by Equation 10. It is written in terms of the current density ( $j$ ) of the membrane. That is the quotient of the electric current over the membrane surface area. When

working with this model, it is imperative that the current density ( $j$ ) and the control volume potential ( $\Delta E_{CEM}$ ) be coupled. When one changes the other is directly affected. A simple way to couple the two variables is to set the membrane potential equal to the product of the current density and the membrane area resistance ( $\Delta E_{CEM} = j \times R_A$ ). However, the area resistance of the membrane will change with the composition of the electrolytes in contact with the two surfaces.

$$A \cdot \frac{j}{F} = \text{Rate of OH}^- \text{ generation}$$

Equation 10: Rate of generation of OH<sup>-</sup> ions by the electrochemical reduction of water

The rate of OH<sup>-</sup> accumulation is equal to the rate of generation minus the rate of diffusional and migrational loss. Equation 11 is the complete OH<sup>-</sup> material balance.

$$V \cdot \frac{dC_{OH^-}}{dt} = -A \cdot D_{OH^-}^{CEM} \cdot \frac{C_{OH^-}}{\delta_{CEM}} - A \cdot D_{OH^-}^{CEM} \cdot C_{OH^-} \cdot \frac{z_{OH^-} F}{RT} \frac{\Delta E_{CEM}}{\delta_{CEM}} + A \cdot \frac{j}{F}$$

Equation 11: Material balance of OH<sup>-</sup> ions in the cathode compartment of a batch operation salt-splitting cell

Rearranging the material balance yields a standard form first order linear differential equation given by Equation 12.

$$\frac{dC_{OH^-}}{dt} + \frac{A}{V} \cdot \frac{D_{OH^-}^{CEM}}{\delta_{CEM}} \left( 1 + \frac{z_{OH^-} F}{RT} \cdot \Delta E_{CEM} \right) \cdot C_{OH^-} = \frac{A}{V} \cdot \frac{j}{F}$$

Equation 12: Standard form material balance of OH<sup>-</sup> ions in the cathode compartment of a batch operation salt-splitting cell

Integrating this differential equation will result in the concentration of OH<sup>-</sup> ions as a function of time, current density, and various membrane properties. The initial condition necessary to find an analytical solution to this differential equation is that at time  $t = 0$ , the bulk OH<sup>-</sup> concentration is equal to a specified value,  $C_{OH^-}^{t=0}$ . The result is given by Equation 13.

$$C_{OH^-} = C_{OH^-}^{t=0} \cdot \exp(-pt) + \frac{q}{p} \cdot (1 - \exp(-pt))$$

$$q = \frac{A}{V} \cdot \frac{j}{F}$$

$$p = \frac{A}{V} \cdot \frac{D_{OH^-}^{CEM}}{\delta_{CEM}} \left( 1 + \frac{z_{OH^-} F}{RT} \cdot \Delta E_{CEM} \right)$$

Equation 13: Concentration of OH<sup>-</sup> ions in the cathode compartment of a batch operation salt-splitting cell.

The model combined with the data from the experimental data from Figure 4.3.1 was used to back calculate the diffusion coefficient at the five NaOH product concentrations. Table 6.1.1 shows that the diffusion coefficient becomes larger (diffusion occurs more readily) as the NaOH catholyte concentration is increased.

Table: 6.1.1 Predicted diffusion coefficient given by the model of a transient, batch operation salt-splitting cell.

NaOH Concentration (M)	$D_{[OH^-]}$ ( $\text{cm}^2 \text{s}^{-1}$ )
1	1.6E-07
2	1.6E-07
3	1.6E-07
4	1.9E-07
5	2.1E-07
5 M NaOH experimentally determined value	4.1E-07

The diffusion coefficient calculated at 1 M NaOH concentration validates the first diffusion only experiment that is shown in Table 4.5.1. When  $D_{OH^-} = 1.6 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$  is used to calculate the catholyte concentration change after 20 minutes of diffusion, no observable change is expected. However, comparing the diffusion coefficient calculated at 5 M NaOH concentration to the results of the corresponding diffusion only experiment there is a mismatch. Calculating from the results of the experiment, the diffusion coefficient at 5 M NaOH  $D_{OH^-} = 4.1 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Whereas the model figures,  $D_{OH^-} = 2.1 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ . It is likely that this discrepancy stems from the value of the voltage drop across the membrane,  $\Delta E_{CEM}$ , used in the model. The value used in the model is calculated from the area resistance of the membrane reported by the manufacturer multiplied by the current. The manufacturers' data in Tables 4.1.1 and 4.2.1 are found using various concentrations of NaCl solution. Changing the composition of the electrolyte will change the conductivity of the membrane among other membrane properties. To improve the model, membrane conductivities should be measured under  $\text{Na}_2\text{SO}_4$  electrolysis conditions. Dammak et al [1] find co-ion diffusion coefficients in CEMs to be in the range of  $8.0 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$  to  $1.2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  using potassium chloride solutions of 2 M concentration and less.

## 6.2 Steady-State Flow Cell

Additionally a full cell analytical model of a salt-splitting flow cell operating at steady-state has been written by performing a material balance on OH<sup>-</sup> ion similar to the balance used to create the previous transient batch operation model. The steady-state flow model also predicts the OH<sup>-</sup> concentration of the cathode compartment. The balance is given by Equation 14.

$$V \frac{\partial C_i}{\partial t} = \dot{V} C_i^{in} - \dot{V} C_i - A \cdot D_i \frac{\partial C_i}{\partial x} - A \cdot D_i \cdot C_i \frac{z_i F}{RT} \frac{\Delta E}{l} + A \cdot \frac{j}{F}$$

Equation 14: General material balance of an ion in a salt-splitting flow cell

The control volume is same as the batch operation model, the ion exchange membrane. The electrolyte solutions are assumed to be well mixed so that at  $x = 0$  the OH<sup>-</sup> concentration is equal to that of the bulk concentration of the catholyte. At  $x = \delta$ , the concentration is equal to that of the bulk concentration of the center electrolyte. Since the center compartment is generally acidic, the concentration of OH<sup>-</sup> in the center compartment, ( $C_{OH^-}^{Center}$ ) is conservatively taken to be zero for added simplicity. Steady-state operation ( $dC_i/dt = 0$ ) and pure water feed ( $C_i^{in} = 0$ ) assumptions simplify the material balance. Equation 15 is the simplified material balance. Slowing the volumetric flowrate,  $\dot{V}$ , or increasing the current density,  $j$ , will increase the product concentration but decrease the current efficiency. Figure 6.2.1 shows the predicted CEM current efficiency as a function of NaOH product concentration of a steady-state flow cell and the experimental behavior of the batch-operation cell. The model suggests linear behavior while the experiments suggest quadratic behavior. The model would likely be improved by linking the diffusion coefficient to the electrolyte concentration. Dammak et al [1] suggest an analytical formula for calculating the value of diffusion coefficients. This

formula would be very useful in improving both the steady-state flow and batch-operation models. However, the formula contains some variables, such as concentration of fixed sites per unit volume and volume of absorbed electrolyte. These variables are not listed by manufacturers and were not determined in this work.

$$\dot{V}C_i + A \cdot D_i \cdot \frac{\Delta C_i}{\delta_{Membrane}} + A \cdot D_i C_i \cdot \frac{z_i F}{RT} \cdot \frac{\Delta E}{\delta_{Membrane}} - \frac{j}{F} = 0$$

Equation 15: Steady-state, pure water feed material balance of an ion in a salt-splitting cell.

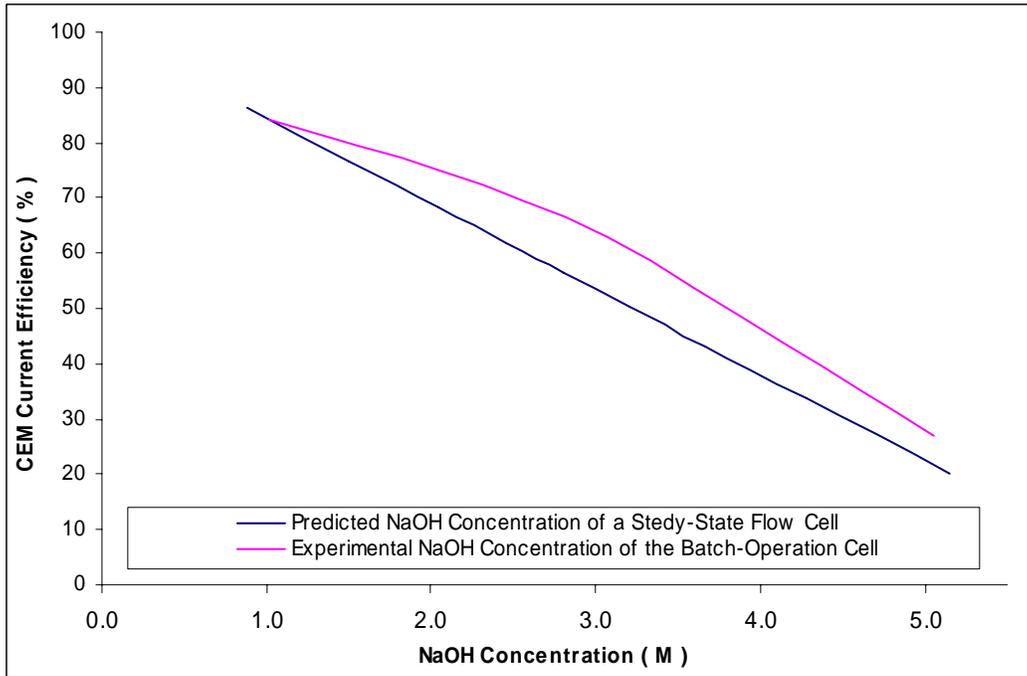


Figure 6.2.1: CEM current efficiency vs. NaOH product concentration (M).

There are many improvements to make to both models. A future version should be a full cell model instead of a half cell model. That is to say, the balance will consider events that occur in the anode and center compartment such as the transport of other ions.

## CHAPTER 7

### RECOMMENDATIONS FOR FUTURE WORK

#### 7.1 Multi-Compartment Electrodialysis Flow Cell

A multi-compartment electrodialysis cell has been designed to increase the NaOH product concentration. The design is shown in figure 7.1.1. By definition, electrodialysis facilitates a separation. The cations are separated from the anions. By alternating CEMs and AEMs, dilution and concentration compartments are created. This type of cell allows for control over electrolyte composition in contact with each membrane; permitting the use of DuPont Nafion 982 and the possibility of a 32% wt/wt NaOH product. Dilute NaOH is fed to a dilution compartment and to the center concentration compartment. Because  $\text{Na}_2\text{SO}_4$  is not fed to a compartment bounded by DuPont Nafion 982, polymer disruption will not occur. In addition, a diaphragm similar to those within chlor-alkali cells is used in place of an AEM separating the NaOH dilution compartment from the center concentration compartment. This is because an AEM cannot tolerate high pH environments, as shown in Figure 5.8.1. One investigation that should be made with this type of cell is the possibility of a recycle stream. The product NaOH of the center concentration compartment is likely to be dilute. However, the dilute NaOH product from the center compartment may be an acceptable feed stream to the cathode electrolysis compartment.

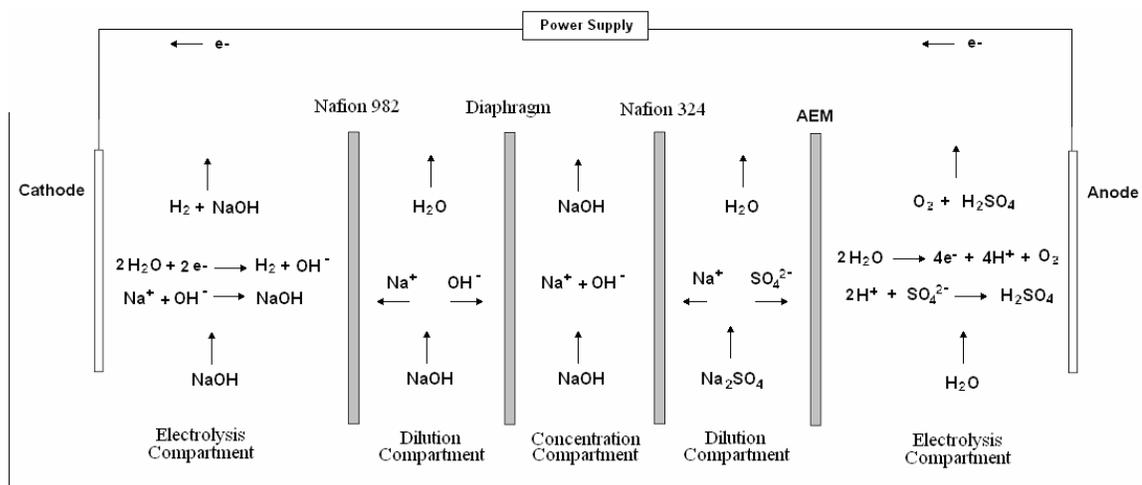


Figure 7.1.1: Schematic of a multi-compartment electrodiolysis cell for higher concentration NaOH product.

## 7.2 Three-Electrode Salt-Splitting Cell

Addition of a third electrode allows for pH control of center compartment. Figure 7.2.1 is a schematic of a three-electrode salt-splitting cell. Martin expressed the need for pH control to sustain the lifetime of the ion exchange membranes. It is also possible that pH control would also result in higher current efficiency. The third electrode could be operated cathodically, anodically, or with alternating polarity.

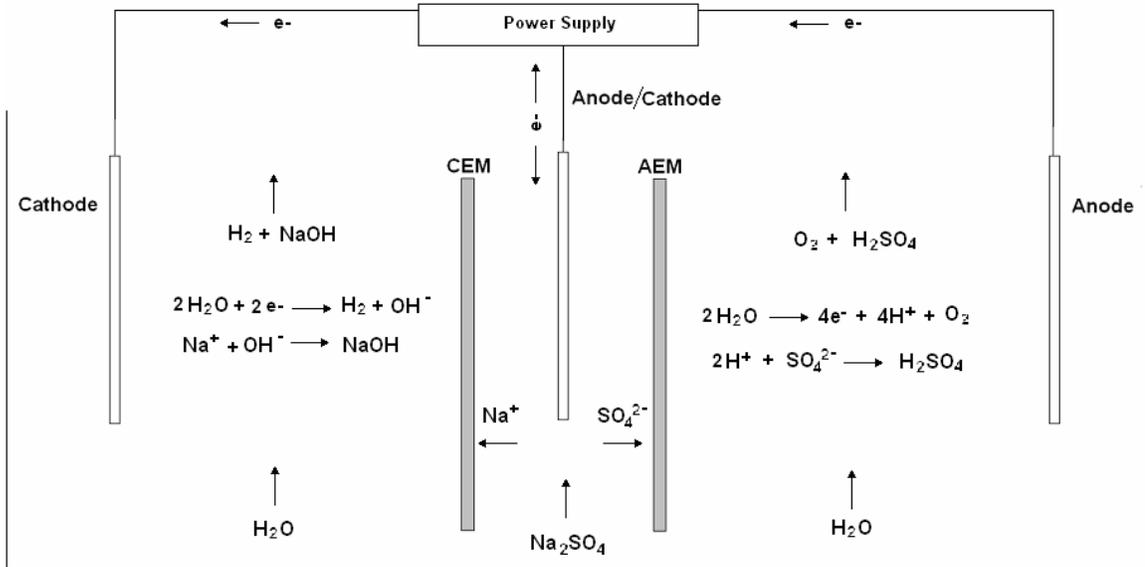


Figure 7.2.1: A three-electrode salt-splitting cell.

## CHAPTER 8

### CONCLUSIONS

This work details a three-compartment salt-splitting electrolysis cell for the recycle of  $\text{Na}_2\text{SO}_4$  waste saltcake from pulp mills into  $\text{NaOH}$  and  $\text{H}_2\text{SO}_4$ . Various CEMs and AEMs were tested to examine which membrane properties must be optimized to improve the counter-ion to co-ion selectivity of the membranes and increase the overall current efficiency of the cell.

It is observed that DuPont Nafion 324 is the best suited CEM for a three-compartment cell. The Sybron Ionac MA-7500 is the most counter-ion to co-ion selective AEMs tested in this work.

The DuPont Nafion 324 is based on a perfluorinated polymer backbone; which does not absorb electrolyte as styrene divinylbenzene based membranes. Therefore DuPont Nafion membranes maintain a higher counter-ion to co-ion selectivity. Additionally, the DuPont Nafion 324 is tolerant of the  $\text{SO}_4^{2-}$  anion, because it contains only  $\text{SO}_3^-$  fixed ionic sites; whereas the DuPont Nafion 982 CEM contains both  $\text{SO}_3^-$  and  $\text{COO}^-$  fixed ionic sites. The  $\text{COO}^-$  layer is extremely sensitive to  $\text{SO}_4^{2-}$  anions.

It is observed that increasing the ion exchange capacity of a styrene divinylbenzene membrane does not increase the counter-ion to co-ion selectivity of the membrane. It is also observed that the current efficiency of styrene divinylbenzene membranes increased with electrical resistance. It is believed that the co-ion diffusion coefficient decreases more rapidly with increasing electrical resistance than the counter-ion diffusion coefficient. The result is improved counter-ion to co-ion selectivity. Exchange capacity and electrical resistance are not the sole figures of merit when determining a membrane's counter-ion to co-ion selectivity and usefulness in a salt-splitting cell.

Using the DuPont Nafion 324 CEM and Sybron Ionac Ma-7500 AEM, the CEM current efficiency was tested using concentrations of NaOH catholyte from 1 to 5 M. During these experiments the anolyte is buffered in order to regulate the AEM current efficiency. However, it is observed that the CEM current efficiency decreases with increasing NaOH catholyte concentration. A 1 M NaOH product is made at 85% current efficiency. The production of 5 M NaOH is achieved at 27% current efficiency with a single layer of CEM and 48% current efficiency using a double layer of CEM. A result of the 5 M NaOH product is the center compartment becomes alkaline due to the diffusion of OH<sup>-</sup> across the CEM and lowers the AEM current efficiency. The CEM counter-ion to co-ion selectivity declines with increasing NaOH catholyte concentration. The coefficient of diffusion, and therefore the overall effects of diffusion, increases with the concentration differential of the solutions that contact the membrane surfaces.

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